SEARCH FOR SHOCK-METAMORPHOSED GRAINS IN PRECAMBRIAN SPHERULE LAYERS

by

Frank C. Smith

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Geology

Fall 2014

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by

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ABSTRACT

Several lines of evidence suggest that the ~17 Precambrian spherule layers known at present are related to large terrestrial impact events. However, there is minimal physical evidence in only a few of the layers to support an impact origin. The primary objective of this research was to search for shock-metamorphosed grains in the Neoarchean Carawine, Jeerinah, and Bee Gorge (formerly Wittenoom) spherule layers (Western Australia), the Neoarchean Monteville spherule layer (South Africa), and the Paleoproterozoic Grænsesø spherule layer (South-West Greenland). The documentation of shock-metamorphosed grains in a spherule layer would provide physical evidence to support an impact origin. A secondary objective was to evaluate the possibility that heavy mineral assemblages may provide a tool to test the recently proposed correlation of the Carawine, Jeerinah, and Monteville spherule layers.

Twenty-five spherule layer and context hand samples from surface outcrops went through acid digestion, and the residues were wet sieved, typically into five size fractions. The 63-125 μ m size fractions, and, for most samples, the 125-250 μ m size fractions, went through heavy liquid ($\rho = 2.96 \text{ g/cm}^3$) separation. Micro-Raman spectroscopy and X-ray diffraction were used to identify the heavy mineral phases, and to search for high-pressure polymorphs. The heavy mineral assemblages for 23 samples were determined by grain counts using a binocular microscope. A white opaque zircon grain and six white, translucent-to-opaque, or opaque, zircon grains from a sample of the Carawine spherule layer were analyzed by transmission and scanning electron microscopy, respectively, to search for shock-metamorphic effects.

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Twelve light fraction grain mounts for another sample from the Carawine spherule layer were searched for quartz grains with planar microstructures using optical microscopy.

The acid-insoluble weight data confirm that all the samples have a significant (\geq 33 wt%) carbonate component. The acid-insoluble material for the context samples/layers is mostly in the <63 µm size fraction, whereas that for the spherule layer samples is mostly in the >63 µm size fraction. These results are consistent with the previously proposed interpretations that these spherule layers were deposited by high-energy events in low-energy, deep-shelf or slope marine environments.

For most samples, the heavy mineral assemblages consist predominantly of anatase, rutile, tourmaline, and zircon (\pm chrome spinel) grains that are mostly in the 63-125 µm size fraction. At least some of the anatase is of secondary origin. Using micro-Raman spectroscopy, the high-pressure, α -PbO₂-structured polymorph of TiO₂ (TiO₂ II) was identified in 27 buff rutile grains from a total of five samples from the Carawine, Jeerinah, Bee Gorge, and Monteville spherule layers. For a sample or sublayers subdivision within a sample, rutile + TiO₂ II grains comprise ~1-5% of the rutile population. No rutile + TiO₂ II grains were identified in the context layers.

For two Bee Gorge samples from the same rock, rutile + TiO_2 II grains are confined to the upper part of the spherule layer interval. For the Monteville spherule layer, rutile + TiO_2 II grains were identified in the sample from the upper part of the layer, but no rutile + TiO_2 II grains were identified in the sample from the lower part of the layer. The stratigraphic position of the rutile + TiO_2 II grains within the Bee Gorge and Monteville spherule layers is somewhat analogous to that for shockmetamorphosed grains within the Cretaceous-Paleogene impact ejecta couplet layers.

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On the basis of geologic and petrologic evidence, the TiO_2 II polymorph is interpreted as a shock-induced phase that is syngenetic with respect to its host spherule layer, and therefore, the rutile + TiO_2 II grains provide physical evidence to support an impact origin for the Carawine, Jeerinah, Bee Gorge, and Monteville spherule layers.

Multiple analytical methods revealed no unequivocal evidence of shockmetamorphism of the white, translucent-to-opaque, or opaque zircon grains, and the results suggest that these grains have varying degrees of metamictization. About 1.6% (n = 14) of the ~875 quartz grains (63-125 µm size fraction) examined in the light fraction grain mounts contain planar microstructures. Seven sets of these structures in three quartz grains were measured using the universal stage microscope, and five of the sets were indexed to rational crystallographic planes having orientations that are commonly observed for shock-induced planar deformation features. These results provide additional support for an impact origin of the Carawine spherule layer.

The Carawine, Jeerinah, and Monteville spherule layer samples, and one sample from the Bee Gorge spherule layer, have similar heavy mineral assemblages. In the former three spherule layers, chrome spinel, rutile, and zircon grains each show a similar range in their physical properties. In the sample from the Bee Gorge spherule layer, the chrome spinel grains have a different color, and the rutile and zircon grains each show a different range in their physical properties, as compared to those for their respective phases in the Carawine, Jeerinah, and Monteville spherule layers. Therefore, the heavy mineral data support the previously proposed correlation of the Carawine, Jeerinah, and Monteville spherule layers.

This study has documented, apparently for the first time, a shock-induced highpressure polymorph (TiO₂ II) from Archean terrestrial rocks. It has now been shown that the TiO_2 II phase can survive in Archean rocks that have undergone low-strain deformation and low greenschist facies metamorphism. The rutile + TiO_2 II grains provide physical evidence to support an impact origin of four Neoarchean spherule layers, and the heavy mineral data support previous proposals that these four spherule layers actually record two separate impact events. The hypothesis that Precambrian spherule layers are of impact origin now has firmer support, and the spherule layers can serve as terrestrial constraints for the post-Late Heavy Bombardment cratering flux for Earth well into the Paleoproterozoic. Heavy minerals appear to provide another tool, not only for the correlation of spherule layers, but also for understanding the depositional processes that formed the spherule layers.

Field observation and hand samples have documented, apparently for the first time, that the Grænsesø spherule layer contains cm-to-dm-sized chert and carbonate intraclasts, a characteristic feature of many of the Precambrian spherule layers. The sampled interval of the Grænsesø spherule layer consists of a massive dolomixtite that appears to have been deposited by a single debris flow. The Grænsesø spherule layer records a singular, high-energy event that occurred in a low-energy marine environment. The white opaque zircons in the Grænsesø spherule layer are interpreted as epiclastic grains that have varying degrees of metamictization. At least eight of the 17 samples from the five spherule layers contain ~100-7300 zircon grains/kilogram, so Precambrian spherule layers may be very useful for zircon provenance studies.

Chapter 1

INTRODUCTION

1.1 Importance of Impact Events

Hypervelocity impact events have played an important role in the formation and the evolution of the planets, their satellites, and the asteroids (Taylor, 2001). Spacecraft have imaged impact structures on numerous bodies throughout the solar system (French, 1998), including very large (diameter (D) >1,500 km) impact basins on Mercury (Solomon et al., 2008; Murchie et al., 2008), the Moon (Stuart-Alexander, 1978; Wilhelms et al., 1979; Spudis et al., 1994), and Mars (Wilhelms, 1973; Schultz and Frey, 1990; Frey, 2008). Detailed studies of lunar samples gave rise to the "giant impact hypothesis" for the origin of the Moon (Hartmann and Davis, 1975; Cameron and Ward, 1976; Canup and Asphaug, 2001), and the "lunar cataclysm" (Tera et al., 1974) or "Late Heavy Bombardment" (LHB) hypothesis (Wetherill, 1975). The LHB hypothesis proposes that a sharp spike in the crater production rate at $\sim 3.85 \pm 0.10$ Ga (billion years ago) formed many of the large impact basins on the Moon (Dalrymple and Ryder, 1993, 1996; Cohen et al., 2000; Norman et al., 2006). If the LHB hypothesis is correct, then the Earth was also subject to an enhanced impact cratering flux at this time (e.g., Koeberl, 2006). There is a minimal terrestrial rock record for this time period, and terrestrial evidence for the LHB is equivocal (Koeberl, 2006; cf., Jørgensen et al., 2009). Prior to \sim 3.8 Ga, the differentiation of large terrestrial impact melt pools may have produced a significant volume of felsic crust (Grieve et al., 2006).

Hypervelocity impact events are now known to have been a factor in the geological and biological evolution of the post-Archean terrestrial environment (e.g., Grieve and Masaitis, 1994; French, 1998; Schulte et al., 2010). The number of confirmed terrestrial impact structures has risen from about a dozen in 1960 (Grieve, 1991) to 184 at present (Earth Impact Database, 2014). The Vredefort structure in South Africa has a diameter of ~180-300 km (Turtle et al., 2005), and it is the oldest (2023 ± 4 Ma (million years ago); Kamo et al., 1996), well-studied, confirmed terrestrial impact structure (Reimold and Gibson, 1996). Since 1960, the confirmation of an impact origin for most putative impact structures was primarily due to the development of diagnostic criteria for the detection of shock-metamorphic effects and/or an extraterrestrial component (ETC) in minerals and rocks (French, 1998).

It was the discovery of an ETC (positive iridium (Ir) anomaly) in a thin clay layer at the Cretaceous-Tertiary (K-T) boundary (e.g., Alvarez et al., 1980) that eventually led to the recognition that a large impact event at ~66 Ma (Jourdan et al., 2012) triggered the mass extinction (including the dinosaurs) that ended the Mesozoic Era and changed the course of terrestrial biological evolution (Schulte et al., 2010, and references therein). The K-T boundary is now formalized as the Cretaceous-Paleogene (K-Pg) boundary (e.g., Gradstein and Ogg, 2004), and the K-Pg boundary event deposit has been linked (Sharpton et al., 1992; Swisher et al., 1992; Krogh et al., 1993; Schulte et al., 2010) to the large Chicxulub impact structure (D ~180 km) that is now buried under the northern part of the Yucatán Peninsula, Mexico (Hildebrand et al., 1991; Sharpton et al., 1992; Swisher et al., 1992).

Three other large impact events may be linked to changes in the terrestrial environment. An impact ejecta layer that is probably linked (e.g., Addison et al., 2005;

Pufahl et al., 2007) to the ~1.85 Ga Sudbury impact structure (D ~130-260 km; Turtle et al., 2005) occurs at a stratigraphic horizon that marks the transition from the deposition of banded iron formation (BIF) to younger fine-grained clastic rocks (Cannon et al., 2010). The impact ejecta layer linked to the Ediacaran Acraman impact structure (D ~85-90 km; Williams and Wallace, 2003) coincides with palynological, biomarker, and carbon isotope anomalies (Hill et al., 2007). These data suggest that a period of biospheric impairment immediately after the impact event that formed the Acraman structure was succeeded by a period that included the diversification of large complex acritarchs (Grey et al., 2003; Willman et al., 2006; Hill et al., 2007).

The upper Eocene clinopyroxene-bearing (cpx) spherule layer (see section 1.2.3) may have been derived from the Popigai impact structure (D ~100 km) in Siberia (Whitehead et al., 2000; Liu et al., 2009). The cpx spherule layer appears to be associated with both a sharp decline in the abundance of several radiolarian species, and a drop in temperature of marine surface waters and/or an increase in ice volume (Liu et al., 2009, and references therein). These data are intriguing, but at present, only the Chicxulub impact event has been robustly linked to major changes in the terrestrial environment. These examples, however, illustrate the importance of impact event and changes in the terrestrial environment.

1.2 Terrestrial Impact Ejecta Layers

1.2.1 Ejecta Formation and Launch

The physical processes that form a hypervelocity impact crater and its concomitant ejecta are described by Melosh (1989) and reviewed by French (1998) and Koeberl (2002). Impact ejecta may consist of very highly shocked (melted/vaporized) to unshocked materials (French, 1998). For terrestrial impact events that produce craters with diameters \geq 1-2 km (Grieve, 1991), the projectile is essentially melted and vaporized during the short, initial contact and compression stage of crater formation (Melosh, 1989; French, 1998). Near the point of impact, shock pressures in the target may be >100 GPa, resulting in vaporization of the material (Melosh, 1989; French, 1998). In a surrounding, quasi-hemispherical volume of the target, partial to complete melting of nonporous crystalline rocks occurs at peak shock pressures of ~35-100 GPa (Melosh, 1989; French, 1998).

At lower shock pressures (~8-40 GPa), minerals in nonporous crystalline rocks remain solid, but they commonly show a range of distinctive shock-metamorphic effects (French, 1998). Common shock-metamorphic effects include planar deformation features (PDFs) in quartz and feldspar, diaplectic glasses, and high-pressure polymorphs (French, 1998). Planar deformation features in quartz are narrow ($<2-3 \mu m$) straight planes consisting of highly deformed or amorphous material, and the PDFs are generally oriented parallel to specific rational crystallographic planes (French, 1998). Highpressure polymorphs include coesite and stishovite (both SiO₂; French, 1998), reidite (ZrSiO₄; Glass et al., 2002), and TiO₂ II, the α -PbO₂-structured polymorph of TiO₂ (El Goresy et al., 2001; Jackson et al., 2006).

At relatively low shock pressures, perhaps as low as ~2 GPa, shatter cones form in rocks, and they represent a unique megascopic criterion for shock metamorphism (French, 1998). At pressures less than ~2 GPa, target materials undergo deformation, e.g., fracturing and brecciation, that is not unique to shock metamorphism (French, 1998).

Most of the impact ejecta are derived from approximately the upper one-third to one-half (excavation zone) of the expanding transient cavity, primarily during the excavation stage of crater formation (Melosh, 1989; French, 1998). Proximal impact ejecta are deposited up to five crater radii (R_c) from the rim of the final crater (Glass and Simonson, 2012) by several different mechanisms (e.g., Meyer et al., 2011, and references therein). Distal impact ejecta, the focus of this dissertation, are deposited beyond 5 R_c from the rim of the final crater (Glass and Simonson, 2012).

Distal impact ejecta from large impact events are primarily dispersed from the growing crater by two main mechanisms: ballistic transport associated with the expanding ejecta curtain, and the rise of a very hot plume that consists of vaporized projectile and target materials, melt particles, and unmelted components (Melosh, 1989; Alvarez, 1996). In large impacts, the "vapor plume" accelerates upward, blows out the top of the atmosphere, and the entrained particles are launched on ballistic trajectories (Jones and Kodis, 1982; Alvarez, 1996). The following discussion briefly examines the characteristics of proximal impact ejecta layers, and then provides a more detailed examination of distal impact ejecta layers.

1.2.2 Proximal Impact Ejecta Layers

Proximal ejecta comprise ~90 vol% of the total ejecta, and about half of the total ejecta is deposited within 1 crater radius (R_c) of the final crater rim to form the continuous ejecta blanket (Melosh, 1989, p. 90; French, 1998). Beyond the continuous

ejecta blanket, the ejecta become thinner and more discontinuous (French, 1998). The following discussion focuses on four proximal impact ejecta layers, three of which have been linked to large (D >20 km) impact structures.

Proximal and proximal-to-distal impact ejecta layers are associated with the Miocene Ries (D ~24 km; von Engelhardt, 1990), the Chicxulub (e.g., Ocampo et al., 1996; Schulte et al., 2010) and the Sudbury (e.g., Cannon et al., 2010) impact structures. The Stac Fada Member (SFM) of the Mesoproterozoic Stoer Group in northwest Scotland was recently reinterpreted to be part of a proximal impact ejecta blanket (Amor et al., 2008). Proximal impact ejecta layers commonly consist of coarse lithic and impact meltbearing breccias (suevite) that are on the order of 10 to >80 m thick (Amor et al., 2008; Cannon et al., 2010; Schulte et al., 2010). Proximal impact ejecta layers commonly contain unshocked materials that were derived both from the source crater and from the underlying substrate during emplacement of the ejecta (e.g., von Engelhardt, 1990; von Engelhardt et al., 1995; Cannon et al., 2010).

Pebble-to-boulder-sized clasts commonly show varying degrees of shock metamorphism (e.g., von Engelhardt et al., 1995). Sand-sized (>63 µm to 2 mm), shockmetamorphosed grains (e.g., quartz and feldspar with PDFs) are commonly a very minor component of proximal impact ejecta layers (e.g., Addison et al., 2005; Amor et al., 2008). For example, only one quartz grain (~100 µm long) containing putative PDFs was found in the acid leach residue of a sample (>1 kg) from the K-Pg carbonate diamictite unit (\geq 15 m thick) on Albion Island, Belize, a site that is located ~274 km (~3 R_c) from the rim of the Chicxulub impact structure (Pope et al., 1999). Shock-metamorphosed quartz grains have been found in the Mesoproterozoic SFM breccias in northwest

Scotland (Amor et al., 2008; Osinski et al., 2011), but not in every sample of the breccias (Osinski et al., 2011).

Proximal impact ejecta layers commonly contain impact melt particles that may include tiny angular shards, mm-sized spheroids, and mm-to-dm-sized glassy fragments and bombs (von Engelhardt, 1990; von Engelhardt et al., 1995; Pope et al., 1999; Amor et al., 2008; Cannon et al., 2010). Glassy impact melt particles are typically devitrified and/or replaced by secondary phases, especially in the pre-Miocene layers (e.g., Pope et al., 1999; Cannon et al., 2010). In addition to impact melt particles, accretionary lapilli, commonly ~0.5-2 cm in diameter, are a minor component in all four of these proximal impact ejecta layers (Graup, 1981; Schulte et al., 2010; Amor et al., 2008; Cannon et al., 2010). Shock-metamorphosed grains occur in some accretionary lapilli in the Sudbury impact ejecta layer (e.g., Addison et al., 2005; Cannon et al., 2010). The presence of shock-metamorphosed grains and clasts (e.g., von Engelhardt et al., 1995) in these layers provides strong evidence for their impact origin (e.g., Amor et al., 2008; Cannon et al., 2010). Nickel (Ni)-rich spinel crystals and a small positive Ir anomaly in the K-Pg proximal ejecta (Schulte et al., 2010, and references therein), and chromium (Cr) isotopic data from the Mesoproterozoic SFM breccias in northwest Scotland (Amor et al., 2008), provide further support for an impact origin of these layers.

Proximal impact ejecta layers commonly show a complex internal stratigraphy that records multiple depositional events and emplacement processes (e.g., von Engelhardt et al., 1995; Pope et al., 1999; Branney and Brown, 2011). The discovery of shock-metamorphosed grains within several of these layers was the key to the correct interpretation of their origin (e.g., Amor et al., 2008; Cannon et al., 2010). Proximal impact ejecta layers well illustrate the importance of searching for shock-metamorphosed

grains in strata (especially breccias) that appear to be unique horizons in their host successions.

1.2.3 Distal Impact Ejecta Layers

At distances greater than~20 R_c from the rim of the source crater, distal impact ejecta layers mainly consist of glassy impact spherules, commonly <1 mm in size, that are termed microtektites and microkrystites (see below; Glass and Simonson, 2012). These layers have been termed "impact spherule layers" (Simonson and Glass, 2004). At present, there is no precise definition of an impact spherule layer in terms of the minimum abundance of spherules by volume, the aggregate thickness of spherules within a layer, or the maximum thickness of the layer (Simonson and Glass, 2004). A working definition is that impact "spherule layers are discrete beds or very thin stratigraphic intervals containing large numbers of impact spherules" (Simonson and Glass, 2004, p. 343).

There are eleven presently confirmed distal impact ejecta/spherule layers that range in age from ~1850-0.8 Ma, and eight of the layers have been linked to source craters (Table 1). Spherules have not been reported in the Late Cretaceous Crow Creek Member distal impact ejecta layer (Izett et al., 1998), and they are minor components in the Sudbury (Addison et al., 2005; Cannon et al., 2010) and the Acraman (Haines, 2005; Hill et al., 2007) impact ejecta layers. To provide a context for the Precambrian spherule layers, I first review tektites, microtektites, and microkrystites, and then describe three well-studied Cenozoic distal impact ejecta/spherule layers.

| Layer | Location | Aggregate thickness* (cm) | Age (Ma) | Unmelted shock- produced components | Proposed source crater (Location) | Refs. |
|---|---|---------------------------------|-------------|---|---|----------------------------------|
| Australasian microtektite | Indian Ocean; West equatorial Pacific Ocean and adjacent seas; Antarctica | <0.0001- 0.17 | ~0.8 | Quartz with PDFs; coesite, stishovite, TiO ₂ II | Unknown (probably in Indochina) | 1, 6, 18 |
| Ivory Coast microtektite | Eastern equatorial Atlantic Ocean | <0.001 | ~1.1 | None yet reported | Bosumtwi (Ghana) | 1,6 |
| North American microtektite | Gulf of Mexico, Caribbean Sea, Barbados, Northwestern Atlantic Ocean | <0.01-8 | ~35 | Quartz and feldspar with PDFs; coesite, stishovite, reidite | Chesapeake Bay (Virginia, USA) | 1,6 |
| Cpx spherule | Global | <0.0001- 0.06 | ~35 | Quartz with PDFs; coesite | Popigai (Russia) | 1, 6, 17 |
| K-Pg boundary event deposit | Global | ~0.2-25 | ~66 | Quartz and feldspar with PDFs; zircon with planar microdeformation features and granular texture; stishovite | Chicxulub (Mexico) | 1, 6, 13, 14, 15, 16 |
| Crow Creek Member of Pierre Shale | Eastern South Dakota and northeastern Nebraska, USA | Unknown | ~74 | Quartz and feldspar with PDFs; zircon with planar microdeformation features | Manson (Iowa, USA) | 11, 12 |

 Table 1:
 Confirmed distal impact ejecta/spherule layers.

Table 1: continued

| Layer | Location | Aggregate thickness* (cm) | Age (Ma) | Unmelted shock- produced components | Proposed source crater (Location) | Refs. |
|---------------------------------|---|---------------------------------|-------------|---|---|---------------------|
| Late Triassic spherule | Southwest England, near Bristol | ~1.6 | ~214 | Shocked mineral grains including quartz with PDFs | Manicouagan (Canada) | 1, 9, 10 |
| Qidong spherule | Qidong, South China | Unknown | ~372 | None yet reported | Unknown | 1,6 |
| Senzeilles/Hony microtektite | Belgium | <0.001 | ~374 | None yet reported | Unknown | 1,6 |
| Acraman | Adelaide Geosyncline & Officer Basin, South Australia | Up to ~3.5 | ~580 | Quartz with PDFs; rare shatter cones in clasts | Acraman (South Australia) | 1, 6, 7, 8 |
| Sudbury | Lake Superior region, USA and Canada | Up to ~4000 | ~1850 | Quartz and feldspar with PDFs | Sudbury (Canada) | 1, 2, 3, 4, 5 |

*The aggregate thicknesses are estimated from layer thickness and percent spherules (Glass and Simonson, 2012), except for the Sudbury and Acraman layers. The value for the Sudbury layer refers to the total thickness of the layer (Cannon et al., 2010). The value for the Acraman layer refers to the actual thickness of the ejecta where the layer is not reworked (see Williams and Wallace, 2003).

Abbreviations: Cpx = clinopyroxene-bearing; PDFs = planar deformation features; K-Pg = Cretaceous-Paleogene; Refs. = References.

References: ¹Glass and Simonson, 2012; ²Addison et al., 2005; ³Turtle et al., 2005; ⁴Pufahl et al., 2007; ⁵Cannon et al., 2010; ⁶Simonson and Glass, 2004, and references therein; ⁷Haines, 2005; ⁸Williams and Wallace, 2003; ⁹Walkden et al., 2002; ¹⁰Thackrey et al., 2009; ¹¹Izett et al., 1998; ¹²Weber and Watkins, 2007; ¹³Bohor et al., 1984; ¹⁴Bohor et al., 1993; ¹⁵Smit, 1999; ¹⁶Schulte et al., 2010; ¹⁷Liu et al., 2009; ¹⁸Glass and Fries, 2008.

Tektites are naturally occurring, enigmatic glassy bodies that are typically >1 cm in size (Glass, 1990; Glass and Simonson, 2012). By the 1960s, tektites had been found scattered over the land surface in four large regions known as strewn fields (Barnes, 1963). Tektites are typically black and opaque, but they can be brown or green and translucent (Glass, 1990). Tektites are commonly spherical, but they may have other "splash form" shapes (e.g., spheroid, dumbbell, teardrop, disc) that are produced by the rapid rotation of molten droplets (Baker, 1963; Glass, 1984). There are also blocky (layered or Muong Nong-type) and ablated (remelted splash forms) tektites (Baker, 1963; Glass, 1990).

The origin of tektites was a scientific controversy for about two centuries (e.g., O'Keefe, 1963, 1976; Barnes, 1989, 1990; Glass, 1990, and references therein). However, by the late 1960s, tektites were generally considered to represent either distal impact melt ejecta from terrestrial hypervelocity impact events (Cohen, 1963), or impact melt ejecta from impact events that occurred on the Moon (e.g., O'Keefe, 1963). The lunar hypothesis persisted to some degree even after the return of the lunar samples (e.g., O'Keefe, 1976). However, petrographic, geochemical, and isotopic data support the hypothesis that tektites represent very high temperature (~1,500-2,000 °C; Chao, 1963; Clarke and Wosinski, 1967) distal impact melt ejecta that were derived from highly shocked upper crustal materials during terrestrial impact events (e.g., Glass, 1990; Koeberl, 1994). The North American, Central European, and Ivory Coast tektite strewn fields have been linked to the Chesapeake Bay (Poag et al., 1994; Koeberl et al., 1996), the Ries (e.g., Koeberl, 1994), and the Bosumtwi (e.g., Koeberl, 1994) impact structures, respectively. The source crater for the large Australasian strewn field has not yet been

identified, but it is probably located in the Indochina region (Ma et al., 2004; Glass and Koeberl, 2006).

Beginning in the 1960s, glassy spherules interpreted as microtektites (Glass, 1967) were discovered in several horizons within Cenozoic sediments in deep-sea cores (e.g., Glass, 1967, 1968; Glass et al., 1973). The microtektites were linked to the Australasian (Glass, 1967, 1972; Cassidy et al., 1969; Glass et al., 1979), the Ivory Coast (Glass, 1968, 1969), and the North American (Glass et al., 1973; Koeberl and Glass, 1988) tektite strewn fields. The microtektite occurrences have greatly enlarged the sizes of these three tektite strewn fields (Glass, 1990; Koeberl, 1994).

Microtektites are commonly <1 mm in size (Glass et al., 1979), but a few microtektites range up to ~2 mm in size (Simonson and Glass, 2004). Microtektites are essentially holohyaline (Glass, 1967), and they commonly contain vesicles (Glass and Simonson, 2012). Some microtektites contain clear inclusions of silica glass (lechatelierite) that formed by the melting of quartz grains (Glass and Burns, 1988; Glass and Simonson, 2012). Relict mineral inclusions are present in some microtektites (Glass and Zwart, 1979; Folco et al., 2010a). Unbroken microtektites commonly have shapes ("splash forms") that are very similar to those of tektites (Glass et al., 1979). Geochemical and petrographic data indicate that microtektites, like tektites, represent highly shocked distal impact melt ejecta that are associated with terrestrial impact events (e.g., Koeberl, 1994; Montanari and Koeberl, 2000; Glass et al., 2004a).

In contrast to microtektites, microkrystites are glassy impact spherules that contain primary microlites/crystallites (Glass and Burns, 1988). The late Eocene cpx spherules, and the diagenetically-altered microcrystalline spherules containing relict quench textures (Glass and Burns, 1988) from the K-Pg boundary event deposit

(e.g., Montanari et al., 1983; Smit and Kyte, 1984) are microkrystites (e.g., Glass and Simonson, 2012). The late Eocene and K-Pg microkrystites are described in more detail in the appropriate sections of the following discussion.

The Australasian microtektite layer (~0.8 Ma), the upper Eocene (~35 Ma) cpx spherule layer, and the K-Pg (~66 Ma) boundary event deposit are the most widespread spherule layers (Simonson and Glass, 2004). Microtektites (or microtektite-like spherules) are present in all three layers (Glass and Simonson, 2012), but no microkrystites have yet been found in the Australasian microtektite layer (Simonson and Glass, 2004; Lui et al., 2009). From youngest to oldest, these spherule layers appear to be associated with source craters of increasing size (Smit, 1999; Lui et al., 2009). These spherule layers well illustrate the components of distal impact ejecta, and how the relative proportion of the components changes with increasing distance from the source crater.

The Australasian strewn field covers more than 10% of the Earth's surface (Glass et al., 1979). Australasian microtektites were recently discovered in Victoria Land in Antarctica, and the strewn field now extends in a southerly direction more than 10,000 km from the probable location of its source crater in the area of Indochina (Folco et al., 2008, 2009, and references therein). Australasian microtektites have been found in more than 60 deep-sea cores (Glass and Koeberl, 2006; Prasad et al., 2007).

In the deep-sea cores from a semicircular area that extends up to ~3,500 km from a center in northern Vietnam, microtektites (D >125 μ m) have their highest abundance (>200/cm²), and many of these microtektites contain vesicles (Glass and Koeberl, 2006) and/or relict mineral inclusions (D ≤20 μ m), including apparently shock-metamorphosed quartz (Folco et al., 2010a). Fragments of microtektites and tektites, partially melted vesicular particles, and unmelted impact ejecta (see below) are also present in the cores

from this semicircular area (Glass and Koeberl, 2006). In one core from this area, concentrations of iridium up to 0.16-0.19 ppb are coincident with the peak abundance of microtektites, and these values provide evidence for an ETC in the microtektite layer (Koeberl, 1993; Schmidt et al., 1993).

For most of the cores within this semicircular area, the estimated maximum thickness of the microtektite/impact ejecta layer prior to bioturbation is $\leq 300 \ \mu m$ (Glass and Koeberl, 2006). In the core that is probably the closest to the source crater, the original thickness of the microtektite/impact ejecta layer reaches a maximum of ~2 mm, and the abundance of microtektites (9,834/cm²), the ratio of unmelted/melted impact ejecta (43%), and the ratio of microtektite fragments/whole splash forms (75%) have the highest values of any microtektite-bearing site in the strewn field (Glass and Koeberl, 2006). These data are in accord with previous data from the microtektite portions of the Australasian, Ivory Coast, and North American strewn fields that show that these four parameters all increase with decreasing distance to the source crater (Glass et al., 1997; Glass and Simonson, 2013).

The unmelted impact ejecta from the deep-sea cores within this semicircular area consist of silt-to-sand-sized rock fragments and mineral grains, most of which exhibit evidence of shock metamorphism (Glass and Koeberl, 2006). Most of the shock-metamorphosed mineral fragments are white opaque, and they typically contain quartz, coesite, and rare stishovite (Glass and Wu, 1993; Glass and Koeberl, 2006). Some shock-metamorphosed quartz grains contain PDFs (Wu, 1995). Most of the rock fragments are small (D <50 μ m), but a few are up to ~600-700 μ m in size (Glass and Koeberl, 2006). The rock fragments contain grains of quartz, feldspar, carbonate, coesite, stishovite (rare), and a phyllosilicate phase, and they show evidence of partial melting and vesiculation

(Glass and Koeberl, 2006; Glass and Fries, 2008). The TiO_2 II phase (see section 1.2.1) was identified in several of these rock fragments using micro-Raman spectroscopy (Glass and Fries, 2008).

The abundance (Glass and Koeberl, 2006), vesicularity (Folco et al., 2010a), and average total alkali (Na₂O + K₂O) concentration (Folco et al., 2010b) of Australasian microtektites (D >125 μ m) decrease, and their internal homogeneity increases (Folco et al., 2010a) with increasing distance from Indochina. The microtektites from Antarctica show the greatest depletion in volatile elements (Folco et al., 2008, 2009). No unmelted impact ejecta have yet been found beyond the semicircular area described above (Glass and Koeberl, 2006). The mineralogical, petrographic, and geochemical data show that with increasing distance from the source crater, the impact ejecta experienced a greater intensity and/or duration of heating (Folco et al., 2010b). These data support the theoretical concept (Melosh, 1989, p. 91) that the average degree of shock metamorphism of distal impact ejecta increases with distance from the source crater (Glass and Simonson, 2012). Recently, the diameter of the source crater for the Australasian strewn field has been estimated to be ~25-50 km (Glass and Koeberl, 2006; Prasad et al., 2007; Liu et al., 2009).

The cpx spherules, termed microkrystites by Glass and Burns (1988), were first found in upper Eocene sediments in a deep-sea core from the Caribbean Sea (e.g., John and Glass, 1974). At present, the cpx spherule layer has been found in ~25 deep-sea cores and at Massignano, Italy, and the cpx spherule layer has a near-global extent (Liu et al., 2009, and references therein). It was first thought that the cpx spherules were part of the North American strewn field (John and Glass, 1974), but numerous studies have now

shown that the cpx spherules were formed during a slightly older impact event (Liu et al., 2009, and references therein).

All unbroken cpx spherules are spherical (Glass and Simonson, 2012), and most of the spherules are <200-400 μ m in diameter (e.g., John and Glass, 1974; Glass and Simonson, 2012), but a few cpx spherules are up to ~900 μ m in diameter (Simonson and Glass, 2004). In contrast to microtektites, cpx spherules do not contain vesicles, lechatelierite, or relict mineral inclusions (Glass and Simonson, 2012). At five sites, the cpx spherules have been partly or completely replaced by clay or pyrite (Liu et al., 2009). Many cpx spherules contain Ni- and/or Cr-rich spinel crystals (Glass et al., 1985, 2004b).

The cpx spherule layer is typically associated with a positive Ir anomaly with typical Ir concentrations of ~100-666 pg/g and peak values of 1046 and 4100 pg/g at two sites (Liu et al., 2009, and references therein). Recent chemical and Cr-isotopic data confirm an ETC in the cpx spherule layer, and these data suggest that the impactor was an ordinary chondrite from the main asteroid belt (Kyte et al., 2011). The mineralogical, petrographic, and geochemical data suggest that the cpx spherules represent droplets that condensed from vaporized target and impactor materials (Glass and Simonson, 2012).

At several sites, the cpx spherules are associated with microtektites that appear to be part of the same impact event (Liu et al., 2009). At present, unmelted shockmetamorphosed impact ejecta (coesite and/or quartz with PDFs) have been found at only three sites: in two deep-sea cores from the northern Indian Ocean (Liu et al., 2009), and at Massignano, Italy (Clymer et al., 1996; Glass et al., 2004b). The Ni-rich spinels, shock-metamorphosed grains, positive Ir anomalies, and Cr-isotopic data support an impact origin for the cpx spherule layer (Glass et al., 2004b; Clymer et al., 1996; Liu et al., 2009; Kyte et al., 2011).
Liu et al. (2009) proposed that all the cpx spherule layer sites occur within three ejecta rays that radiate from the Popigai impact structure in Siberia. At the two sites in the Indian Ocean-South Atlantic ray that are closest to the Popigai impact structure, shock-metamorphosed grains are present, and the abundance of impact spherules $(D > 125 \ \mu\text{m})$ is the highest (2,274 and 9,570/cm²) for the entire cpx spherule layer (Liu et al., 2009). Along this ray, the ratio of microtektites ($D > 125 \ \mu\text{m}$)/total spherules increases from 4% and 9% at the two sites in the northern Indian Ocean that are closest to the Popigai impact structure to 100% at a site in the South Atlantic (Liu et al., 2009). Within the North Atlantic-equatorial Pacific ray, shock-metamorphosed grains only occur at the site (Massignano) that is the closest to the Popigai impact structure (Liu et al., 2009). These data from the cpx spherule layer support the concept that the relative proportion of highly shocked materials (e.g., impact spherules) in distal impact ejecta increases with increasing distance from the source crater (Melosh, 1989, p. 91; Glass and Simonson, 2013).

The K-Pg boundary event deposit has a global distribution, and there are more than 350 presently known occurrences in deep-sea cores, cores on land, and outcrops (Schulte et al., 2010). There are distinct changes in the nature, thickness, type of ejecta, and relative proportion of ejecta components of the K-Pg boundary event deposit with increasing distance from the Chicxulub impact structure (e.g., Smit, 1999; Schulte et al., 2010). Smit (1999) and Schulte et al. (2010) group the K-Pg boundary event deposit sites into three and four regions, respectively, with increasing distance from the Chicxulub impact structure. Most of the "proximal" and all of the "intermediate" sites of Smit (1999) and Schulte et al. (2010) are actually distal sites since they are >5 R_c (~450 km) from the rim of the Chicxulub impact structure. Estimated paleodistances

from the center of the Chicxulub impact structure (Schulte et al., 2010) are given for sites in the following discussion.

At the sites (~500-900 km) around the Gulf of Mexico, the K-Pg boundary event deposit typically consists of dm-to-10 m-thick, high-energy, fining-upward sequences of coarse sandstone-to-siltstone beds that were deposited in neritic-to-bathyal environments (Smit, 1999; Schulte et al., 2010). The sequences commonly exhibit a complex internal stratigraphy, and sedimentary structures at several sites suggest bimodal current directions (Smit, 1999). Several sites show evidence of soft-sediment deformation, including slump folds (e.g., Smit, 1999; Schulte and Kontny, 2005). The sequences are generally interpreted as having been rapidly deposited by impact-induced tsunami waves and sediment gravity flows, and the sequences commonly contain abundant materials of local/regional derivation (Smit, 1999; Schulte et al., 2010).

The sequences typically include a cm-to-dm-thick basal ejecta-rich unit that contains abundant spherules, angular or irregularly-shaped fragments (originally glassy), accretionary lapilli, carbonate ejecta fragments, and, locally, shock-metamorphosed grains (Smit, 1999; Schulte and Kontny, 2005; Schulte et al., 2010). At the Brazos River, Texas site, carbonate accretionary lapilli (D ~0.05-3 cm) comprise ~25% of the coarse ejecta fraction in the basal ejecta-rich beds (Yancey and Guillemette, 2008). Similar lapilli occur at several of the sites in northeast Mexico (Schulte et al., 2010, and references therein). A positive Ir anomaly and Ni-rich spinels are locally present near/at the top of the sequences (Smit, 1999; Schulte et al., 2010).

The spherules in the sequences have splash form shapes, and most of the spherules are $\leq 1-2$ mm in diameter (e.g., Bohor and Glass, 1995). The spherules and angular or irregularly-shaped fragments, the latter components being up to $\sim 1-2$ cm in

size, are mostly altered, commonly to clay minerals, micas, chlorite, and calcite, but a few spherules contain remnant glass cores (e.g., Kring and Boynton, 1991; Smit, 1999; Schulte and Kontny, 2005). The spherules may exhibit schlieren or flowlines, and many spherules have a vesicular texture (Smit et al., 1992; Smit, 1999; Schulte and Kontny, 2005). Most of the spherules appear to be similar to microtektites (e.g., Kring and Boynton, 1991; Bohor and Betterton, 1991; Simonson and Glass, 2004), and they probably formed by rapid quenching of impact melt droplets (e.g., Smit et al., 1992). The variable mineralogy and geochemistry of the spherules reflect a compositionally heterogeneous target that included supracrustal carbonate rocks and mafic-to-felsic crystalline basement rocks (e.g., Schulte and Kontny, 2005). Microkrystites (e.g., Schulte and Kontny, 2005, their Fig. 6D) appear to be rare or absent at these and other sites within and near North America (Smit et al., 1992; Smit, 1999).

At marine sites near the east coast of the United States (~2,500 km), the K-Pg boundary event deposit typically consists of a cm-to-dm-thick, locally reworked, spherule-rich clay layer that contains shock-metamorphosed quartz grains (Smit, 1999; Schulte and Kontny, 2005; Schulte et al., 2010). The spherules are altered, vesicular, up to ~1-2 mm in diameter, and have splash form shapes (Smit, 1999). At the Blake Nose site east of Florida, the strata beneath the K-Pg boundary event deposit show evidence of impact-induced large-scale soft-sediment deformation, including slump folding (Smit, 1999). In the 6-cm-thick spherule layer at the Bass River, New Jersey site, carbonate accretionary lapilli, similar to those at the Brazos River, Texas site, are present (Yancey and Guillemette, 2008), and shock-metamorphosed quartz grains occur in the uppermost centimeter (Olsson et al., 1997).

At the Western Interior sites that extend from northern New Mexico to southern Canada (~2,100-3,400 km), the K-Pg boundary event deposit commonly consists of duallayer claystone couplets (~0.5-3 cm thick) that were deposited in low-energy coal-swamp environments (Smit, 1999; Schulte et al., 2009). The lower claystone layer (~1.5 to 2.5 cm thick) is massive and kaolinitic, and it contains spherules (D <1 mm) and fragments (originally glassy), rare shock-metamorphosed grains, and a small positive Ir anomaly (Bohor and Glass, 1995, and references therein). The spherules have splash form shapes, and many spherules are now hollow with shells composed of kaolinite or goyazite (Bohor and Glass, 1995). The spherules are interpreted as diagenetically-altered, quenched impact melt droplets that were similar to microtektites (Bohor and Glass, 1995). The spherules are interpreted as ballistic impact ejecta that were associated with an expanding ejecta curtain (Bohor and Glass, 1995, and references therein).

The upper, thin (~5-12 mm thick), laminated, smectitic layer of the couplet commonly contains a larger positive Ir anomaly (~1-56 ppb), Ni-rich spinel crystals, and shock-metamorphosed grains (Bohor and Foord, 1987; Bohor and Glass, 1995, and references therein; Schulte et al., 2010, and references therein). The Ni-rich spinel crystals are interpreted to have originally been associated with spheroids that were destroyed by weathering and diagenesis (Bohor and Glass, 1995). The spinel-bearing spheroids are interpreted to correlate with the microkrystites (see below) that are common in the very distal sites (>7,000 km), and many of these spherules may have formed by condensation within the impact vapor plume (Bohor and Glass, 1995, and references therein).

Shock-metamorphosed grains comprise about 2% of the thin upper layer of the couplet, and they consist of quartz, sodic plagioclase, microcline, metaquartzite, quartz-sericite schist, granite-like material (Izett, 1987), and zircon (Bohor et al., 1993; Kamo and Krogh, 1995). Trace amounts of stishovite were identified in bulk samples of the boundary claystone at the Brownie Butte, Montana (Bohor et al., 1984) and Raton, New Mexico (McHone et al., 1989) sites. At the Brownie Butte, Montana site, stishovite occurs in quartz grains that contain PDFs (Bohor et al., 1984).

The first known marine site of the K-Pg boundary event deposit that exhibits a dual-layer stratigraphy occurs at Demerara Rise (~4,500 km) in the western tropical North Atlantic (MacLeod et al., 2007; Schulte et al., 2009). A normally graded, 1.5-2-cm-thick spherule layer that shows no evidence of bioturbation, post-depositional reworking, or traction transport, occurs precisely at the K-Pg biostratigraphic boundary (MacLeod et al., 2007; Schulte et al., 2007; Schulte et al., 2009). Spherules comprise about two thirds of the layer, and they occur within a phyllosilicate matrix (Berndt et al., 2011). The spherules are generally spheroidal, and they decrease in size from an average of ~0.5 mm in diameter (maximum D ~1 mm) at the base of the layer to <0.1 mm at the top (Schulte et al., 2009). Spherules can be hollow, vesicular, or massive, and they consist mostly of smectite with rare relict hydrated glass (Schulte et al., 2009). The geochemistry of the relict glass suggests that most of the spherules were derived from Si- and Al-rich lithologies (Schulte et al., 2009). Most spherules appear to be altered microtektites, but a few spherules are interpreted as microkrystites (Schulte et al., 2009).

The uppermost 0.5 to 0.7 mm of the spherule layer consists of spherules (~40%) that are generally enriched in FeO and MgO, carbonate clasts and accretionary lapilli

(totaling >50%), shock-metamorphosed quartz and feldspar grains (~10%), and minor lithic fragments (Schulte et al., 2009). The spherules enriched in FeO and MgO may have an ETC, and the silt-to-fine-sand-sized carbonate clasts appear to represent unshocked to highly shocked (melted?) materials (Schulte et al., 2009). Shock-metamorphosed quartz grains contain PDFs and "strawberry" texture, while gneissic lithic fragments show fractures but no PDFs (Schulte et al., 2009). The spherule layer has a positive Ir anomaly (MacLeod et al., 2007), and recent microchemical data reveal that platinum (Pt) group elements (PGEs) are enriched in the top 2 mm of the spherule layer (Berndt et al., 2011).

Most of the spherules are interpreted as impact melt droplets that were derived from crystalline basement rocks and launched on ballistic trajectories (Schulte et al., 2009). The components in the uppermost 0.5-0.7 mm of the spherule layer consist of unshocked-to-highly shocked materials that were derived from both crystalline basement and supracrustal target rocks, and these components were transported in a hot vapor plume that was contaminated with meteoritic material (Schulte et al., 2009; Berndt et al., 2011). The microkrystites are interpreted as reflecting differences in the cooling rate of the impact melt droplets instead of differences in their chemistry (Schulte et al., 2009).

At sites at paleodistances greater than ~7,000 km from the Chicxulub impact structure (e.g., El Kef, Tunisia; Caravaca, Spain), the K-Pg boundary event deposit typically consists of a reddish, thin (~2-5 mm thick) basal impact ejecta clay layer that is directly overlain by a 1 to 25 cm-thick, carbonate-poor, detrital clay layer (Izett, 1987; Smit, 1999; Schulte et al., 2010). The basal impact ejecta layer commonly contains abundant spherules, many of which contain Ni-rich spinels (e.g., Kyte and Bostwick 1995), a positive Ir anomaly, shock-metamorphosed quartz grains, and impact diamonds (Smit, 1999, and references therein). At a few sites in the North Pacific and in Spain

(~7,000-8,000 km), both microtektite-like spherules, some having rotational splash form shapes, and microkrystites are present, but only microkrystites have been reported from most of the sites (Smit, 1999, and references therein).

The microkrystites are spherical with typical diameters $\leq 0.5 \text{ mm}$ (mean D ~0.25 mm), and they are invariably altered to secondary phases (e.g., K-feldspar, smectite, pyrite, glauconite, and goethite) (Smit; 1999; Simonson and Glass, 2004). The internal crystallite pseudomorphs exhibit skeletal, dendritic, feathery, fibroradial and fan-shaped quench textures (Montanari et al., 1983; Smit, 1999, and references therein), and remnant dendritic clinopyroxene crystallites occur in a few spherules at a site in the North Pacific (Smit et al., 1992). Other precursor minerals may have been plagioclase (Smit et al., 1992) and olivine (Smit, 1999). Different groups of microkrystites can occur in a single sample (Smit, 1999), and dendritic and skeletal Ni-rich spinel crystals commonly occur in microkrystites that have a more mafic composition (Smit, 1999) and may have a positive Ir anomaly (e.g., Montanari et al., 1983; Kyte and Bostwick, 1995).

The maximum Ir concentrations in the ejecta layer at ~20 sites (~6,450-11,000 km) range from 0.49 to 70 ppb (Schulte et al., 2010, and references therein). The chromium isotopic method (see Shukolyukov and Lugmair, 1998; Lugmair and Shukolyukov, 1998; Trinquier et al., 2006, for analytical methodology) has been used to confirm an ETC within the K-Pg ejecta layer (Shukolyukov and Lugmair, 1998; Trinquier et al., 2006). The chromium isotopic data suggest a carbonaceous chondrite-type impactor (Shukolyukov and Lugmair, 1998), possibly of CM2 type (Trinquier et al., 2006), for the K-Pg impact event.

Shock-metamorphosed quartz grains with PDFs have a global distribution, and the maximum grain size decreases with increasing distance from North America

(Bohor and Izett, 1986; Bohor et al., 1987; Bohor, 1990). A recent systematic study on a global scale of shock-metamorphosed quartz grains shows that their size (mean and maximum) and abundance (number of grains/g and number of grains/cm²) decrease fairly symmetrically with increasing paleodistance from the Chicxulub impact structure (Morgan et al., 2006). The abundance of shock-metamorphosed quartz grains at the North American sites is much higher than at all other sites (Bostwick and Kyte, 1996; Morgan et al., 2006). The degree of shock metamorphism of the quartz grains, as measured by the average number of sets of PDFs/grain, appears to increase with increasing paleodistance from the Chicxulub impact structure (Morgan et al., 2006). These data support the hypothesis that the Chicxulub impact structure is the source crater for the K-Pg boundary event deposit (Morgan et al., 2006).

The Australasian microtektite layer, the cpx spherule layer, and the K-Pg boundary event deposit illustrate the following characteristics of Phanerozoic confirmed distal impact ejecta/spherule layers. The geographic distribution of an impact ejecta layer appears to be proportional to the size of the source crater, and large craters ($D \ge 100 \text{ km}$) have global-scale impact ejecta layers (Simonson and Glass, 2004). The thickness of an impact ejecta/spherule layer decreases with increasing distance from the source crater (Glass and Simonson, 2013), but for Chicxulub-sized impact events, the spherule layer has a fairly constant mm-scale thickness at very distal (>7,000 km) sites (Smit, 1999). The size and abundance of unmelted shock-metamorphosed grains decrease with increasing distance from the source crater (e.g., Morgan et al., 2006), but for Chicxulub-sized and larger impact events, shock-metamorphosed grains have a global distribution (Morgan et al., 2006; Glass and Simonson, 2013). The average degree of shock metamorphism of the impact ejecta increases with increasing distance from the source

crater (Morgan et al., 2006; Glass and Simonson, 2013), such that beyond a distance of ~20 R_c from the rim of the crater, an unreworked impact ejecta layer consists mostly of spherules, and beyond ~200 R_c, there are little, if any, unmelted impact ejecta that are >125 μ m in size (Glass and Simonson, 2013).

Microkrystites have only been found in impact ejecta layers that are associated with very large (D \geq 100 km) impact structures (Simonson and Glass, 2004; Liu et al., 2009). In the upper Eocene cpx spherule layer, there is no clearly defined geographic separation of microtektites and microkrystites (e.g., Liu et al., 2009). In contrast, in the K-Pg boundary event deposit, only microkrystites have yet been found at paleodistances of greater than ~7,000-8,000 km from the Chicxulub impact structure (Smit, 1999).

Microkrystites commonly contain, or are closely associated with, Ni-rich spinel crystals (e.g., Kyte and Bostwick, 1995; Smit, 1999, and references therein), and microkrystites may have a positive Ir anomaly (e.g., Kyte and Bostwick, 1995; Simonson and Glass, 2004). Microkrystites are generally interpreted to represent condensate droplets from the hot vapor plume that is contaminated with meteoritic material (Smit et al., 1992; Simonson and Glass, 2004; Ebel and Grossman, 2005). Microkrystites would therefore be formed from the most highly shocked material (rock vapor), and their distribution in the K-Pg boundary event deposit supports the concept that the average degree of shock metamorphism of impact ejecta increases with increasing distance from the source crater (Melosh, 1989; Smit et al., 1992; Glass and Simonson, 2013). In contrast, microtektites are generally interpreted to represent rapidly quenched impact melt droplets that were ballistically ejected from the source crater (Smit et al., 1992; Simonson and Glass, 2004). However, it is possible that some microtektites may form as vapor condensates (e.g., Elkins Tanton et al., 2002; Kelly and Elkins-Tanton, 2004; Glass

and Simonson, 2013), and that some microkrystites may form as impact melt droplets (Schulte et al., 2009; Glass and Simonson, 2013), so the formation of these impact spherules is still an open question.

The five Cenozoic impact ejecta/spherule layers (Table 1) are the best characterized of the Phanerozoic impact ejecta/spherule layers, and for four of these layers, the approximate aggregate thickness of spherules is typically <0.1 cm (Simonson and Glass, 2004). Only the microtektite-like spherules in the K-Pg boundary event deposit have an appreciable aggregate thickness of up to 18 cm (Simonson and Glass, 2004). For these spherules, aggregate thicknesses on the order of a decimeter typically occur at sites that are within ~1,000 km of the Chicxulub impact structure (Schulte et al., 2010, and references therein). Of all the Phanerozoic confirmed impact ejecta/spherule layers (Table 1), only the microtektite-like spherules in the K-Pg boundary event deposit have aggregate thicknesses that are comparable to those of the Precambrian spherule layers (Simonson and Glass, 2004).

1.3 Precambrian Spherule Layers

Seventeen spherule layers of putative impact origin are presently known from Archean and Paleoproterozoic stratigraphic successions. The Acraman and Sudbury impact ejecta layers (Table 1), and a Paleoarchean spherule-bearing diamictite layer of putative impact origin, termed the Antarctic Chert Member (ACM)-S2 by Glikson et al. (2004), are not included in this discussion, since spherules appear to be a very minor component in these layers. In Paleoarchean rocks, seven spherule layers (S1-S7; ~3470-3230 Ma; Table 2) occur in the Barberton Greenstone Belt (BGB) of South Africa (SA) (Fig. 1; Lowe and Byerly, 1986, 2010; Lowe et al., 1989, 2003), and the Warrawoona spherule layer (~3470 Ma; Table 2) occurs in the Pilbara craton of Western Australia (WA) (Fig. 1; Lowe and Byerly, 1986; Byerly et al., 2002; Glikson et al., 2004). The Warrawoona spherule layer has been correlated with the S1 spherule layer in the BGB (Byerly et al., 2002).

| Layer/Host Formation (Group) | Location | Aggregate thickness* (cm) | Age (Ma) | Elemental, isotopic, and mineralogical evidence for an impact origin | Refs. |
|---|--------------------------|---------------------------------|-------------|---|------------------------------|
| S5/At contact between the Sheba Fm. and Belvue Road Fm. (Fig Tree) | BGB, SA | <22 | ~3230 | None yet reported | 5, 6, 7 |
| S4/Mapepe (Fig Tree) | BGB, SA | 12 | ~3243 | Ir, PGE, Cr | 1, 4, 5, 8, 10, 11, 12 |
| S3/Various (Fig Tree) | BGB, SA | ~30 | ~3243 | Ir, Cr, NiSp | 1, 4, 8, 9 |
| S2/Mapepe (Fig Tree) | BGB, SA | ~10-70 | ~3260 | Ir?, Cr | 1, 4, 8 |
| S6/Mendon (Onverwacht) | BGB, SA | ~25 | ~3300 | None yet reported | 5, 6, 7 |
| S7/Kromberg (Onverwacht) | BGB, SA | ? | ~3400 | None yet reported | 1, 5, 6, 7 |
| S1/Hooggenoeg (Onverwacht) | BGB, SA | ~6 | ~3470 | Ir? | 1, 3, 4 |
| Warrawoona/Apex Basalt (Warrawoona) | Pilbara craton, WA | ~5 | ~3470 | None yet reported | 1, 2, 3 |

Table 2:Paleoarchean spherule layers.

*The aggregate thicknesses are estimated from layer thickness and percent spherules, and most of the values are from Glass and Simonson (2012).

Abbreviations: BGB = Barberton Greenstone Belt; Cr = Chromium isotopic data; Fm. = Formation; Ir = Positive iridium anomaly; NiSp = Nickel-rich spinel;

PGE = Platinum Group Elements with close to chondritic ratios; Refs. = References; SA = South Africa; WA = Western Australia.

References: ¹Glass and Simonson, 2012; ²Lowe and Byerly, 1986; ³Byerly et al., 2002; ⁴Lowe et al., 2003; ⁵Lowe and Byerly, 2010; ⁶Byerly and Lowe, 2010; ⁷D. R. Lowe, personal communication, 2011; ⁸Kyte et al., 2003; ⁹Byerly and Lowe, 1994; ¹⁰Lowe et al., 1989; ¹¹Kyte et al., 1992; ¹²Shukolyukov et al., 2000.



Figure 1: Generalized location map for the Precambrian spherule layers. Modified after Glass and Simonson (2012, their Fig. 1B), and used with permission from the Mineralogical Society of America.

In Neoarchean to early Paleoproterozoic rocks (~2630-2490 Ma), five spherule layers (Table 3) occur in the Hamersley Basin of Western Australia (Fig. 1; Simonson et al., 2009a, 2009b, and references therein; Hassler et al., 2011), and three spherule layers (Table 3) occur in the Griqualand West Basin of South Africa (Fig. 1; Simonson et al., 2009a, 2009b, and references therein). The Grænsesø spherule layer (Table 3) occurs in South-West Greenland (SWG) (Fig. 1; Chadwick et al., 2001; Smith et al., 2006). The age of the Grænsesø spherule layer is not well-known, but its host strata were probably deposited between ~2030-1848 Ma (see section 2.4). The proposed correlations for the Neoarchean to early Paleoproterozoic spherule layers in the Hamersley Basin (WA) and Griqualand West Basin (SA) (Rasmussen et al., 2005; Simonson et al., 1999, 2009a, 2009b, and references therein; Hassler et al., 2011; Goderis et al., 2013) are shown in Figure 2. If all the proposed correlations are correct, then the 17 Precambrian spherule layers actually record 12 separate impact events.

| Layer/Host Formation (Group) | Location | Aggregate thickness* (cm) | Age (Ma) | Elemental, isotopic, and mineralogical evidence for an impact origin | Refs. |
|---|----------|---------------------------------|----------------|---|-----------------------------------|
| Grænsesø/Grænsesø (Vallen) | SWG | ~25 | ~2030- 1848 | None yet detected | 7, 28, 29, 30, 31 |
| Kuruman/Kuruman Iron Fm. (Ghaap) | GWB, SA | ~0.5 | ~2490 | None yet reported | 3, 4, 7, 19, 25, 26, 27 |
| Dales Gorge/Dales Gorge Member, Brockman Iron Fm. (Hamersley) | HB, WA | ~6 | ~2490 | Ir, PGE, Cr, NiP | 4, 7, 12, 20, 22, 23, 24 |
| Bee Gorge/Wittenoom (Hamersley) | HB, WA | ~1-3 | ~2540 | Ir, PGE | 4, 7, 15, 17, 20, 21 |
| Reivilo/Reivilo (Ghaap) | GWB, SA | 2-2.5 | ~2560 | Ir, PGE | 3, 4, 7, 18, 19 |
| Paraburdoo/Wittenoom (Hamersley) | HB, WA | 2 | ~2570 | Ir, PGE, NiSp | 7, 15, 16, 17, 18 |

 Table 3:
 Neoarchean and Paleoproterozoic spherule layers.

Table 3: continued

| Layer/Host Formation (Group) | Location | Aggregate thickness* (cm) | Age (Ma) | Elemental, isotopic, and mineralogical evidence for an impact origin | Refs. |
|---|----------|---------------------------------|----------------|---|--------------------------------------|
| Jeerinah/Jeerinah (Fortescue) | HB, WA | 0.4-20 | ~2630 | Ir, PGE, Cr, ShQ | 4, 7, 8, 10, 11, 12, 13, 14 |
| Carawine/Carawine Dolomite (Hamersley) | HB, WA | ~30 | ~2630 | Ir, PGE, Cr | 3, 4, 7, 8, 9 |
| Monteville/Monteville (Ghaap) | GWB, SA | ~6 | ~2650- 2588 | Ir, PGE | 1, 2, 3, 4, 5, 6, 7 |

*The aggregate thicknesses are estimated from layer thickness and percent spherules, and the values are from Glass and Simonson (2012).

Abbreviations: Cr = Chromium isotopic data; Fm. = Formation; GWB = Griqualand West Basin; HB = Hamersley Basin; Ir = Positive iridium anomaly; NiP = Ni-rich phases; NiSp = Nickel-rich spinel; PGE = Platinum Group Elements with close to chondritic ratios; Refs. = References; SA = South Africa; ShQ = One shock-metamorphosed quartz grain with PDFs; SWG = South-West Greenland; WA = Western Australia. References: ¹Simonson et al., 1999; ²Simonson et al., 2000a; ³Simonson et al., 2009a, and references therein; ⁴Simonson et al., 2009b; ⁵Gutzmer and Beukes, 1998; ⁶Martin et al., 1998; ⁷Glass and Simonson, 2012; ⁸Rasmussen et al., 2005; ⁹Simonson and Hassler, 1997; ¹⁰Rasmussen and Koeberl, 2004; ¹¹Simonson et al., 2000b; ¹²Trendall et al., 2004; ¹³Hassler et al., 2005; ¹⁴Rasmussen and Fletcher, 2010; ¹⁵Hassler et al., 2011; ¹⁶Trendall et al., 1998; ¹⁷Woodhead et al., 1998; ¹⁸Goderis et al., 2013; ¹⁹Schröder et al., 2006; ²⁰Simonson, 1992; ²¹Simonson et al., 1998; ²²Pickard, 2002; ²³Simonson et al., 2002; ²⁴Glikson and Allen, 2004; ²⁵Sumner and Bowring, 1996; ²⁶Altermann and Nelson, 1998; ²⁷Pickard, 2003; ²⁸Chadwick et al., 2001; ²⁹Smith et al., 2006; ³⁰Kalsbeek and Taylor, 1985; ³¹Nilsson et al., 2010.



Figure 2: Proposed correlation chart for Neoarchean and early Paleoproterozoic spherule layers from the Hamersley Basin (two columns on left) of Western Australia and the Griqualand West Basin (column on right) of South Africa. The dashed lines show the proposed correlations. Fm. = Formation; SL = spherule layer. Modified after Hassler et al. (2011, their Fig. 1), and used with permission from the Geological Society of America.

The Precambrian spherule layers are distinctive discrete beds or sequences of related beds that are ~3 mm up to 24.7 m thick, but most of the layers are a few decimeters to ~100-300 cm thick (Lowe et al., 2003; Simonson and Glass, 2004; Glikson et al., 2004; Simonson et al., 2009a; Lowe and Byerly, 2010; Byerly and Lowe, 2010; Hassler et al., 2011). Twelve of the spherule layers are presently known to have a

minimum lateral persistence of 12-330 km (Simonson and Glass, 2004; Simonson et al., 2009a; Hassler et al., 2011). Most of the spherule layers appear to have been deposited in below-wave base marine paleoenvironments along continental margins (Simonson and Glass, 2004). However, many of the spherule layers appear to represent discrete high-energy events in their host successions (Simonson and Glass, 2004).

Many of the spherule layers contain granule-to-boulder-sized, intrabasinal rip-up clasts, and/or silt-to-coarse sand-sized terrigenous grains (Simonson and Glass, 2004). The rip-up clasts are typically angular and tabular, and they commonly consist of chert, argillite, and carbonate lithologies that are similar to those of the subjacent strata (Simonson and Glass, 2004). The high-energy, reworked spherule layers are generally interpreted as having been deposited by several impact-induced mechanisms, including tsunami waves, currents, bottom return flow and/or turbidity currents, and sediment gravity flows (e.g., Simonson et al., 1999, 2009a; Hassler et al., 2000; Hassler and Simonson, 2001; Lowe et al., 2003; Simonson and Glass, 2004; Lowe and Byerly, 2010).

In the reworked spherule layers, spherules typically comprise ~1-50 vol%, and they typically have aggregate thicknesses of ~0.4-30 cm (Simonson and Glass, 2004; Glass and Simonson, 2012). A few spherule layers, at least locally, consist of essentially unreworked spherules that show normal grading, and these layers appear to be suspension-settling fallout deposits (Lowe et al., 2003; Simonson et al., 2009a; Lowe and Byerly, 2010; Hassler et al., 2011). The Paleoarchean fallout spherule layers are typically 25-40 cm thick (Lowe et al., 2003; Lowe and Byerly, 2010), whereas the Neoarchean fallout layers are ~2 cm thick (Simonson et al., 2009a; Hassler et al., 2011).

Most of the Precambrian spherules are $\leq 1-2$ mm in diameter (Fig. 3), but spherules in some of the Paleoarchean layers are up to 2-4 mm in diameter (Lowe et al., 2003; Simonson and Glass, 2004). Most spherules have spherical-to-ovoid shapes, but rare teardrops and dumbbells have been reported (e.g., Chadwick et al., 2001; Lowe et al., 2003; Simonson, 2003; Simonson et al., 2009a). The spherules have been replaced by secondary phases, most commonly, quartz, sericite, chlorite, K-feldspar, and carbonates (Lowe et al., 2003; Simonson, 2003). The only remnant primary phases that have been recognized to date are Ni-rich spinel crystals in some spherules in both the S3 spherule layer in the BGB (Table 2; Byerly and Lowe, 1994; Lowe et al., 2003) and the Paraburdoo spherule layer in the Hamersley Basin (Table 3; Goderis et al., 2013), and submicron-sized Ni-rich phases in the rims of some spherules in the Dales Gorge spherule layer in the Hamersley Basin (Table 3; Glikson and Allen, 2004).



Figure 3: Spherules replaced by K-feldspar from HCl-insoluble residue of the Bee Gorge (Wittenoom) spherule layer. The figure is from Glass and Simonson (2013, their Fig. 8.9), and is used with permission from Springer.

Although the spherules now consist of secondary phases, they commonly exhibit well-preserved, original internal textures, especially in spherules that are replaced by K-feldspar (Simonson, 2003). The spherules commonly exhibit quench and devitrification textures, and clear spots that are interpreted to represent original bubble cavities or glass cores (e.g., Lowe et al., 2003; Simonson, 2003; Simonson et al., 2009b). Internal textures can be quite diverse, but they commonly include inward-radiating fibrous aggregates that nucleated on the edges of spherules, and/or randomly oriented laths, the latter texture being similar to those in finely crystallized basalts (Simonson and Harnik, 2000, and references therein; Simonson, 2003; Hassler et al., 2011, and references therein). Pseudomorphs of primary crystallites are common in many spherules (Simonson and Glass, 2004), and their shapes suggest that many of the original crystallites were plagioclase (Simonson and Harnik, 2000, and references therein; Simonson, 2003; Simonson et al., 2009a, 2009b, and references therein; Hassler et al., 2011), but some may have been olivine or pyroxene (e.g., Lowe et al., 2003; Hassler et al., 2011). The petrographic data support a melt origin for the spherules, and they suggest that many spherules were originally mafic or ultramafic in composition (Simonson and Harnik, 2000; Lowe et al., 2003; Simonson et al., 2009a; Hassler et al., 2011).

In addition to spherules, the Carawine, Jeerinah, and Monteville spherule layers (Table 3) contain fairly abundant irregular melt particles (Simonson et al., 2009b, and references therein). The irregular melt particles have been replaced by secondary phases that are similar to those that replaced the spherules, and the irregular melt particles commonly exhibit diverse internal textures (e.g., Simonson et al., 2000c). The irregular melt particles are commonly larger (up to ~0.7-2 cm in size) and more angular than the spherules, and they typically contain infilled bubble cavities and/or fine-scale relict flow

banding (Simonson et al., 2000c, 2001; Jones-Zimberlin et al., 2006; Kohl et al., 2006). Many irregular melt particles contain minute lath-shaped to acicular crystallite pseudomorphs that commonly exhibit randomly oriented or parallel-fibrous textures (Simonson et al., 2000c, 2009b). Spherules are present in a few of the irregular melt particles and vice versa, an observation that suggests simultaneous formation of the two types of melt particles (Simonson et al., 2001).

Several lines of evidence support an impact origin for the Precambrian spherule layers. The spherules are similar in size and shape to Phanerozoic microtektites and microkrystites (Simonson, 2003). Many spherules exhibit relict internal textures that are similar to those produced by quenching and/or devitrification of silicate melts (Simonson, 2003). The internal textures are quite heterogeneous, but some textures are similar to those observed in the K-Pg spherules from the Gulf of Mexico sites (Simonson, 2003; cf., Schulte and Kontny, 2005). However, many of the spherules have textures that do not closely match those of the Phanerozoic microkrystites (Simonson, 2003).

It should be noted that volcanic basaltic glassy spherules may have similar sizes, shapes, and internal textures (von der Borch, 1971; Melson et al., 1988) to those of the Precambrian spherules, and that pyroclastic layers are present in many of the successions that host the spherule layers (e.g., Hassler and Simonson, 2001; Lowe et al., 2003). However, unlike pyroclastic layers, the spherule layers typically do not contain obvious volcanic materials, e.g., pumice/scoria fragments, shards, Pele's Hair, broken phenocrysts, or accretionary lapilli (Hassler and Simonson, 2001; Chadwick et al., 2001; Lowe et al., 2003; Simonson, 2003). Furthermore, volcanic basaltic glassy spherules typically occur quite near to their source vent, whereas many of the spherule layers

persist for distances of tens to hundreds of kilometers (Simonson, 2003; Lowe et al., 2003; Simonson et al., 2009a; Hassler et al., 2011).

The Ni-rich spinels in spherules from the S3 (Byerly and Lowe, 1994) and Paraburdoo (Goderis et al., 2013) spherule layers, and the Ni-rich particles in spherules from the Dales Gorge spherule layer (Glikson and Allen, 2004) provide further support for an impact origin of the spherule layers. Many of the spherule layers represent highenergy, reworked marine deposits that are similar to the high-energy K-Pg boundary event deposit at the Gulf of Mexico sites (Simonson and Glass, 2004). Therefore, an impact origin for the spherule layers is suggested by their discrete nature, lateral persistence, evidence of high-energy deposition, and the mineralogy and petrography of the spherules (e.g., Byerly and Lowe, 1994; Glikson and Allen, 2004; Simonson and Glass, 2004).

Trace element and chromium isotopic data further support an impact origin for the Precambrian spherule layers. Nine of the 17 spherule layers are known to have positive Ir anomalies (Tables 2 and 3; Lowe et al., 2003, and references therein; Simonson and Glass, 2004, and references therein; Glikson and Allen, 2004; Simonson et al., 2009b; Goderis et al., 2013), and most of the Neoarchean-to-early Paleoproterozoic spherule layers have CI-chondrite-normalized PGE patterns defined by Ir, ruthenium (Ru), Pt, and rhodium (Rh) that strongly suggest the presence of an ETC (Table 3; Simonson et al., 2009b; Goderis et al., 2013). Chromium isotopic compositions confirm an ETC in the S2, S3, and S4 spherule layers of the BGB (Table 2), and these data suggest that the spherule layers were formed by carbonaceous chondrite-type impactors (Shukolyukov et al., 2000; Kyte et al., 2003). Chromium isotopic compositions confirm an ETC in the Carawine, Jeerinah, and Dales Gorge spherule layers in the Hamersley Basin (WA), but not in the

Monteville spherule layer in the Griqualand West Basin, South Africa (Table 3), and these data suggest that most, if not all, of these spherule layers were formed by ordinary chondrite-type impactors (Shukolyukov et al., 2002; Simonson et al., 2009b).

At present, no unmelted shock-metamorphosed grains have been documented from the Paleoarchean spherule layers (Lowe et al., 2003; Lowe and Byerly, 2010; López et al., 2011). One shock-metamorphosed angular quartz grain (~100 μ m in size) containing at least two sets of PDFs was found in a polished thin section made from a drill core sample of the Jeerinah spherule layer (Hamersley Basin) where the layer is 1-2 mm thick (Rasmussen and Koeberl, 2004). This shock-metamorphosed quartz grain supports an impact origin of the Jeerinah spherule layer, and it indicates the presence of quartz in at least some of the target rocks (Rasmussen and Koeberl, 2004). Furthermore, this discovery shows that shock-metamorphosed quartz grains are able to survive in Neoarchean rocks that have undergone diagenesis and low-grade metamorphism (Rasmussen and Koeberl, 2004).

On the basis of one or more of the following parameters, i.e., spherule layer thickness, aggregate thickness of spherules, spherule size, Ir fluence, and extraterrestrial Cr fluence, and using certain assumptions (e.g., see Lowe et al., 2003; Glikson, 2005), the diameters of the impactors that produced several of the Paleoarchean to Paleoproterozoic spherule layers have been estimated at ~5-70 km (Lowe et al., 1989, 2003, and references therein; Byerly and Lowe, 1994; Shukolyukov et al., 2000; Hassler et al., 2000; Kyte et al., 2003; Glikson et al., 2004; Glikson, 2005; Johnson and Melosh, 2012). The diameters of the impactors that formed the Popigai and Chicxulub impact structures are estimated at ~5-7 km (Vishnevsky and Montanari, 1999, and references therein; Johnson and Melosh, 2012) and 10 ± 4 km (Alvarez et al., 1980; Johnson and Melosh, 2012), respectively, so

many, if not all, of the Precambrian spherule layers should have had a global extent and source craters with $Ds \ge 100$ km (e.g., Simonson et al., 2009b). The fact that many of the Precambrian spherules appear to have had primary microlites/crystallites (Simonson and Glass, 2004), i.e., they are microkrystites, provides further support for the hypothesis that many, if not all, of the Precambrian spherule layers originally had a global extent (see section 1.2.3).

1.4 Statement of the Problem

At present, eight of the 11 confirmed distal impact ejecta/spherule layers are known to contain shock-metamorphosed quartz grains with PDFs, and four of these eight layers also contain one or more high-pressure polymorphs (Table 1). Furthermore, eight of these 11 layers have been linked to source craters, all of which occur on continental crust (Table 1, and references therein). Therefore, shock-metamorphosed grains (commonly SiO₂ phases) have been readily discovered in distal impact ejecta/spherule layers that have source craters on continental crust.

If most, or all, of the 17 Precambrian spherule layers were formed by Chicxulubsized or larger impact events (Simonson et al., 2009b, and references therein; Johnson and Melosh, 2012; Goderis et al., 2013), then shock-metamorphosed grains in the spherule layers should have a global extent (e.g., Glass and Simonson, 2013). Despite ~25 years of research, however, only one unmelted shock-metamorphosed (quartz) grain has been documented (Rasmussen and Koeberl, 2004) in any of the 17 Precambrian spherule layers. This dissertation addresses this conundrum: if the Precambrian spherule layers were formed by large impact events that distributed shock-metamorphosed grains on a global scale, then where are the shock-metamorphosed grains in the spherule layers?

The Sudbury and Acraman impact ejecta layers are not included in the following discussion, since spherules are a minor component in the presently known occurrences of these layers. There are several possible reasons for the apparent near-absence of shockmetamorphosed grains in the Precambrian spherule layers. First, the spherule layers are not of impact origin (e.g., Buick, 1987; Koeberl et al., 1993; Koeberl and Reimold, 1995; Reimold et al., 2000). Second, shock-metamorphosed grains produced during the very early stages of the impact events (French, 1998) were somehow modified (e.g., Croskell et al., 2002) or destroyed during their flight, perhaps due to thermal and/or physical effects concomitant with very large impact events. Third, most, if not all, of the impact events occurred on oceanic mafic/ultramafic crust, thereby producing little, if any, shockmetamorphosed quartz or zircon (e.g., Simonson et al., 1998; Simonson and Harnik, 2000; Lowe et al., 2003). Fourth, diagenetic and/or metamorphic processes destroyed the shock-metamorphosed grains or their shock-metamorphic effects. This possibility is more likely for mafic/ultramafic ejecta (e.g., Lowe et al., 2003; Simonson and Glass, 2004). Fifth, the samples that have been searched for shock-metamorphosed grains are from stratigraphic levels within the spherule layers that do not contain shock-metamorphosed grains. Sixth, the number and mass of samples that have been searched for shockmetamorphosed grains have been insufficient to find these grains. Seventh, shockmetamorphosed grains, especially quartz and feldspar, are very difficult to find due to the presence of epiclastic quartzo-feldspathic sand-sized grains in many of the spherule layers (e.g., Simonson et al., 1998; Morgan et al., 2006). Eighth, search techniques have focused on finding sand-sized grains of shock-metamorphosed quartz (e.g., Simonson et al., 1998) and/or zircon (Lowe et al., 2003, and references therein; López et al., 2011). However, many silt-sized (<63 µm) shock-metamorphosed quartz grains were discovered

in the K-Pg boundary event deposit using a scanning electron microscope (SEM) (Morgan et al., 2006).

1.5 Focus of this Research

The primary focus of this research was to search for shock-metamorphosed grains in the Carawine, Jeerinah, Monteville, Bee Gorge, and Grænsesø spherule layers (Table 3). The secondary focus of this research was to test the proposed correlation (e.g., Simonson et al., 2009a, 2009b, and references therein) of the Carawine, Jeerinah, and Monteville spherule layers (Fig. 2). The Carawine spherule layer was originally correlated with the "spherule marker bed" in the Bee Gorge Member of the Wittenoom Formation (Simonson, 1992). The "spherule marker bed" was later termed the Wittenoom spherule layer (e.g., Simonson et al., 2009a, and references therein), but upon the discovery of a new spherule layer in the Paraburdoo Member of the Wittenoom Formation, the Wittenoom spherule layer is now termed the Bee Gorge spherule layer (Hassler et al., 2011). The Carawine spherule layer was later correlated (Simonson et al., 2001) with the newly discovered Jeerinah spherule layer (Simonson et al., 2000b).

Subsequent to the discovery of the Monteville spherule layer (Simonson et al., 1997), it was suggested that this spherule layer may correlate with the "spherule marker bed" (Simonson et al., 1999), but shortly thereafter, the Monteville spherule layer was correlated with the Jeerinah spherule layer (Simonson et al., 2001). Detailed stratigraphic, sedimentologic, petrographic, geochemical, isotopic, and geochronologic data on the spherule layers from the Hamersley Basin and Griqualand West Basin (Table 3) and their host strata, support the correlation of the Carawine, Jeerinah, and Monteville spherule layers (Simonson et al., 2009a, 2009b, and references therein; Hassler et al., 2011; Goderis et al., 2013).

The present research focused on the heavy mineral fraction ($\rho > 2.96 \text{ g/cm}^3$) of the spherule layers for the following reasons. First, petrographic studies of samples from the Carawine (e.g., Simonson, 1992; Simonson et al., 1998; Jones-Zimberlin et al., 2006), Jeerinah (Simonson et al., 2000b; Rasmussen and Koeberl, 2004; Jones-Zimberlin et al., 2006), Monteville (Simonson et al., 1999; Kohl et al., 2006; Jones-Zimberlin et al., 2006), Bee Gorge (Wittenoom) (Simonson, 1992; Simonson et al., 1998), and Grænsesø (Chadwick et al., 2001) spherule layers have to date resulted in the discovery of a single shock-metamorphosed (quartz) grain (Rasmussen and Koeberl, 2004). Therefore, a search for shock-metamorphosed quartz and feldspar grains that would yield grain abundances in more than trace amounts may have a small probability of success. Second, the discovery of shock-metamorphosed zircons would support an impact origin for the spherule layers (e.g., Bohor et al., 1993; Glass and Liu, 2001; Glass et al., 2002). Furthermore, uranium-lead (U-Pb) geochronology on shock-metamorphosed zircons could potentially provide the age(s) of the target rocks and the impact event(s) (e.g., Krogh et al., 1993), and these data could test the proposed correlation of the spherule layers. Third, given the fact that the spherule layers occur in successions that have undergone diagenesis and low-grade metamorphism (Higgins, 1970; Smith et al., 1982; Beukes, 1987; Rasmussen et al., 2001; Sumner and Beukes, 2006, and references therein), and the possibility that they formed from impact events into oceanic mafic/ultramafic rocks (e.g., Simonson et al., 1998; Simonson and Harnik, 2000), it is possible that remnant shock-metamorphosed grains may largely consist of resistant heavy minerals, e.g., anatase, chromite, garnet, ilmenite, and rutile. Fourth, the characterization of the heavy mineral assemblages of the spherule layers may provide a test of the proposed correlation of the Carawine, Jeerinah, and Monteville spherule layers (Fig. 2).

1.6 Significance of this Research

The Precambrian spherule layers have generally been interpreted as of impact origin since their recognition by Lowe and Byerly (1986), but definitive physical evidence for their impact origin (see French, 1998) has been limited to the discovery of a single quartz grain with PDFs in the Jeerinah spherule layer (Table 3; Rasmussen and Koeberl, 2004). It has been proposed that several of the Paleoarchean to early Paleoproterozoic spherule layers may record "mega-impacts" that triggered tectonic and magmatic events that led to abrupt lithologic changes, e.g., the deposition of BIFs and/or other ferruginous sediments (Glikson and Vickers, 2006, 2007, 2010; Glikson, 2006, 2008). However, Simonson et al. (2009c) concluded that most of the Precambrian spherule layers do not exactly coincide with dramatic lithologic or stratigraphic changes in their host successions. Recently, the Paleoarchean to Paleoproterozoic spherule layers (Tables 2 and 3) have been used as terrestrial evidence to support the cratering flux rates that are predicted by computer simulations (Bottke et al., 2012), as well as to estimate the sizes and impact velocities of asteroids that created global-scale spherule layers (Johnson and Melosh, 2012). The implicit assumption of an impact origin for the Precambrian spherule layers should be verified by the discovery of shock-metamorphosed grains in these layers (see French, 1998).

Precambrian spherule layers have great potential to serve as chronostratigraphic horizons for the correlation of well-preserved unfossiliferous supracrustal successions on a global scale (e.g., Simonson et al., 2009a, 2009b). The correlation of spherule layers is not straightforward, and it requires the integration of different types of datasets (e.g., Simonson et al., 2009a, 2009b, and references therein). The fact that new spherule layers continue to be discovered in well-studied successions (e.g., Simonson et al., 2009a; Lowe and Byerly, 2010; Hassler et al., 2011) requires that caution be used in the correlation of

spherule layers (Simonson et al., 2009a, 2009b). This dissertation involves the first detailed attempt at using heavy mineral assemblages as a potential tool to evaluate the proposed correlation of the Carawine, Jeerinah, and Monteville spherule layers (Fig. 2).

Chapter 2

SAMPLES AND THEIR GEOLOGICAL CONTEXT

2.1 Introduction

Twenty-five spherule layer and context hand samples were used for this study. Twenty-two of the samples were collected from surface outcrops, and three of the samples consist of one or two pieces of float that were collected from slopes directly in front of the outcrops. Dr. Bruce M. Simonson provided all the samples from the Carawine Dolomite, Jeerinah Formation, and the Bee Gorge Member of the Wittenoom Formation in the Hamersley Basin, Western Australia (Fig. 4; Tables 4, 5, and 6) and the Monteville Formation in the Griqualand West Basin, South Africa (Fig. 5; Table 7). I collected the four spherule layer samples and one context sample from the Grænsesø Formation in South-West Greenland (see Higgins, 1970), and Dr. Mark T. Hutchison of the Geological Survey of Denmark and Greenland (GEUS) kindly provided the other context sample from the Grænsesø Formation (Fig. 6; Table 8).

All the samples were photographed, weighed, and described, and these data are given in Appendices A-H. Twenty-three samples were weighed either on an Ohaus Triple Beam balance in our laboratory, or on a Sartorius I4800P balance at the Department of Biological Sciences at the University of Delaware. Both balances have a readability of 0.1 g. Context samples X68-1 (Carawine) and II67-1B (Monteville) were weighed at Oberlin College. Descriptions of the spherule layers and their local/regional geological context are given in numerous references (see sections 2.2, 2.3, and 2.4).



Figure 4: Generalized location map for the Carawine (RH, RS, RE, and TTT sites), Jeerinah (Hesta site), and Bee Gorge (BB, TP, and WG sites) samples (see Tables 4, 5, and 6) that were used in this study. DDH186 and WRL-1 are sites of drill cores discussed in Rasmussen and Koeberl (2004). Abbreviations: BB = Bacon Bore; Gp = Group; RE = Ripon Hills southeast; RH = Ripon Hills; RS = Ripon Hills south; TP = Tom Price; TTT = Tarra Tarra turnoff; WG = Wittenoom Gorge. Modified after Simonson et al. (2009a, their Fig. 1A), and used with permission from Elsevier.

| opneraie | Buyer | | | |
|------------------|------------------------------------|----------------------------------|--|------------------------|
| Sample number | Informal site name ¹ | Latitude, longitude ¹ | Position within the spherule layer | Lithology |
| X38-2 | Tarra Tarra turnoff (TTT) | 21°48′S, 121°13′30″E | Sandy upper part of dolomixtite | Dolomixtite |
| 42-1A | Ripon Hills south (RS) | 21°18′S, 120°46′30″E | Within 75 cm of top of layer | Sandy dolomixtite |
| 43-1 | Ripon Hills south (RS) | 21°18′S, 120°46′30″E | Finer zone near top of lowermost subunit | Dolomixtite |
| X24-1 | Ripon Hills (RH) | 21°20.085′S, 120°45.547′E | Lower part | Dolomixtite |
| 84-1 | Ripon Hills south (RS) | 21°18′S, 120°46′30″E | Within 20 cm of base of layer | Calcareous dolomixtite |
| W85-2 | Ripon Hills (RH) | 21°18.661′S, 120°46.356′E | Float from lower part of layer | Dolomixtite |

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| opneru | | |

¹Data are from B. M. Simonson (personal communication, 2013).

Context

| Sample number | Informal site name ¹ | Latitude, longitude ¹ | Position with respect to the spherule layer | Lithology |
|------------------|------------------------------------|----------------------------------|---|--------------------|
| 104175 | Ripon Hills south (RS) | 21°18′S, 120°46′30″E | ~20 m above | Laminated dolomite |
| 104141 | Ripon Hills southeast (RE) | 21°18′30″S, 120°52′E | ~5 m below | Laminated dolomite |
| X68-1 | Tarra Tarra turnoff (TTT) | 21°48′S, 121°13′30″E | 10-20 m below | Laminated dolomite |

¹Data are from B. M. Simonson (personal communication, 2013).

| Sample number | Location | Latitude, longitude ¹ | Position within the spherule layer | Lithology |
|------------------|-----------------|-------------------------------------|--|---|
| X21-1 | Hesta siding | 22°11.8′S, 119°1.6′E | Float from in front of the outcrop that was derived (B. M. Simonson, personal communication, 2013) from the basal thin-bedded zone of the layer (see Hassler et al., 2005) | Melt particle- bearing gravelly sandstone |
| W94-1Q | Hesta siding | 22°11.8′S, 119°1.6′E | Float from in front of the outcrop that was derived (B. M. Simonson, personal communication, 2013) from the basal thin-bedded zone of the layer (see Hassler et al., 2005) | Melt particle- bearing gravelly sandstone |

Table 5:Jeerinah spherule layer samples.

¹Data are from Hassler et al. (2005). Note: Under "Lithology", "Melt particle" refers to both spherules and irregular melt particles (see section 1.3).

 Table 6:
 Bee Gorge Member (Wittenoom Formation) samples.

Spherule layer + Context layer(s)

| Sample number | Informal site name | Latitude, longitude ¹ | Lithologies |
|------------------|------------------------------|-------------------------------------|--|
| 96714A | Tom Price (TP) water tank | 22°45′S, 117°45′E | Basal carbonate lutite (context layer) and spherule-bearing dolomitic lutite |
| 96714B | Tom Price (TP) water tank | 22°45′S, 117°45′E | Basal carbonate lutite (context layer) and spherule-bearing dolomitic lutite |
| BB | Bacon Bore (BB) | 21°58′S, 117°36′E | Spherule-rich layer with carbonate lutite sandwiched between two carbonate lutite context layers |

¹Data are from Simonson et al. (1993a).

Context

| Sample number | Informal site name | Latitude, longitude ¹ | Position with respect to the spherule layer | Lithology |
|------------------|--|-------------------------------------|---|--------------------------|
| 92058 | Wittenoom Gorge (WG) (Cathedral Pool) | 22°19′S, 118°20′E | ~1 m above | Fine-grained calcarenite |

¹Data are from Simonson et al. (1993a).



Figure 5: Generalized location map for the Monteville spherule layer samples (U63-1 and V111; see Table 7) and Monteville context samples (T149-1 and II67-1B; see Table 7) that were used in this study. The samples are from the Monteville farm (MF) site in the Griqualand West Basin, South Africa. Prieska is a town. Fm = Formation. Modified after Simonson et al. (2009a, their Fig. 1B), and used with permission from Elsevier.

Table 7:Monteville Formation samples.

| Spherale L | Ju y CI | | | |
|------------------|--------------------|----------------------------------|------------------------------------|--------------------|
| Sample number | Location | Latitude, longitude ¹ | Position within the spherule layer | Lithology |
| V111 | Monteville farm | 28°36′S, 23°58.5′E | Upper part | Dolomite |
| U63-1 | Monteville farm | 28°36′S, 23°58.5′E | Lower part | Impure dolomite |

Spherule Layer

¹Data are from B. M. Simonson (personal communication, 2013).

Context

| Sample number | Location | Latitude, longitude ¹ | Position with respect to the spherule layer | Lithology |
|------------------|--------------------|----------------------------------|---|-----------|
| II67-1B | Monteville farm | 28°36′S, 23°58.5′E | ~20 cm above | Dolomite |
| T149-1 | Monteville farm | 28°36′S, 23°58.5′E | ~1 m below | Limestone |

¹Data are from B. M. Simonson (personal communication, 2013).



 Figure 6: Location maps for the Grænsesø spherule layer in South-West Greenland. The six samples from the Grænsesø Formation that were used in this study (see Table 8) are from the Midternæs (northernmost) spherule locality. The spherule localities are from Bondesen et al. (1967). K = Ketilidian orogen. Modified after Chadwick et al. (2001, their Fig. 1).

Table 8:Grænsesø Formation samples.

| | Spherule Euger | | | | | | | |
|--|------------------|-----------|----------------------------------|------------------------------------|-------------|--|--|--|
| | Sample number | Location | Latitude, longitude ¹ | Position within the spherule layer | Lithology | | | |
| | GL8904-4 | Midternæs | 61°40′11.3″N, 47°48′9.6″W | Near the top | Dolomixtite | | | |
| | GL8904-3 | Midternæs | 61°40′11.3″N, 47°48′9.6″W | Lower part of upper part | Dolomixtite | | | |
| | GL8904-2 | Midternæs | 61°40′11.3″N, 47°48′9.6″W | Lower part | Dolomixtite | | | |
| | GL8904-1 | Midternæs | 61°40′11.3″N, 47°48′9.6″W | Lower part | Dolomixtite | | | |

Spherule Layer

¹Latitude and longitude were obtained by Global Positioning System (GPS).

Context

| Sample number | Location | Latitude, longitude ¹ | Position with respect to the spherule layer | Lithology |
|------------------|-----------|----------------------------------|---|-----------|
| GL8904-6 | Midternæs | 61°40′11.3″N, 47°48′9.6″W | <1 m above the top | Dolomite |
| SP3 ² | Midternæs | 61.6699432°N, 47.8025431°W | A few meters below | Dolomite |

¹Latitude and longitude were obtained by Global Positioning System (GPS).

²This sample and its location information were provided by Dr. Mark T. Hutchison.

2.2 Western Australia

The Carawine spherule layer and its host formation are characterized in, e.g., Simonson (1992, 2003), Simonson et al. (1993b, 1998, 2000c, 2009b), Simonson and Hassler (1997), Hassler and Simonson (2001), and Hassler et al. (2005). Two measured sections of the Carawine spherule layer in the Ripon Hills area (Fig. 4; Table 4) are given in Hassler and Simonson (2001, their Fig. 5). An outcrop of the Carawine spherule layer in the Ripon Hills area is shown in Simonson (1992, his Fig. 8). A detailed description and a schematic diagram of the Carawine spherule layer at the Tarra Tarra turnoff (TTT) locality (Fig. 4; Table 4) are given in Hassler et al. (2005, p. 766-768).
The Jeerinah spherule layer and its host formation are characterized in, e.g., Simonson et al. (2000b, 2001, 2009b), Simonson (2003), Rasmussen and Koeberl (2004), Hassler et al. (2005), Jones-Zimberlin et al. (2006), Glikson and Vickers (2007), and Rasmussen and Fletcher (2010). A detailed description and a schematic diagram of the Jeerinah spherule layer at the Hesta locality (Fig. 4; Table 5) are given in Hassler et al. (2005, p. 764-766). The outcrop at the Hesta locality is shown in Glikson (2006, his Fig. 4B).

The Bee Gorge (Wittenoom) spherule layer and its host formation (Wittenoom) are characterized in, e.g., Simonson (1992, 2003), Simonson et al. (1993a, 1993b, 1998, 2009b), Simonson and Hassler (1997), Hassler et al. (2000, 2005), Hassler and Simonson (2001), Simonson and Glass (2004), and Scally and Simonson (2005). A measured section of the Wittenoom Formation at the Tom Price (TP) locality (Fig. 4; Table 6) is given in Simonson et al. (1993a, their Fig. 2). An outcrop of the Bee Gorge (Wittenoom) spherule layer and the enclosing strata at the TP locality is shown in Simonson and Glass (2004, their Fig. 8). The Bee Gorge (Wittenoom) spherule layer at the Bacon Bore (BB) locality (Fig. 4; Table 6) is described and illustrated in Simonson (1992, his Fig. 6C) and Hassler et al. (2000, their Fig. 3).

2.3 South Africa

The Monteville Formation is characterized in, e.g., Beukes (1987), Altermann and Siegfried (1997), Sumner and Beukes (2006), and Schröder et al. (2006), and the Monteville spherule layer is characterized in Simonson et al. (1999, 2000a, 2009a, 2009b) and Kohl et al. (2006). The Monteville spherule layer at the Monteville farm locality (Fig. 5; Table 7) is described in detail in Simonson et al. (1999) and Kohl et al. (2006). The lower part of the Monteville spherule layer from which sample U63-1

(Table 7) was collected is shown in Simonson et al. (1999, their Fig. 7A), and a sample from the upper part of the Monteville spherule layer that is similar to sample V111 (Table 7) is shown in Simonson et al. (1999, their Fig. 7B).

2.4 South-West Greenland

The Grænsesø Formation predominantly consists of pelite, shale, and dolomite, with minor chert and cherty quartzite in the Grænseland (Bondesen, 1970) and Midternæs (Higgins, 1970) areas of South-West Greenland (Fig. 6). The Grænsesø Formation contains very minor coarse clastic material in the Midternæs area (Higgins, 1970). The Grænsesø Formation has undergone low greenschist facies metamorphism in the Grænseland (Bondesen, 1970) and Midternæs (Higgins, 1970) areas.

The Grænsesø Formation is the uppermost formation of the Vallen Group (e.g., Higgins, 1970, his Table 2), and schematic stratigraphic sections of the Vallen Group in the Midternæs area are given in Higgins (1970, his Fig. 6). The Vallen Group is overlain by the Sortis Group that primarily consists of pillow lavas, pillow breccias, gabbroic sills, felsic pyroclastic rocks, and sedimentary rocks (Bondesen, 1970; Higgins, 1970). In the Midternæs area, the contact between the Vallen and Sortis Groups was locally mapped as a thrust (Higgins, 1970).

The ages of the Vallen and Sortis Groups are not well-known (Garde et al., 2002), but they are in the interval of ~2130-1848 Ma (see discussion in Chadwick et al., 2001, p. 332; Garde et al., 2002). The older date $(2130 \pm 65 \text{ Ma})$ was obtained on two regional sets of dolerite dikes that cut the Archean basement rocks, and the samples are from an area that is ~50 km west of the Midternæs area (Kalsbeek and Taylor, 1985). These dolerite dikes are correlated with amphibolite dikes that cut the Archean basement but not the Vallen and Sortis Groups (Chadwick et al., 2001, p. 332). Recently, Nilsson et al.

(2010) obtained U-Pb baddeleyite ages of ~2030-2050 Ma on one of the dolerite dike sets that was dated by Kalsbeek and Taylor (1985). These recently dated samples are from areas that are farther north (Nilsson et al., 2010) than the area that was sampled by Kalsbeek and Taylor (1985). Therefore, the ages of the Vallen and Sortis Groups may fall within the interval of ~2030-1848 Ma, but radiometric dating of samples from the two groups is necessary for more accurate ages.

A spherule layer ("spherule-bearing dolomite layer") that is ~1 m thick was described from the upper part of the Grænsesø Formation at two localities in Grænseland and one locality in Midternæs (Fig. 6; Bondesen et al., 1967; Bondesen, 1970; Higgins, 1970). Two additional localities of the spherule-bearing dolomite layer were found near the locality in northernmost Grænseland near Sioralik glacier (Fig. 6) in the summers of 1966 (Raunsgaard Pedersen, 1966; Lam and Raunsgaard Pedersen, 1968) and 1967 (Raunsgaard Pedersen, 1968), thus bringing the total number of localities of the spherule-bearing dolomite layer to five (Higgins, 1970). The five localities span a distance of ~25 km, and the spherule-bearing dolomite layer occurs at the same stratigraphic position in the Grænsesø Formation at all five localities (Bondesen et al., 1967; Raunsgaard Pedersen, 1968).

The texture and mineralogy of the spherule-bearing dolomite layer are described in Bondesen et al. (1967, p. 20). Petrographic descriptions of the spherules ("globular structures"; D ~0.25-1.5 mm), preliminary results on the types of organic compounds associated with the spherules, and carbon isotopic analyses of the carbonaceous matter and carbonate in the spherule-bearing dolomite layer are given in Bondesen et al. (1967). A detailed analysis of the organic compounds is given in Lam and Raunsgaard Pedersen (1968). The spherules were interpreted as microfossils (*Vallenia* sp.), an interpretation

that was supported by their close association with, and the carbon isotopic composition of, the organic compounds (Bondesen et al., 1967, Lam and Raunsgaard Pedersen, 1968).

On the basis of petrographic analysis of thin sections, as well as the stratigraphic and sedimentologic characteristics of the spherule-bearing dolomite layer, the spherules were reinterpreted as distal impact melt ejecta that have been replaced by secondary phases (Chadwick et al., 2001). In thin section, cherty fragments up to ~4 mm in size, and well-sorted epiclastic quartzose sand (mostly <250 μ m in size) were also observed in the Grænsesø spherule layer (Chadwick et al., 2001). At the beginning of the present research project, only a very small amount of material from the Grænsesø spherule layer was available for study. In order to obtain more material of the Grænsesø spherule layer, as well as context samples from the Grænsesø Formation, and to examine the Grænsesø spherule layer in the field, I made two attempts to relocate the Grænsesø spherule layer.

In early August, 2003, I reached the area of the southernmost locality of the Grænsesø spherule layer in Grænseland (Fig. 6). I found an old campsite (rusty cans and a tent ring) situated in the upper part of the Grænsesø Formation at the *Vallenia* locality shown in Bondesen et al. (1967, their Fig. 2), but after two days of careful examination of these strata, I was unable to relocate the Grænsesø spherule layer. I collected three context samples of different lithologies from the upper part of the Grænsesø Formation, but these samples are not included in the present research.

In early August, 2004, using a map kindly provided by Dr. A. K. Higgins of the Geological Survey of Denmark and Greenland, I relocated the single known locality of the Grænsesø spherule layer in the Midternæs area (Fig. 6; Higgins, 1970). I first encountered float of the Grænsesø spherule layer, and I collected five float samples of the Grænsesø spherule layer (Table 9). In the following discussion, as well as in other parts

of this dissertation (e.g., Appendices A-H), colors with codes (e.g., N3 or 10YR 8/2) are from the rock-color chart (Geological Society of America, The Rock-Color Chart Committee, 1991). The float of the Grænsesø spherule layer typically has a distinctive pink coloration and very noticeable dark gray (N3), cm-sized, cherty clasts (Fig. 7). The fine-grained, crystalline dolomitic matrix is medium gray (N5) on a fresh surface. Dark gray (N3)-to-black (N1) spherules (D ~0.5-1 mm) are dispersed through the matrix (Fig. 8), and they comprise up to ~20 vol% of the rock. Some float also contains minor cm-to-dm-sized, subrounded-to-angular clasts of buff, laminated dolomite, and the chert and dolomite clasts can have tabular or elongate shapes (Fig. 8). The dolomite clasts appear to be similar to dolomite beds that occur lower in the stratigraphic section (Fig. 9).

| Float sample | Site | Latitude, longitude (GPS) |
|--------------------|------|----------------------------|
| GL8804-1, GL8804-2 | 1 | 61°40'8.3"N, 47°48'17.0"W |
| GL8804-3 | 2 | 61°40'8.8"N, 47°48'13.5"W |
| GL8804-4 | 3 | 61°40'9.4"N, 47°48'12.7"W |
| GL8804-5 | 4 | 61°40'10.1"N, 47°48'12.2"W |

 Table 9:
 Float samples of the Grænsesø spherule layer and their GPS coordinates.



Figure 7: Grænsesø spherule layer float (slf) at site 2 (Table 9). The float has a distinctive pink color and abundant gray chert (ch) clasts. The pick is ~33 cm long.



Figure 8: Grænsesø spherule layer float about 9 m uphill from site 1 (Table 9). The rock consists of tabular chert (ch) and dolomite (dol) clasts that are set in a dolomitic matrix that contains mm-sized dark gray (N3) spherules and chert grains. The pen is ~15 cm long.



Figure 9: Outcrop (61°40'11.9"N 47°48'15.1"W) of buff-weathering, laminated, finegrained dolomite that is stratigraphically below the Grænsesø spherule layer. The pick is ~33 cm long.

The float of the Grænsesø spherule layer occurs in a narrow band that is ~15-18 m northwest of, stratigraphically below, and parallel to, a resistant outcrop of dolomite (Fig. 10). The strata in this immediate area generally strike northeast and dip at moderate angles to the southeast (Higgins, 1970). I traced the float of the Grænsesø spherule layer uphill (Fig. 10) towards the northeast for ~140 m, and relocated the outcrop of the Grænsesø spherule layer at the axis of a northwest-trending spur. Due to an approaching storm system and minimal rations, I had only one day to examine and sample the outcrop of the Grænsesø spherule layer.



Figure 10: Grænsesø spherule layer float band looking northeast (uphill) from site 2 toward site 3 (Table 9). Dark lines mark the edges of the float band.At right is a resistant outcrop of dolomite that is stratigraphically above the Grænsesø spherule layer.

The Grænsesø spherule layer outcrop is situated at $61^{\circ}40'11.3"N 47^{\circ}48'9.6"W$, and it is marked by a cairn that I constructed ~1 m above it. This is a low outcrop that is ~4 m long, and it appears to be truncated on its northeast side by a fault (low-angle?) that juxtaposes the Grænsesø spherule layer to the southwest against dark gray chert beds to the northeast (Fig. 11). White quartz veinlets are present in the chert beds and the Grænsesø spherule layer near the suspected fault.



Figure 11: Grænsesø spherule layer (sl) outcrop (looking southeast) that is apparently in fault (heavy black line) contact with dark gray chert (ch) beds (on left). The fault is concealed by rubble. An outcrop of interbedded dolomite (dol), chert, and shale that is above the Grænsesø spherule layer is at the upper right. The base of the escarpment that is formed from the igneous rocks of the Sortis Group is in the background. The pick (~33 cm long) is at the base of the outcrop, and the pink flagging is near the top of the outcrop. I briefly examined the area along strike to the northeast and saw no evidence of the Grænsesø spherule layer, but this area requires further examination. Southeast of the Grænsesø spherule layer, and stratigraphically above it, are outcrops and bands of interbedded dolomite, shale, and chert (Fig. 11) of the uppermost Grænsesø Formation (Higgins, 1970). A few tens of meters farther uphill to the southeast is an escarpment that is formed from the basal igneous rocks of the Sortis Group (Fig. 11; Higgins, 1970). The following discussion of the Grænsesø spherule layer outcrop includes data from Smith et al. (2006).

The outcrop is partially obscured by rubble, and the Grænsesø spherule layer appears to dip (<15°) to the southeast. The lower and upper contacts of the Grænsesø spherule layer are covered by rubble, but the Grænsesø spherule layer has a minimum thickness of 145 cm. In outcrop, the Grænsesø spherule layer weathers a very pale orange (10YR 8/2)-to-grayish orange (10YR 7/4) color, and it typically does not show the intensity of the pink coloration that is characteristic of the float.

The Grænsesø spherule layer is a massive dolomixtite with subrounded-to-angular clasts of medium dark gray (N4)-to-black (N1) chert and grayish orange (10YR 7/4)-to-pale yellowish brown (10YR 6/2) dolomite that are supported by a medium dark gray (N4), fine-grained dolomitic matrix that comprises ~40-50 vol% of the rock. The chert and dolomite clasts are generally \leq 10 cm in size, but several large dolomite clasts (~8 by 30-60 cm) occur in the upper part of the outcrop. A decimeter-sized dolomite clast within a piece of float that lies at the base of the outcrop is shown in Figure 12. The largest clast that I observed is a dolomite clast that occurs near the top of the outcrop at its northeast margin (Fig. 13). This is a wedge-shaped clast that is ~15-40 cm thick and

 \sim 110 cm long. The clast consists of two adjoining dolomite layers, one light gray (N7) and the other grayish orange (10YR 7/4).

No spherules were observed within any of the dolomite or chert clasts in the outcrop. Locally, chert and dolomite clasts appear to have been disrupted and injected by matrix material (Fig. 14). The long axes of some of the tabular and elongate chert clasts show an alignment that is roughly parallel to the contacts of the Grænsesø spherule layer. The alignment of tabular chert clasts in a piece of float is shown in Figure 15.



Figure 12: Buff-weathering dolomite clast (~53 cm long) within a piece of Grænsesø spherule layer float that is just below the spherule layer outcrop. Note the absence of spherules and chert debris in the dolomite clast. The pick is ~33 cm long.



Figure 13: Large dolomite clast (dc) within the Grænsesø spherule layer (sl) outcrop at its northeast margin. The heavy black dashed lines delineate the clast. The pink flagging is along or near the upper margin of the clast. Subvertical quartz \pm carbonate veinlets (vnlts) cut the clast and the spherule layer matrix (upper right). The pick (in the shadow at the lower right) is ~33 cm long.



Figure 14: Buff, subrounded dolomite clast (dc) in the upper part of the Grænsesø spherule layer outcrop. The clast has been disrupted and cross-cut by the matrix that contains spherules and chert debris.



Figure 15: Elongated chert clasts that show an alignment of their long axes in a piece of Grænsesø spherule layer float that occurs just below the spherule layer outcrop. The pick is ~33 cm long.

Evenly dispersed in the matrix of the Grænsesø spherule layer are grayish-black spherules and subrounded-to-angular, coarse sand-to-pebble-sized chert grains, each of which comprises ~15-20 vol% of the rock, and very fine-to-coarse sand-sized, subangular epiclastic quartz grains that comprise ~1-2 vol% of the rock. No obvious volcanic material, e.g., pumice, scoria, shards, or volcanic lithic clasts, and no distinctive bedding were observed in the Grænsesø spherule layer. The larger dolomite clasts appear to be concentrated in the upper part of the Grænsesø spherule layer, but this observation needs to be verified by further study of the outcrop after the rubble has been removed. Both the clasts and the matrix of the Grænsesø spherule layer are cut by a set of subvertical, light gray (N7)-to-grayish pink (5R 8/2), quartz \pm carbonate veinlets that are typically less than ~5 mm wide (Fig. 13). The locations of the four Grænsesø spherule layer samples (see Table 8) that were analyzed in this study are shown in outcrop in Figure 16. On the basis of hand sample descriptions (Appendix G), the maximum size of the mm-sized chert grains or fragments steadily decreases upward in the Grænsesø spherule layer from ~7-8 mm (sample GL8904-1) near the base to ~2 mm (sample GL8904-4) near the top.

About 3 m southeast of the top of the Grænsesø spherule layer outcrop, and just southwest of the cairn, there is a small outcrop of a dolomite layer (~20 cm thick) that appears to directly overlie the Grænsesø spherule layer, although the contact is covered by rubble (Fig. 17). This is a medium dark gray (N4), fine-grained, dense dolomite that is very light gray (N8) and yellowish gray (5Y 8/1) on the weathered surface. This bed appears to be massive, but it may be faintly laminated in part. No spherules, clasts, or siliciclastic grains were observed in this dolomite. Grænsesø context sample GL8904-6 (Table 8 and Appendix H) was collected from this outcrop. During a cursory examination of the strata both above and below the Grænsesø spherule layer over an interval of a few tens of meters, no other layer was found that contains spherules and/or gravelly debris.

On August 10, 2006, Dr. Mark T. Hutchison of the Geological Survey of Denmark and Greenland and Louise Nielsen (University of Copenhagen) accessed the Grænsesø spherule layer outcrop by helicopter, using my GPS coordinates, and they spent 1.5 hours describing and sampling the outcrop and nearby rocks. The location and identity of the Grænsesø spherule layer outcrop were confirmed, as was the observation that the spherules appear to be restricted to this single horizon (Hutchison, personal communication, 2006). Grænsesø context sample SP3 (Table 8 and Appendix H) was collected from an outcrop of thin-to-medium-bedded, fine-grained, massive dolomite

(Fig. 18) that occurs a few meters stratigraphically below the Grænsesø spherule layer (Hutchison, personal communication, 2006).



Figure 16: Locations in the Grænsesø spherule layer outcrop of the four samples (see Table 8) that were analyzed in this study. View is to the southeast. The pick (lower right) is ~33 cm long, and it is at the base of the outcrop. The pink flagging (upper center) is near the top of the outcrop.



Figure 17: Outcrop of fine-grained dolomite that is just above the Grænsesø spherule layer. Grænsesø context sample GL8904-6 (see Table 8) was collected from this outcrop. The pick is ~33 cm long.



Figure 18: Thin-to-medium beds of fine-grained dolomite that are a few meters stratigraphically below the Grænsesø spherule layer. Grænsesø context sample SP3 (see Table 8) was collected from this outcrop. The sledge hammer is ~70 cm long. The photograph was taken by Dr. Mark T. Hutchison and it is used with his permission.

Chapter 3

METHODS

3.1 Sample Preparation

The preparation of the 25 samples (Appendices I-P) turned out to be a slow and laborious process that took several years to complete. During the process, care was taken to minimize contamination of the samples. The trim saw table and blade were washed and brushed before each sample was sawn and/or trimmed. All glassware was washed with soap and warm water and then rinsed with acetone just prior to use. Separatory funnels were likewise thoroughly cleaned between the heavy liquid separations involving different samples, layers/sublayers within a sample, subsamples, and size fractions. All sample crushing was done with a steel mortar and pestle that were cleaned with acetone. All sieving (wet and dry) was done with W. S. Tyler standard 3-inch brass sieves, and just prior to use, the sieves were ultrasonically cleaned, and they were checked for grains or flaws in the mesh using a binocular microscope. The binocular microscopes that were used in this study have up to 50× magnification.

The magnets that were put in the beakers during acid dissolution were washed with soap and warm water and rinsed with acetone. The beakers were covered with plastic wrap during acid dissolution, the dilution and decantation process, and settling of the $<38 \mu m$ acid-insoluble material. Heavy liquid was filtered just before it was poured into a separatory funnel, and typically, it was filtered again before it was returned to the bottle. The boxes containing filters, weighing paper, and vials were always kept closed.

Prior to the weighing, transfer, and alignment of grains, or the weighing of the $<38 \mu m$ acid-insoluble material, the small brushes used in these steps were ultrasonically cleaned, and they were checked for grains using a binocular microscope.

The minor laboratory contamination that was noted consisted of a few malachite and solder particles from the laboratory water pipes, rust particles from the fume hood and/or the separatory funnel stands, and plastic material/fibers. Early in the project, subsample 9.5938 g of Jeerinah spherule layer sample W94-1Q (Appendix K), and the >38 μ m size fractions of the two context layers in Bee Gorge sample BB (Appendix L), each went through a warm bath of 1,2,4 trichlorobenzene for four days in order to dissolve the plastic fibers. These attempts to dissolve the fibers were unsuccessful, and they were discontinued.

Seventeen samples were not crushed at any time during preparation, but eight samples (W94-1Q, X21-1, BB, 96714A, 96714B, X68-1, 92058, V111) underwent varying degrees of crushing at one or more stages of sample preparation. The eight samples typically contained abundant fine-grained matrix, carbonate lutite, or mm-sized (and smaller) acid-resistant grains. The Jeerinah spherule layer samples W94-1Q and X21-1 did not react with room-temperature HCl, and prior to acid dissolution on the hotplate (see below), they were crushed so that most of the material would pass through a 250 µm sieve (Appendix K). The spherule layer and the two context layers in Bee Gorge sample BB each underwent minor crushing prior to acid dissolution (Appendix L).

The basal carbonate lutite layers in Bee Gorge samples 96714A and 96714B underwent minor crushing prior to acid dissolution, and later, the acid-insoluble material was crushed below 125 μ m (Appendix L). Subsample 10.3574 g from the spherule layer part of sample 96714A underwent minor crushing prior to acid dissolution. After acid

dissolution, the acid-insoluble material of subsample 10.3574 g was crushed below 125 μ m before the spherules could be handpicked from the >250 μ m size fraction, so there are no weight data available for the spherules in this subsample (Appendix L). The acid-insoluble material in the >250 μ m size fractions of subsamples 7.3433 g and 8.5769 g of sample 96714A underwent minor crushing, followed by handpicking of the spherules and spherule fragments, and the material was then crushed below 125 μ m (Appendix L). Each of the remaining six subsamples from the spherule layer parts of samples 96714A and 96714B were crushed below 125 μ m after the spherules had been handpicked from the acid-insoluble material in the >250 μ m size fractions (Appendix L).

Millimeter-sized (and smaller) acid-resistant grains in subsample 304.7 g of Carawine context sample X68-1 were crushed after acid dissolution, and the acidinsoluble material was wet sieved again (Appendix J). Millimeter-sized (and smaller) acid-resistant grains in the two subsamples of Bee Gorge context sample 92058 were crushed in between acid dissolution (Appendix L). Millimeter-sized (and smaller) acidresistant grains in the >250 μ m size fraction of subsample 106.1 g of Monteville spherule layer sample V111 were largely crushed below 250 μ m, and the acid-insoluble material was wet sieved again (Appendix M). In the following discussion, I summarize the general sample preparation procedure.

The samples were typically sawn into smaller pieces, and the weathering rinds and associated oxidized zones were trimmed off using a water-cooled trim saw with a diamond-tipped blade. The sawn pieces were rinsed with tap and/or distilled water. For about two-thirds of the samples, the pieces were immersed in concentrated HCl or HNO₃ (see below) for ~10-30 seconds with hand agitation, and then rinsed with tap and/or distilled water. For about half of the samples, the pieces were put in a glass beaker, and the beaker was largely filled with tap or distilled water. The contents of the beaker underwent several minutes of ultrasonic agitation, and the pieces were then removed from the beaker and rinsed with tap and/or distilled water. For all 25 samples, after the pieces had been rinsed with tap and/or distilled water, the wet pieces were placed in a glass beaker, and this beaker was put in an oven at a temperature (T) of ~60-70 °C. The minimum drying time was overnight.

Subsamples, or pieces combined into a subsample, were weighed with either an Ohaus Triple Beam balance with a readability of 0.1 g, or a Sartorius 1801 MP8 electronic analytical balance with a readability of 0.1 mg. The analytical balance has a weighing range of 111 g, and most of the smaller pieces (<100 g) were weighed on the analytical balance. All the larger pieces (>100 g) were weighed on the Ohaus Triple Beam balance. After weighing, a subsample was immediately put in an acid bath, or it was returned to the oven. For four samples, in order to break up the clay material, some or all of the subsamples were boiled in either a saturated solution of sodium pyrophosphate (Na₄P₂O₇·10H₂O) or water, typically for 1-4 days. The four subsamples of Jeerinah spherule layer sample W94-1Q were boiled in sodium pyrophosphate prior to acid dissolution (Appendix K), whereas for Bee Gorge samples 96714A and 96714B (Appendix L) and Monteville spherule layer sample V111 (Appendix M), all the boiling was done after acid dissolution.

All samples went through one or more warm acid baths. The acids used were Certified A.C.S. Plus concentrated (12.1 N) HCl, Certified A.C.S. Plus concentrated (15.8 N) HNO₃, and muriatic acid (31.45% HCl). During the early part of the project, most samples went through baths of 20% HCl and/or concentrated HCl (Appendices I, K, L, M). Initial heavy liquid separations (see below) during the early part of the project

revealed the presence of pyrite in Carawine spherule layer samples W85-2, X24-1, and 43-1 (Appendix I). In order to dissolve the pyrite, the HCl-insoluble materials in the 63-125 μ m and 125-250 μ m heavy mineral separates of sample W85-2, and the HCl-insoluble materials in the 63-125 μ m heavy mineral separates of sample X24-1 went through HNO₃ baths. The HCl-insoluble materials in the 63-125 μ m and 125-250 μ m size fractions of sample 43-1 went through HNO₃ baths.

For Jeerinah spherule layer sample W94-1Q, the >38 μ m size fractions went through muriatic acid baths, and later, the <38 μ m material went through concentrated HCl baths (Appendix K). The Grænsesø spherule layer samples sequentially went through concentrated HCl and concentrated HNO₃ baths (Appendix O). Nine samples that were processed during the latter part of the project, including most of the context samples, went through concentrated HNO₃ baths (Appendices I, J, L, N, and P).

For acid dissolution, each subsample was put in a glass beaker (\pm a magnet), a few hundred milliliters of acid were added, and the beaker was put on a hotplate that usually had a magnetic stirrer. Additional acid was added to the beaker as needed, and the hotplate was usually on for ~4-10 hours during the work day, but not overnight. The time required for complete dissolution of the carbonate \pm sulfide components varied from ~1-10 days, but most samples took ~2-7 days. When acid dissolution was complete, the beaker was removed from the hotplate, topped off with tap or distilled water, and the acid-insoluble material was allowed to settle.

A suction device attached to a sink faucet was used to decant the acidic water. The beaker was again filled with tap or distilled water, and the material was allowed to resettle. The dilution and decantation cycle was repeated up to \sim 15 times to completely remove the acid, but most samples were free of acid after 4-8 cycles. For Carawine

context sample 104175 (Appendix J), dilution was done using only distilled water. All sample preparation of the sawn pieces of Carawine spherule layer sample 42-1A (Appendix I) was done with distilled water.

The acid-insoluble residues were wet sieved in conjunction with ultrasonic agitation. Most of the samples were wet sieved into five size fractions (<38 μ m, 38-63 μ m, 63-125 μ m, 125-250 μ m, and >250 μ m). The acid-insoluble residues of the samples from the Grænsesø Formation contain appreciable secondary quartz material, and five of these six samples (Appendices O and P) were wet sieved into seven size fractions (<38 μ m, 38-63 μ m, 63-125 μ m, 125-250 μ m, 125-250 μ m, 250-500 μ m, 500-1000 μ m, and >1000 μ m). The >38 μ m size fractions were dried under a heat lamp, and each size fraction was weighed on the analytical balance, and the material was put in a vial.

For each sample, all, or part, of the $<38 \ \mu\text{m}$ acid-insoluble material was recovered in 1L, 2L, or 4L glass beakers. The $<38 \ \mu\text{m}$ acid-insoluble material was allowed to settle, or it was centrifuged at 3000 rpm for 10-15 minutes. Centrifuge runs were repeated until the water in the centrifuge tubes was clear or fairly clear. During the settling process, the $<38 \ \mu\text{m}$ acid-insoluble material was progressively put in smaller beakers. The $<38 \ \mu\text{m}}$ acid-insoluble material was dried in the oven, weighed on the analytical balance, and put in vials.

Using a binocular microscope, spherules \pm irregular melt particles in the >250 µm size fractions were handpicked from the six Carawine (Appendix I) and three Bee Gorge (Appendix L) spherule layer samples. No spherules or irregular melt particles were handpicked from the two Jeerinah spherule layer samples, since the samples were mostly crushed below 250 µm (Appendix K). The spherules and irregular melt particles were

each dry sieved using 250 μ m, \pm 500 μ m, \pm 1000 μ m sieves, and each size fraction was weighed on the analytical balance and put in vials.

All samples went through heavy liquid separation using laboratory grade s-tetrabromoethane ($\rho = 2.96 \text{ g/cm}^3$) in 500 ml or 1000 ml separatory funnels. Most of the separations were done on the 63-125 µm and 125-250 µm size fractions. During the early part of the project, separations were done on many, if not all, of the 38-63 µm size fractions of Carawine spherule layer samples X38-2, W85-2, X24-1 (Appendix I), Jeerinah spherule layer sample W94-1Q (Appendix K), and Bee Gorge samples BB, 96714A, and 96714B (Appendix L), but no further work was done on the 38-63 µm-sized heavy mineral separates because of time limitations. Each separation was allowed to settle overnight, and the heavy mineral separate was collected in a filter. The acidinsoluble materials in the 63-125 µm and 125-250 µm size fractions each went through 1-3 separations, and the light fractions ($\rho < 2.96 \text{ g/cm}^3$) were then collected in filters. All the filters were rinsed with acetone three or four times a day for several days in order to remove as much of the s-tetrabromoethane as possible. Filters were stored upright, kept closed with paper clips, and covered with plastic wrap until their contents were either weighed and put in vials or transferred directly to cavity slides.

All light fractions were weighed on the analytical balance, and they were put in vials. Most of the heavy mineral separates were transferred directly from the filters to cavity slides. For Carawine spherule layer sample 42-1A (Appendix I), Carawine context sample 104175 (Appendix J), and Monteville context samples T149-1 and II67-1B (Appendix N), the heavy mineral separates were weighed on the analytical balance before they were transferred to cavity slides. However, the weights of most of the heavy mineral separates are reported as derived weights. For a given size fraction of a given subsample,

a derived weight is obtained by subtracting the weight of the light fraction from the weight of the acid-insoluble material.

Seven samples (84-1, 42-1A, X68-1, 92058, U63-1, T149-1, and II67-1B) had abundant secondary iron \pm manganese oxide/oxyhydroxide grains in the heavy mineral separates (Appendices I, J, L, M, and N), and these separates were generally transferred from the filters to vials. Using a binocular microscope, I handpicked the grains that were not obvious secondary iron \pm manganese oxide/oxyhydroxide grains from these heavy mineral separates, and I transferred the handpicked grains to cavity slides. Using a binocular microscope, the heavy mineral grains were sorted, and for most of the separates, the grains were aligned in rows in the cavity slides in preparation for micro-Raman study and grain counts.

Hydrofluoric acid (HF) was used to etch grains (Appendix Q) from a 63-125 µmsized light fraction of a subsample from Carawine spherule layer sample 43-1 prior to examination by SEM (see section 3.2). It was thought that SEM examination of quartz grains etched in HF may increase the chance of detecting PDFs in the quartz grains (e.g., see Bohor et al., 1984; Morgan et al., 2006). Three heavy mineral separates (63-125 µm size fractions) from two Grænsesø spherule layer samples went through HF treatment (Appendix Q) prior to micro-Raman spectroscopy (see section 3.2) in order to remove the secondary quartz that typically mantles the grains in the Grænsesø samples.

In order to search for PDFs in quartz by optical microscopy, twelve grain mounts were made from portions of the light fractions of five subsamples (987.4 g, 1046.2 g, 1078.1 g, 1114.1 g, and 1136.4 g) of Carawine spherule layer sample 43-1 (Appendix I). Eleven of the grain mounts are of the 63-125 μ m size fractions, and one grain mount is of the 125-250 μ m size fraction. The following procedure was used to make the light

fraction grain mounts. A 76 by 25 mm glass slide was heated on a hotplate for a few minutes, and 2-4 drops of Piccolyte (60% in xylene) mounting medium was put on the slide with a glass stirring rod. The mounting medium was smeared around to cover about one-third of the slide, and then the slide was quickly removed from the hotplate. The grains were sprinkled on the mounting medium and quickly spread out with a needle. A 40 by 23 mm cover slide was placed on the grains and gently tapped down. Problems encountered during the preparation of the grain mounts included: failure of the cover slide to bond with the medium due to excess heating, excess bubbles in the medium due to stirring, and failure of the medium to fully harden, thereby allowing the grains to rotate within the mounting medium.

A grain mount of a white opaque zircon grain from the 63-125 μ m size fraction of subsample 144.3 g of Carawine spherule layer sample X38-2 (Appendix I) was made by the following procedure, and it was sent to Dr. Hugues Leroux at the Université de Lille for analysis by Transmission Electron Microscope (TEM). A few drops of thin-section epoxy were put around the periphery of a circular (D = 25.4 mm) glass slide in order to provide balance during the grinding and polishing steps, as well as across the center of the slide in order to hold the grain. Using a binocular microscope, the grain was placed on the slide and a sketch was made of the drops and grain. The mounting medium was allowed to harden overnight. Grinding by hand on a wetted 600 grit paper strip was done until the grain was slightly exposed as determined by examining the slide using a binocular microscope. The grain was polished by hand on a 6 μ m grit paper strip that was wetted with a solution of water, detergent, and glycerol. A final polish was done by hand using 0.05 μ m Al₂O₃ powder that was wetted with water.

3.2 Analytical Techniques

Single-grain X-ray diffraction (XRD) data were obtained for ~195 heavy mineral grains from eight samples of the Carawine (W85-2, X24-1, 43-1, X38-2), Jeerinah (W94-1Q, X21-1), Bee Gorge (96714A), and Grænsesø (GL8904-2) spherule layers, and Grænsesø context sample GL8904-6. About 85% of the grains are from the four Carawine spherule layer samples, and ~96% of the grains are from the 63-125 μ m size fractions. The XRD analyses were done to help characterize the heavy mineral assemblages, and to search for shock-induced high-pressure polymorphs and baddeleyite.

The XRD analyses were done at the Department of Geological Sciences at the University of Delaware using Philips PW 1729 and XRG 3100 generators, and Gandolfi (G) and Debye-Scherrer (D-S) film cameras, with each camera having a diameter of 115 mm. The generators were operated at 40 kV and 30 mA using Cu K α radiation and a nickel filter. Each grain was X-rayed for ~20-26 hours, and then it was removed from the camera and put in a micropaleontology slide. With the aid of a head-mounted magnifying visor, the d-spacings of the lines, arcs, or dots on the film strips were determined using a template mounted on a backlight, and the intensities were estimated visually. Phase identification was determined by reference to the powder diffraction data for minerals that are given in Berry (1974). No standard for actinolite is given in Berry (1974), so X-ray powder diffraction data for an actinolite sample from Sobotín, Czechoslovakia, that are reported in Dostál (1965) are used in lieu of an actinolite standard.

In the XRD data tables given below, the identification (ID) of a grain is indicated by the type of camera used for the analysis (G or D-S) and the start date of the analysis. For a few grains, the abbreviation for the camera is followed by two hyphenated numbers, e.g., D-S 2-3, or by a single number, e.g., D-S #2. The first number, or the single number, indicates the generator that was used (1 = PW 1729; 2 = XRG 3100), and

the second number indicates the port on the generator. Unless otherwise indicated, the grain is 63-125 μ m in size. Except for actinolite, the phase used as a standard is followed by its card identification number (see Berry, 1974). The XRD data consist of the d-spacings (Å) and the relative intensities (I/I_o) of the lines.

In order to decrease the time for phase identification, and to significantly increase the number of grains to be searched for shock-metamorphic effects, we arranged with Professor Karl Booksh of the Department of Chemistry and Biochemistry at the University of Delaware for the use of their micro-Raman instrument. Using a binocular microscope and a small wetted brush, the grains to be analyzed by micro-Raman spectroscopy were handpicked from the heavy mineral separates that were stored in cavity slides. The selected grains were put in a row on a flat glass microscope slide, and the slide was placed on the stage of the micro-Raman instrument.

Raman spectra were acquired with a commercial Bruker Senterra (Billerica, Massachusetts) micro-Raman setup using a Nd:YAG laser frequency-doubled to 532 nm as the excitation source. Incident laser power varied from 2-10 mW, with most Raman spectra acquired at 5 mW. The laser beam was focused on the sample using an Olympus MPlan $50\times/0.75$ objective lens that yielded a probed spot diameter of ~2 µm. The Raman spectra were collected at high resolution (~3-5 cm⁻¹) using a 1200 grooves/mm grating, an entrance slit of 50 by 1000 µm, and a thermo-electrically-cooled, charge-coupled device (CCD) detector. Integration times and spectral co-additions were appropriately adjusted to yield satisfactory signal-to-noise ratios. Integration times typically ranged from 20-60 seconds, and the number of co-additions typically ranged from 2-6.

About 3400 grains were analyzed by micro-Raman spectroscopy, including ~536 grains that are either laboratory contaminants (e.g., plastic, solder, and rust particles) or

secondary iron and manganese oxides/oxyhydroxides from the samples. One analysis/grain was obtained for ~95% of the ~3400 grains. Grains that underwent multiple analyses (e.g., white opaque zircons) were generally analyzed 2-3 times, and the rutile grains that contain the TiO₂ II phase were typically analyzed at 3-4 different spots. Upon completion of the XRD and micro-Raman analyses for a given subsample, a grain count of the heavy mineral assemblage for that subsample was done using a binocular microscope.

The identification of a phase or phases in a grain by micro-Raman spectroscopy was done by comparing the acquired Raman spectrum for a grain with one or more Raman spectra of standard materials from the Raman spectral database of the RRUFF Project (Downs, 2006). The Raman spectral database for the standards (RRUFF Project, 2014) was accessed between November, 2012 and April, 2014. All the Raman spectra for the standards (RRUFF Project, 2014) that are shown in the Raman spectral plots were acquired using a 532-nm laser, with the exception of actinolite standard R040063.3, anatase standards R060277.3 and R060277.4, clinozoisite standard R040085.3, and dravite standards R040088.4, R050077.3, R060534.3, and R060534.4. The Raman spectra for these eight standards were acquired using a 514-nm laser (RRUFF Project, 2014). The identification of the TiO₂ II phase was done by comparison of the acquired Raman spectrum with a Raman spectrum for synthetic TiO₂ II (see section 4.2.2.6) that is given in El Goresy et al. (2001, their Fig. 2).

On the Raman spectral plots, the x-axis shows the Raman shift (cm^{-1}) typically in the wavenumber range of ~100/140 up to 1540/1550 cm⁻¹, and the y-axis shows either unnormalized or normalized intensities of the bands in arbitrary units (a.u.). For the plots that show an acquired Raman spectrum and one or more Raman spectra of standard

materials (RRUFF Project, 2014), each of the Raman spectra is normalized to its highest intensity peak in order to account for possible differences in the raw intensities of the acquired and standard Raman spectra. Bands interpreted (Dr. N. Menegazzo, personal communication, 2009) as instrumental peaks (i.p.) commonly occur at wavenumbers of $\sim 120/128$ cm⁻¹ and $\sim 1345/1355$ cm⁻¹, and the former peak can sometimes be of high intensity and broad, with the descending right side of the peak extending to wavenumbers of $\sim 140/155$ cm⁻¹. Cosmic rays striking the detector cause narrow, sharp, cosmic spikes (c.s.) of varying intensity: upward pointing spikes are due to cosmic rays striking the detector during the analysis, whereas downward pointing spikes are due to cosmic rays striking the detector during the background measurement.

Many of the Raman spectra for the samples required baseline correction after their acquisition to correct contributions from fluorescence that is commonly indicated as rising baselines from lower to higher wavenumbers. This processing procedure involved utilizing a routine that is embedded into the spectral acquisition software (OPUS) that is provided by the manufacturer (Bruker Optics) of the micro-Raman instrument. The procedure consists of fixing a minimal number of anchoring points on the Raman spectrum, and then interpolating straight lines between these points. Since contributions from fluorescence are sample dependent, the number of anchoring points varied from two for a linearly-rising baseline up to 10 for Raman spectra that displayed a strong upward curvature at higher wavenumbers. On the Raman spectral plots, the Raman spectrum for a sample has been baseline corrected unless otherwise noted.

An Olympus BH-2 petrographic microscope with an attached mechanical stage was used to search for putative PDFs in quartz grains in the light fraction grain mounts of Carawine spherule layer sample 43-1. A maximum magnification of 400× was obtained

with a DPlan 40 PO objective lens with a numerical aperture of 0.65. Photomicrographs at magnifications of $40-400 \times$ were taken of quartz grains that contain putative PDFs, and the coordinates of these grains were read using the mechanical stage. The grain mount slides had to be cut down to a size of ~35 by 25 mm in order to fit on the universal stage (U-stage).

In the Department of Geological Sciences at the University of Delaware, the U-stage setup consists of a Leitz five-axis U-stage mounted on a Leitz microscope. The magnification of the ocular lens is $8\times$, and the magnification of the high-power objective lens (UM 32/0.30) is $32\times$. The glass hemispheres are of standard size (radius = 13.5 mm), and they have an index of refraction (n) of 1.516. When the grain mount slides were mounted on this U-stage microscope, the quartz grains containing putative PDFs were quickly re-located using the photomicrographs. However, the planar microstructures in the quartz grains were not visible with this U-stage microscope.

The planar microstructures in the quartz grains were visible with the U-stage setup of Dr. Bevan M. French at the Smithsonian Institution, Washington, D. C. This U-stage microscope consists of a Leitz four-axis U-stage mounted on a 5-turret Leitz microscope. The magnification of the ocular lens is $10\times$, and the magnification of the high-power objective lens (UM 4) is $30\times$. The glass hemispheres are of standard size with n = 1.554. This U-stage microscope was used to measure the orientations of planar microstructures relative to the c-axis for three quartz grains from the 63-125 µm size fractions of three subsamples of Carawine spherule layer sample 43-1. The method of determining the crystallographic orientations of the planar microstructures is essentially the same as the method outlined in Ferrière et al. (2009, p. 926). For each grain, the U-stage measurements for the orientations of the c-axis and poles to the planar

microstructures were plotted on a stereographic Wulff net (D = 200 mm), and where possible, the planes were indexed using the template (enlarged to D = 200 mm) shown in Montanari and Koeberl (2000, p. 297; see also von Engelhardt and Bertsch, 1969; Stöffler and Langenhorst, 1994).

The scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analyses were done at the W. M. Keck Electron Microscopy Facility at the University of Delaware under the supervision of Dr. Chaoying Ni and Mr. Frank Kriss. The samples that were analyzed in 2009 and 2010 were coated with gold and carbon, respectively, using a Denton Vacuum Desk IV sputter coater. In February, 2009, 155 grains from a 63-125 μ m-sized light fraction of Carawine spherule layer sample 43-1 that had been etched in HF (Appendix Q) were examined with the JEOL JXA-840 SEM in order to search for putative PDFs in quartz. The grains were sprinkled on double-sided carbon tape attached to an aluminum SEM stub (D = 12.2 mm). The SEM was operated in secondary electron imaging mode at 5-10 kV accelerating voltage, a working distance of 15 mm, and a probe current of 600 pA. A magnification of 1200× was generally used to examine the grains.

In September, 2010, six zircon grains from Carawine spherule layer sample X38-2 that all show arcs on their D-S patterns were analyzed by SEM/EDX to search for possible shock-metamorphic features, e.g., planar microstructures and/or granular texture (see Bohor et al., 1993). The grains were aligned in rows on the double-sided carbon tape on the SEM stubs. The JEOL JSM-7400F field-emission SEM was operated in secondary electron imaging mode at 10 kV accelerating voltage and a probe current of 60-200 pA. The Oxford INCA EDX system was operated at an acquisition rate of ~400-500

counts/second, a live time of 100 seconds, and a working distance of 8 mm. The zircon grains were examined at a magnification of $\sim 1000 \times$.

Chapter 4

RESULTS

4.1 Acid-Insoluble Weights

A summary of the acid-insoluble weight data for the total processed weights of the 25 samples is given in Table 10. The weight data are reported to different decimal places. For a sample consisting of one or more subsamples that were weighed using the Ohaus Triple Beam balance, the total processed weight is reported to the first decimal place (tenth of a gram). For Carawine spherule layer sample X38-2, one subsample was weighed using this balance, and the other subsample was weighed using the analytical balance, so the total processed weight of this sample is also reported to the first decimal place.

For a layer or sublayer(s) consisting of a single subsample that was weighed using the analytical balance (e.g., 14.2225 g), the total processed weight is reported to four decimal places (ten thousandth of a gram). However, sometimes the readout for the analytical balance would not stabilize in the fourth decimal place, so a weight reported to four decimal places may not be accurate to the fourth or even the third (thousandth of a gram) decimal place. For a sample, layer, or sublayer(s) that consists of two or more subsamples that were weighed using the analytical balance, the total processed weight is rounded off to the second decimal place (hundredth of a gram).

The weight percent data in Table 10 are rounded off to the first decimal place (tenth of a gram) in order to be conservative and consistent. Acid-insoluble weight data
by subsample for the 25 samples are given in Appendix R, and acid-insoluble weight data for the size fractions for each subsample are given in Appendices I-P. In the appendices, weights obtained using the analytical balance are reported to the fourth decimal place, but again, these weights may not be very accurate beyond the second decimal place.

| Context | Spherule | Total | Wt% of | Size Fraction Distribution (wt%) of Acid-Insoluble Material | | | | | | |
|-------------------|--|-------------|----------------------|--|------------------|-------------------|------------|------|--|--|
| Sample (Layer) | ample ayer) (Sublayer(s)) (g) Acid- (Sublayer(s)) (g) Material | | <38 µm | 38-63 μm | 63- 125 μm | 125- 250 μm | >250 µm | | | |
| | | mite | | | | | | | | |
| 104175 | | 235.4 | 0.5 ¹ | 97.3 | 2.0 | 0.4 | 0.1 | 0.2 | | |
| | X38-2 | 229.4 | 7.0^{2} | 22.2 | 5.3 | 27.2 | 14.7 | 30.5 | | |
| | 42-1A | 1017.5 | 6.5 ¹ | 27.4 | 2.9 | 3.0 | 4.9 | 61.8 | | |
| | 43-1 | 9573.5 | 4.2 ^{2,3,4} | 19.6 | 3.0 | 2.6 | 2.7 | 72.1 | | |
| | X24-1 | 1937.7 | 9.7 ^{2,3} | 10.5 | 4.5 | 4.3 | 2.6 | 78.1 | | |
| | W85-2 | 649.4 | 9.9 ² | 7.3 | 2.8 | 2.6 | 0.9 | 86.3 | | |
| | 84-1 | 1087.7 | 12.5 ^{2,5} | 21.7 | 4.7 | 5.2 | 4.2 | 64.2 | | |
| 104141 | | 357.2 | 1.8 ¹ | 89.7 | 2.0 | 1.5 | 1.5 | 5.3 | | |
| X68-1 | | 604.7 | 1.1 ¹ | 86.9 | 5.1 | 3.7 | 3.8 | 0.5 | | |
| | | J | eerinah Forma | ation | | | | | | |
| | X21-1 | 353.16 | 67.2 ^{2,6} | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| | W94-1Q | 48.32 | 53.2 ^{2,6} | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| |] | Bee Gorge M | lember (Witter | noom Fo | rmation) | | | | | |
| 92058 | | 452.7 | $10.7^{1,7}$ | 76.1 | 9.4 | 11.2 | 3.1 | 0.2 | | |
| | 96714A (Usplsl) | 17.19 | 47.6 ² | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| | 96714A (Splsl) | 10.3574 | 55.3 ² | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| | 96714A (Lspsl) | 15.92 | 50.6 ² | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| 96714A (Bcl) | | 92.42 | 59.4 ^{2,8} | n.d. | n.d. | n.d. | n.d. | n.d. | | |

 Table 10:
 Acid-insoluble weight data for spherule layer and context samples.

Table 10: continued

| Context | Spherule Layer | Total | Wt% of | Size Fraction Distribution (wt%) of Acid-Insoluble Material | | | | | | |
|-------------------|--|----------------|----------------------------------|--|-------------|------------------|-------------------|------------|--|--|
| Sample (Layer) | Sample Sample (Layer) (Layer/ Sublayer(s)) | | Weight Insoluble (g) Material | | 38-63 μm | 63- 125 μm | 125- 250 μm | >250 µm | | |
| |] | lember (Witter | noom Formation) | | | | | | | |
| | 96714B (Usplsl) | 14.2225 | 51.8 ² | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| | 96714B (Splsl) | 18.58 | 60.4 ² | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| | 96714B (Lspsl) | | 51.3 ² | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| 96714B (Bcl) | | 52.76 | 64.4 ² | n.d. | n.d. | n.d. | n.d. | n.d. | | |
| BB (#1) | | 5.4035 | 19.7 ^{2,9} | 87.1 | 8.4 | 2.1 | 0.4 | 2.0 | | |
| BB (#2) | | 14.89 | 12.6 ² | 92.6 | 5.5 | 0.6 | 0.6 | 0.7 | | |
| | BB (sl) | 31.24 | 32.0^{2} | 16.1 | 8.7 | 10.1 | 12.0 | 53.0 | | |
| | | М | onteville Form | nation | | | | | | |
| II67-1B | | 616.7 | $3.4^{1,10}$ | 88.2 | 4.8 | 1.3 | 0.7 | 4.9 | | |
| | V111 | 326.0 | 9.7 ^{2,11} | 51.4 | 15.6 | 25.7 | 7.0 | 0.3 | | |
| | U63-1 | 593.2 | 18.2^{2} | 31.8 | 3.2 | 2.8 | 2.5 | 59.7 | | |
| T149-1 | | 214.3 | 10.1 ^{1,12} | 78.1 | 16.6 | 4.1 | 0.7 | 0.5 | | |
| | | G | rænsesø Form | ation | | | | | | |
| GL8904-6 | | 321.1 | 3.3 ^{1,13} | 53.2 | 12.4 | 10.9 | 7.0 | 16.5 | | |
| | GL8904-4 | 482.0 | 26.2 ^{1,2,13} | 11.0 | 2.8 | 4.4 | 3.4 | 78.4 | | |
| | GL8904-3 | 808.4 | 20.6 ^{1,2,13} | 9.8 | 5.0 | 7.4 | 6.7 | 71.0 | | |
| | GL8904-2 | 1502.5 | 32.6 ^{1,2,13} | 4.4 | 1.7 | 6.3 | 5.8 | 81.8 | | |
| | GL8904-1 | 1248.4 | 26.2 ^{1,2,13} | 6.0 | 2.5 | 9.4 | 11.8 | 70.3 | | |
| SP3 | | 977.3 | 12.2 ¹ | 21.9 | 2.8 | 3.2 | 3.0 | 69.1 | | |

Notes for superscripts: ¹HNO₃ digestion; ²HCl digestion; ³A little <38 μ m material was lost from one subsample prior to weighing. ⁴A little material was lost from one subsample during acid digestion. ⁵During wet sieving, a little >250 μ m material was lost, and only part of the <38 μ m material was recovered. ⁶Prior to acid digestion, a little material was lost during crushing of the >250 μ m size fractions and dry sieving steps. ⁷For each subsample, only part of the <38 μ m material was recovered, and for one subsample, a little >250 μ m material was lost prior to weighing. ⁸During sample preparation, a little material was lost from three of the nine subsamples. ⁹Prior to weighing, a little <38 μ m material was lost. ¹⁰For one subsample, a little <38 μ m material was not recovered during the second wet sieving of the >38 μ m size fractions. ¹¹For each subsample, some of the <38 μ m material was not recovered. For one subsample that contained abundant millimeter-sized (and smaller) acid-resistant grains, the >250 μ m size fraction was mostly ground below 250 μ m, and the subsample was wet sieved again. ¹²For each subsample, some of the <38 μ m material was not recovered. ¹³Only part of the <38 μ m material was recovered.

Notes for Bee Gorge sample BB: Sample BB consists of a spherule layer sandwiched between two context layers. There is no stratigraphic "up" arrow on the sample, so the relative age of the three layers is unknown. The spherule layer (sl) is referred to as "BB (sl)" in the table. One of the context layers is named "context layer #1" and it is referred to as "BB (#1)" in the table. The other context layer is named "context layer #2" and it is referred to as "BB (#2)" in the table.

Notes for Bee Gorge samples 96714A and 96714B: The samples are from the same rock, and they are mirror images of one another. Each sample consists of a basal carbonate lutite context layer (Bcl) that is directly overlain by a spherule layer. The spherule layer consists of three subdivisions that were processed separately. In ascending stratigraphic order, the three subdivisions are as follows: 1) Lowermost spherule-rich sublayer (Lspsl) 2) Spherule-bearing lutite sublayer (Splsl) 3) Upper spherule/lutite sublayers (Usplsl). Notes for no data (n.d.): There are no weight percent (wt%) data for the original size fraction distribution of acid-insoluble material in Jeerinah spherule layer samples X21-1 and W94-1Q since the two samples were mostly crushed below 250 µm prior to acid digestion. There are no weight percent (wt%) data for the original size fraction distribution of acid-insoluble material in Bee Gorge samples 96714A and 96714B since the two samples were ultimately crushed below 125 µm.

The Carawine context samples are laminated dolomites that have low values (<2 wt%) of acid-insoluble material, and ~92-99 wt% of this material is in the <63 μ m size fraction. The Carawine spherule layer samples are dolomixtites that have higher values of acid-insoluble material, ranging from ~10-12 wt% near the base of the spherule layer, to ~7 wt% near the top of the spherule layer. For each of the Carawine spherule layer samples from the Ripon Hills area (Table 4), ~62-86 wt% of the acid-insoluble material is in the >250 μ m size fraction, whereas for Carawine spherule layer sample X38-2 from the sandy upper part of the dolomixtite at the TTT locality (Table 4), ~30 wt% of the acid-insoluble material is in the >250 μ m size fraction. These results

primarily reflect the much greater weight percent of $63-250 \mu$ m-sized material and lesser abundance of spherules and irregular melt particles in sample X38-2 as compared to the Carawine spherule layer samples from the Ripon Hills area.

Jeerinah spherule layer samples W94-1Q and X21-1 were mostly crushed below 250 µm prior to acid digestion (Appendix K), so only the total weight percents of acidinsoluble material are given in Table 10. The samples are melt-bearing (spherules + irregular melt particles), gravelly sandstones that consist primarily of acid-insoluble components, e.g., secondary iron oxide/oxyhydroxide phases, spherules and irregular melt particles that are chiefly replaced by K-feldspar, and ferruginous, chert, and argillite clasts (see Hassler et al., 2005). The values (~53 and ~67 wt%) of acid-insoluble material for the samples basically agree with the petrographic descriptions for rocks from this part of the spherule layer (see Hassler et al., 2005), but they do show that the samples contain a significant carbonate component by weight.

Bee Gorge samples 96714A and 96714B were ultimately crushed below 125 µm (Appendix L), so only the total weight percents of acid-insoluble material are given in Table 10. Each of the four subdivisions shows comparable weight percent values of acid-insoluble material between the two samples. The basal carbonate lutite layers and the spherule-bearing lutite sublayers have higher values (~55-64 wt%) of acid-insoluble material than the lowermost spherule-rich sublayers (~51 wt%), and the upper spherule/lutite sublayers subdivisions (~47-51 wt%). Like the Jeerinah spherule layer samples, the acid-insoluble weight data show that carbonate is a major component of these lutite-rich samples.

For Bee Gorge sample BB, both the spherule layer and the context layers are more carbonate-rich than their respective layers in Bee Gorge samples 96714A and

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96714B. Bee Gorge context sample 92058 has a weight percent value of acid-insoluble material that is comparable to those for the context layers in sample BB. Both the spherule layers and the context layers of the Bee Gorge samples have much higher weight percent values of acid-insoluble material as compared to their respective layers in the Carawine Dolomite samples. The higher values in the Bee Gorge samples primarily reflect higher proportions of spherules and siliciclastic lutite material.

Monteville spherule layer samples U63-1 and V111 have weight percent values of acid-insoluble material that are comparable to those for samples 84-1, W85-2, and X24-1 from the lower part of the Carawine spherule layer (Table 10). Monteville context samples T149-1 and II67-1B have weight percent values of acid-insoluble material that are higher than those for the three Carawine context samples, but for each of these five samples, >91 wt% of the acid-insoluble material is in the <63 μ m size fraction. The Monteville and Carawine samples show a similar trend in the weight percent values of acid-insoluble material with stratigraphic position: the value(s) in the lower part of the spherule layer is (are) higher than that (those) of the underlying context sample(s), the value decreases upward in the spherule layer, and the overlying context sample has the lowest value.

As compared to the Carawine and Monteville spherule layer samples, the four Grænsesø spherule layer dolomixtite samples have higher values (~20-32 wt%) of acidinsoluble material (Table 10). Furthermore, in contrast to the Carawine and Monteville spherule layers, the weight percent values of acid-insoluble material are fairly constant up through the Grænsesø spherule layer, with an average value of ~26 wt%. This result reflects the rather uniform and massive nature of the Grænsesø spherule layer (see section 2.4). Like the Carawine spherule layer samples from the Ripon Hills area (Table 4), most

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of the acid-insoluble material in the Grænsesø spherule layer samples is in the >250 μ m size fractions. These results primarily reflect the spherules (± irregular melt particles) and the siliceous components (chert clasts/fragments, quartzose sand, ± veinlets) of the dolomixtites that comprise the Grænsesø and Carawine spherule layers. Grænsesø context sample SP3 has a weight percent value of acid-insoluble material that is comparable to those for the context layers in Bee Gorge samples BB and 92058, and Monteville context sample T149-1; all these samples are fine-grained carbonate rocks.

4.2 Heavy Mineral Fractions

4.2.1 Introduction

A summary of the weight data for the heavy mineral fractions for the spherule layer and context samples is given in Table 11. For several samples, layers, or sublayers, the weight listed in Table 11 is less than its respective total processed weight that is listed in Table 10. The reasons for this difference are that for several samples, layers, or sublayers, not all subsamples went through heavy liquid separation, or more commonly, a subsample that has a negative derived weight for the heavy mineral fraction is not included in the weight listed in Table 11. Again, for a given size fraction of a given subsample, a derived weight for the heavy mineral fraction was obtained by subtracting the weight of the light fraction from the weight of the acid-insoluble material. There are no data (n.d.) reported for Bee Gorge context sample 92058, since the derived weights of the heavy mineral fractions are all negative (Appendix L).

For a given sample, layer, sublayer, or sublayers subdivision in Table 11, the weight is reported to one, two, or four decimal places (see discussion for Table 10 in section 4.1), and the weight of the heavy mineral fraction is rounded off to three decimal

places, but again, a weight may not be very accurate beyond two decimal places. The weight percent values are rounded off to two decimal places in order to be conservative and consistent. The weight percent values for the heavy mineral fractions range from <0.01 (63-125 μ m ± 125-250 μ m size fractions) for seven samples to 2.00 (63-125 μ m size fraction) for the upper spherule/lutite sublayers subdivision of Bee Gorge sample 96714A. However, the weight percent values for the heavy mineral fractions are ≤0.03 for 17 samples, and for only seven samples are the weight percent values >0.1 for the whole sample, or for a layer, sublayer or sublayers subdivision within the sample.

| Context Sample (Layer) | Spherule Layer Sample (Layer/ Sublayer(s)) | Weight (g) | Weight (g) of Heavy Mineral Fraction ¹ | Wt% | | | | | |
|------------------------------|---|----------------|--|--------|--|--|--|--|--|
| | (| Carawine Dolo | mite | | | | | | |
| 104175 | | 235.4 | < 0.001 ² | < 0.01 | | | | | |
| | X38-2 | 229.4 | 0.013 ^{3,4} | 0.01 | | | | | |
| | 42-1A | 557.5 | 0.063 ² | 0.01 | | | | | |
| | 43-1 | 2393.1 | < 0.093 ^{4,5} | < 0.01 | | | | | |
| | X24-1 | 758.8 | 0.212 ^{3,4} | 0.03 | | | | | |
| | W85-2 | 649.4 | 0.093 ^{3,4} | 0.01 | | | | | |
| | 84-1 | 430.8 | $0.107^{3,4}$ | 0.02 | | | | | |
| 104141 | | 357.2 | 0.006 ^{2,4} | < 0.01 | | | | | |
| X68-1 | | 604.7 | 0.029 ^{2,4} | < 0.01 | | | | | |
| | Jeerinah Formation | | | | | | | | |
| - | X21-1 | 107.68 | 0.268 ^{3,4,6} | 0.25 | | | | | |
| | W94-1Q | 38.00 | 0.188 ^{3,4} | 0.49 | | | | | |
| | Bee Gorge M | lember (Witter | noom Formation) | | | | | | |
| 92058 | | 452.7 | n.d. | n.d. | | | | | |
| | 96714A (Usplsl) | 17.19 | 0.343 ^{3,4,6} | 2.00 | | | | | |
| | 96714A (Splsl) | 10.3574 | $0.002^{3,4,6}$ | 0.02 | | | | | |
| | 96714A (Lspsl) | 15.92 | 0.218 ^{3,4,6} | 1.37 | | | | | |
| 96714A (Bcl) | | 37.59 | 0.004 ^{3,4,6} | 0.01 | | | | | |
| | 96714B (Usplsl) | 14.2225 | 0.004 ^{3,4,6} | 0.03 | | | | | |
| | 96714B (Splsl) | 12.0772 | < 0.001 ^{3,4,6} | < 0.01 | | | | | |
| | 96714B (Lspsl) | 13.8178 | 0.002 ^{3,4,6} | 0.01 | | | | | |
| 96714B (Bcl) | | 10.7160 | < 0.001 ^{3,4,6} | < 0.01 | | | | | |
| BB (#1) | | 5.4035 | 0.015 ^{3,4,7} | 0.28 | | | | | |
| BB (#2) | | 14.89 | < 0.001 ^{3,4} | < 0.01 | | | | | |
| | BB (sl) | 10.6019 | 0.001 ^{3,4} | 0.01 | | | | | |

Table 11:Summary of weight data for heavy mineral fractions for the spherule layer
and context samples.

| Context Sample | Spherule Layer Sample | Weight (g) | Weight (g) of Heavy Mineral Fraction ¹ | Wt% | | | | | | |
|-------------------|--------------------------|--------------|--|--------|--|--|--|--|--|--|
| | Monteville Formation | | | | | | | | | |
| II67-1B | | 616.7 | 0.037^{2} | 0.01 | | | | | | |
| | V111 | 326.0 | $0.578^{3,4,7}$ | 0.18 | | | | | | |
| | U63-1 | 593.2 | $0.849^{3,4}$ | 0.14 | | | | | | |
| T149-1 | | 214.3 | 0.325^2 | 0.15 | | | | | | |
| | G | rænsesø Form | ation | | | | | | | |
| GL8904-6 | | 321.1 | $0.004^{2,4}$ | < 0.01 | | | | | | |
| | GL8904-4 | 482.0 | $0.005^{4,5}$ | < 0.01 | | | | | | |
| | GL8904-3 | 808.4 | $0.108^{4,5}$ | 0.01 | | | | | | |
| | GL8904-2 | 421.4 | $0.044^{4,5}$ | 0.01 | | | | | | |
| | GL8904-1 | 680.6 | $0.167^{4,5}$ | 0.02 | | | | | | |
| SP3 | | 977.3 | 0.010 ^{2,4,8} | < 0.01 | | | | | | |

Table 11: continued

Notes for superscripts: ¹The value is for the combined 63-125 μm and 125-250 μm size fractions unless otherwise indicated. ²HNO₃ digestion; ³HCl digestion; ⁴A derived weight (see above, p. 94); ⁵HCl and HNO₃ digestion; ⁶63-125 μm size fraction only;

⁷The 125-250 μ m size fraction has a negative derived weight. The reported value is for the 63-125 μ m size fraction. ⁸For the 125-250 μ m size fraction, three subsamples have negative derived weights, and one subsample has a derived weight of 0.0000 g. The reported value is for the 63-125 μ m size fraction.

Notes for Bee Gorge sample BB: Sample BB consists of a spherule layer sandwiched between two context layers. There is no stratigraphic "up" arrow on the sample, so the relative age of the three layers is unknown. The spherule layer (sl) is referred to as "BB (sl)" in the table. One of the context layers is named "context layer #1" and it is referred to as "BB (#1)" in the table. The other context layer is named "context layer #2" and it is referred to as "BB (#2)" in the table.

Notes for Bee Gorge samples 96714A and 96714B: The samples are from the same rock, and they are mirror images of one another. Each sample consists of a basal carbonate lutite context layer (Bcl) that is directly overlain by a spherule layer. The spherule layer consists of three subdivisions that were processed separately. In ascending stratigraphic order, the three subdivisions are as follows: 1) Lowermost spherule-rich sublayer (Lspsl) 2) Spherule-bearing lutite sublayer (Splsl) 3) Upper spherule/lutite sublayers (Usplsl). Notes for no data (n.d.): There are no weight data reported for the heavy mineral fraction of Bee Gorge context sample 92058 since the derived weights (see above, p. 94) for the heavy mineral fractions of the two subsamples are all negative (Appendix L).

XRD analysis, micro-Raman spectroscopy, and SEM/EDX analysis were used to identify the heavy mineral phases. As a total of ~37,000 heavy mineral grains were recovered in the 63-125 μ m size fractions, most of the heavy mineral grains were not analyzed, and their identification was made on the basis of their physical similarities as observed using a binocular microscope to grains that were identified by one or more of the three analytical techniques. For 24 samples, descriptions of the heavy mineral grains that were made using a binocular microscope are given in Appendices S-Z. Grænsesø spherule layer sample GL8904-2 is not included in Appendix Y since no systematic analysis by micro-Raman spectroscopy was done on this sample.

For each of 23 samples, the heavy mineral abundance is shown in a column graph (or graphs). There is no column graph for Carawine context sample 104175 since this sample has only 0-2 primary heavy mineral grains in the 63-250 µm size fraction. For Grænsesø spherule layer sample GL8904-2, no systematic analysis by micro-Raman spectroscopy or grain count was done on the sample, so there is no column graph for this sample. A weight given in a column graph may be different than its respective weight given in Table 10 and/or Table 11. The reason for this difference is that a given weight in a column graph refers only to a subsample(s) that was (were) grain counted after its (their) grains were identified by systematic micro-Raman spectroscopy and (for eight samples) XRD. The subsample(s) that was (were) used to characterize the heavy mineral fraction of a sample, layer, sublayer, or sublayers subdivision is (are) given (enumerated) at the beginning of the following sections. In all the column graphs, except the one for Bee Gorge context sample 92058, the abundance of each phase is plotted as the number of grains per kilogram. Most of the samples contain varying amounts of secondary iron and/or manganese oxide/oxyhydroxide and/or pyrite grains. These phases were identified by micro-Raman spectroscopy and/or XRD analysis, and they are interpreted as secondary grains on the basis of their colors, habit, shapes, angularities, mode of occurrence, and abundance. For example, pyrite grains are typically brassy and angular, and they may occur in crystal aggregates. Hematite and/or goethite can pseudomorphously replace striated cubes or aggregates of cubes that are interpreted as former pyrite crystals. The manganese oxide/oxyhydroxide grains can appear scaly, and these certainly do not appear to be detrital grains. The secondary iron and/or manganese oxide/oxyhydroxide grains can be very abundant, up to 10³ to 10⁵ grains/subsample or sample. These secondary grains are briefly described in the following sections, but they are not included in the descriptions of the heavy mineral grains (Appendices S-Z), or in the grain counts for the heavy mineral abundances that are shown in the column graphs.

In the following sections, for a given sample, layer, sublayer, or sublayers subdivision, a phase is referred to as a trace, minor, or major component if the total number of grains of the phase is <1%, 1-10%, or >10%, respectively, of the total number of grains in that size fraction. For each sample, the results for the phases in the 63-125 μ m size fraction are given first, followed by those for the 125-250 μ m size fraction where appropriate. Several phases can occur as matrix material, e.g., a chrome spinel grain with a muscovite matrix, and the matrix phase is interpreted as adhering to the surface of the grain in question.

Rutile grains that contain the TiO_2 II phase are described in some detail. The white opaque zircon grains were of particular interest in this study, since similar grains in rocks from confirmed impact structures, as well as from distal impact ejecta layers, can

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show shock-metamorphic effects (see Krogh et al., 1984; Bohor et al., 1993; Glass and Liu, 2001). In this study, these zircon grains can be truly white and opaque, but more commonly, the "white opaque" zircon grains are varicolored, e.g., pinkish white, beige, light gray, and clear with light yellow tint, and they are translucent-to-opaque. The white opaque zircon grains vary in shape and roundness from prismatic and euhedral to equant and well-rounded. In the following sections, the variability in wavenumber (cm⁻¹) of a band in the Raman spectra of a given phase is indicated in the following manner: for two or more measured grains, or spots/grain, a band that ranges in wavenumber from, e.g., 216 cm⁻¹ to 224 cm⁻¹ is written as "216/224" cm⁻¹.

4.2.2 Carawine Spherule Layer Samples

4.2.2.1 Sample 84-1

Subsample 268.1 g was used to characterize sample 84-1. For the 63-125 μ m size fraction, there are ~520 secondary iron oxide/oxyhydroxide grains. These secondary grains are typically brown, reddish brown, red, and ochre, and a few of them appear to be pseudomorphs after pyrite. Grains that did not appear to be secondary iron oxide/oxyhydroxide phases were handpicked from the heavy mineral separates, and the phases were identified by micro-Raman spectroscopy. The heavy mineral grains are described in Appendix S, and their abundance is shown in Figure 19. The number of handpicked grains is almost identical to the number of secondary iron oxide/oxyhydroxide grains, but there are far more of the latter grains in the 125-250 μ m size fraction. Therefore, the secondary iron oxide/oxyhydroxide grains probably account for >50 wt% of the heavy mineral fraction.



Figure 19: Heavy mineral abundance for Carawine spherule layer sample 84-1.

For the 63-125 μ m size fraction, anatase (n = 585), clinozoisite/epidote (n = 32), rutile \pm anatase (n = 26), and zircon \pm anatase (n = 20) comprise 86.4%, 4.7%, 3.8%, and 3.0%, respectively, of the total grains (n = 677), and the other phases are each present in trace (<1%) amounts. Most of the grains are subrounded-to-subangular. A Raman spectrum for a green grain has bands at wavenumbers that show a fairly good match with an actinolite standard (Fig. 20), whereas the Raman spectra for two other actinolite grains have only 2-4 bands of low intensities at wavenumbers ~178, 225, 666, and 747 cm⁻¹.



Figure 20: Raman spectra of a green actinolite grain from Carawine spherule layer sample 84-1, and an actinolite standard from the RRUFF Raman spectral database.

For 18 varicolored grains, the Raman spectra are typically very similar, and the Raman spectra have 4-5 bands at wavenumbers ~141 (very strong), ~198, ~395, ~515, and ~637 cm⁻¹ that clearly match the bands in an anatase standard (Fig. 21).



Figure 21: Raman spectra of an anatase grain from Carawine spherule layer sample 84-1, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.

The Raman spectrum for a grain that is clear with a very light yellow tint shows an excellent match with an anglesite standard (Fig. 22).



Figure 22: Raman spectra of an anglesite grain from Carawine spherule layer sample 84-1, and an anglesite standard from the RRUFF Raman spectral database.

The Raman spectrum (Fig. 23) for a black opaque grain has a broad band of moderate intensity at wavenumber 720 cm⁻¹. The match with the Raman spectra for the chromite and magnesiochromite standards is rather poor, but a similar grain in Carawine spherule layer sample X24-1 that was identified as chrome spinel by XRD shows a similar Raman spectrum (see section 4.2.2.3). Therefore, this black opaque grain in Carawine spherule layer sample 84-1 is probably a chrome spinel.



Figure 23: Raman spectra of a chrome spinel grain from Carawine spherule layer sample 84-1, and chromite and magnesiochromite standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for 12 light greenish yellow-to-white grains typically have ~5-8 bands of moderate-to-strong intensities at wavenumbers 230/233, 275/279, 423/436, 450/465, 564/572, 599/608, 882/892, 913/919, and 1086/1093 cm⁻¹. A Raman spectrum (Fig. 24) for one of the grains shows a reasonably good match with an epidote standard, but in the absence of XRD or electron microprobe data for these grains, the grains are referred to as clinozoisite/epidote in Figure 19.



Figure 24: Raman spectra of an epidote grain from Carawine spherule layer sample 84-1, and an epidote standard from the RRUFF Raman spectral database.

For a grain that is clear with a light yellow tint, a Raman spectrum (Fig. 25) shows a good match with an enstatite standard, but in the absence of XRD or electron microprobe data for the grain, the grain is referred to as orthopyroxene in Figure 19.



Figure 25: Raman spectra of an orthopyroxene grain from Carawine spherule layer sample 84-1, and an enstatite standard from the RRUFF Raman spectral database.

For 14 varicolored grains, the Raman spectra for nine of them have bands at wavenumbers that match those of rutile, and the Raman spectra for five of them have bands at wavenumbers that match those of rutile and anatase. The Raman spectra for the rutile grains (e.g., Fig. 26) show an excellent match with those for two rutile standards, and the Raman spectrum for a rutile standard is quite distinct from that for an anatase standard (cf., Fig. 21). Raman spectra for rutile and anatase standards each have a band at wavenumber $\sim 140/143$ cm⁻¹, but for anatase, this band has a very strong intensity, whereas for rutile, this band typically has a very weak-to-weak intensity.



Figure 26: Raman spectra of a rutile grain from Carawine spherule layer sample 84-1, and rutile standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

For a rutile + anatase grain, an unnormalized Raman spectrum is shown in Figure 27, and its normalized Raman spectrum is compared with Raman spectra for anatase and rutile standards in Figure 28. Raman spectra for the rutile + anatase grains typically have

4-8 bands. The bands at wavenumbers 144/148 (very strong), 197/199, 396/397, 513/518, and 635/637 cm⁻¹ match those for an anatase standard, and the bands at wavenumbers 241/244, 441/445, and 609/611 cm⁻¹ match those for a rutile standard. In Figure 27, the band of very low intensity at wavenumber 419 cm⁻¹ is unindexed, and it may possibly be a cosmic spike.



Figure 27: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Carawine spherule layer sample 84-1. The band at wavenumber 419 cm⁻¹ is unindexed (U), and it may possibly be a cosmic spike. No baseline correction was made for the sample spectrum.



Figure 28: Raman spectra of a rutile (R) + anatase (A) grain from Carawine spherule layer sample 84-1, and anatase and rutile standards from the RRUFF Raman spectral database. The unnormalized Raman spectrum of this grain is shown in Figure 27. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser. A Raman spectrum for one of two white opaque grains has three bands at wavenumbers that match those of a rutile standard, and four unindexed bands at wavenumbers 864, 1153, 1181, and 1315 cm⁻¹ (Fig. 29). These grains are referred to as "rutile + unidentified" in Figure 19. Similar-looking grains with similar Raman spectra are present in trace amounts in Carawine spherule layer samples 43-1 and 42-1A (see sections 4.2.2.4 and 4.2.2.5, respectively), and Monteville spherule layer sample U63-1 (see section 4.2.6.1).



Figure 29: Raman spectra of a white opaque rutile grain with unindexed (U) bands ("rutile + unidentified") from Carawine spherule layer sample 84-1, and a rutile standard from the RRUFF Raman spectral database.

A Raman spectrum for an amber translucent grain shows a reasonably good match with a dravite standard (Fig. 30). For two dark green, pleochroic grains, the Raman spectra each have 1-3 bands of very low intensities at wavenumbers 216/224, 369, and 714 cm⁻¹ that suggest that the grains are tourmaline.



Figure 30: Raman spectra of an amber tourmaline grain from Carawine spherule layer sample 84-1, and a dravite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the dravite standard was acquired using a 514-nm laser.

Raman spectra for eight grains that are colorless or clear with a light yellow tint have 2-13 bands at wavenumbers that match those of a zircon standard (Fig. 31). The bands at wavenumbers 350/356 and 999/1006 cm⁻¹ typically have moderate-to-strong intensities, and the bands at wavenumbers 202/204, 221/224, and 437/442 cm⁻¹ have moderate intensities. For two of the zircon grains, the Raman spectra have 4-5 additional bands at wavenumbers 143, 197, 394/396, 514/517, and 638 cm⁻¹ that match those of anatase. For one of these grains, an unnormalized Raman spectrum is shown in Figure 32, and its normalized Raman spectrum is compared with Raman spectra for anatase and zircon standards in Figure 33. The anatase is probably fine-grained matrix material on the surfaces of the zircon grains. No white opaque zircon grains were recovered from Carawine spherule layer sample 84-1.



Figure 31: Raman spectra of a zircon grain from Carawine spherule layer sample 84-1, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 32: Unnormalized Raman spectrum of a zircon (Z) + anatase (A) grain from Carawine spherule layer sample 84-1. No baseline correction was made for the sample spectrum.



Figure 33: Raman spectra of a zircon (Z) + anatase (A) grain from Carawine spherule layer sample 84-1, and anatase and zircon standards from the RRUFF Raman spectral database. The unnormalized Raman spectrum of this grain is shown in Figure 32. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser. Two grains that are dark gray with colorless-to-bright green matrix material on their surfaces remain unidentified (Figure 19). A Raman spectrum for one of the grains has no bands. Similar grains are present in several of the other samples (e.g., see section 4.2.6.2), and Raman spectra identify them as chrome spinels with muscovite matrices.

For the 125-250 μ m size fraction, there are ~210 secondary iron oxide/oxyhydroxide grains that are similar to those in the 63-125 μ m size fraction. Anatase (n = 51) comprises 86.4% of the total grains (n = 59), and the other phases are minor components (Fig. 19). Raman spectra for a forest green grain and two (very) light peach opaque grains have bands at wavenumbers that match those for actinolite and anatase, respectively. Raman spectra for two of three very light yellow grains have bands at wavenumbers that match those for clinozoisite/epidote. A Raman spectrum for one of two grains that are clear with a light yellow tint has bands at wavenumbers that match those for orthopyroxene. For a pale amber grain, a Raman spectrum has bands at wavenumbers that suggest that it is spessartine (Fig. 34). A translucent olive green grain is identified as tourmaline on the basis of its similar appearance to the tourmaline grains in the 63-125 μ m size fraction.



Figure 34: Raman spectra of a spessartine grain from Carawine spherule layer sample 84-1, and a spessartine standard from the RRUFF Raman spectral database.

4.2.2.2 Sample W85-2

Subsamples 277.7 g and 371.7 g ($\Sigma = 649.4$ g) were used to characterize Carawine spherule layer sample W85-2. There are ~25 secondary iron oxide/oxyhydroxide grains in the heavy mineral separates, and almost all of them are in the 63-125 µm size fraction. Pyrite was not observed in the hand sample, but using a binocular microscope, brassy grains that resemble pyrite were observed in the HCl-insoluble heavy mineral separates. The separates went through warm HNO₃ baths in order to dissolve these grains, but ~40 of the brassy grains survived the HNO₃ digestion. XRD patterns of three brassy grains consistently contain lines that match those of pyrite, and the data for two of the grains are given in Table 12. For grain G 7-13-05 (Table 12), the unindexed line at d \sim 3.1 Å may correspond to the line at d = 3.128 Å in the standard. A Raman spectrum for this grain has bands at wavenumbers that match those of pyrite (Fig. 35). For grain G 4-4-05 (Table 12), the unindexed line at d = 3.55 Å may represent the strongest line (d = 3.52 Å) for anatase (see pattern 21-1272 in Berry, 1974). The Raman spectra for six other brassy grains have bands at wavenumbers that match those of pyrite.

| Grain ID: G 7-13-05 | | Grain G 4-4 | ID: -05 | Pyrite 6-0710 | | |
|------------------------|------------------|----------------|------------------|------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| | | 3.55 | 2 | | | |
| | | 3.16 | 3 | 3.128 | 3.5 | |
| ~3.1 | 3 | | | | | |
| 2.7 | 8 | 2.725 | 9 | 2.709 | 8.5 | |
| 2.44 | 4 | 2.425 | 7 | 2.423 | 6.5 | |
| 2.21 | 4 | 2.22 | 7 | 2.2118 | 5 | |
| 1.92 | 3 | 1.92 | 7 | 1.9155 | 4 | |
| 1.63 | 10 | 1.64 | 10 | 1.6332 | 10 | |
| 1.56 | 1 | 1.56 | 2 | 1.5640 | 1.4 | |
| 1.515 | 1 | 1.505 | 2 | 1.5025 | 2 | |
| 1.45 | 1 | 1.455 | 3 | 1.4448 | 2.5 | |
| 1.22 | 1 | ~1.22 | 1 | 1.2113 | 1.4 | |
| ~1.11 | 1 | | | 1.1057 | 0.6 | |
| ~1.044 | 3 | 1.045 | 1 | 1.0427 | 2.5 | |
| 1.01 | 1 | 1.01 | 1 | 1.0060 | 0.8 | |
| | | 0.99 | 1 | 0.9892 | 0.6 | |
| 0.96 | 2 | 0.96 | 2 | 0.9577 | 1.2 | |
| 0.906 | 1 | | | 0.9030 | 1.6 | |

Table 12: XRD data for two pyrite grains from Carawine spherule layer sample W85-2 and a pyrite standard. Lines with intensities ≤1.2 in the standard that were not observed in the patterns for the grains are not listed in the table.



Figure 35: Raman spectra of pyrite grain G 7-13-05 (Table 12) from Carawine spherule layer sample W85-2, and a pyrite standard from the RRUFF Raman spectral database.

The heavy mineral grains are described in Appendix S, and their abundance is shown in Figure 36. For the 63-125 μ m size fraction, anatase (n = 137) and actinolite (n = 11) comprise 85.6% and 6.9%, respectively, of the total grains (n = 160). Almandine (n = 2), anglesite (n = 5), and zircon (n = 2) are minor components, and there is only one grain each of chrome spinel, rutile, and tourmaline. In contrast to Carawine spherule layer sample 84-1, the actinolite grains exhibit more shades of green, the anglesite grains are white, and there is one white, translucent-to-opaque zircon grain. The grains are typically subrounded-to-subangular, but about half of the actinolite grains are angular.



Figure 36: Heavy mineral abundance for Carawine spherule layer sample W85-2.

XRD patterns for four green grains contain lines that suggest that the grains are actinolite (Table 13). The actinolite pattern used in lieu of a standard in Table 13 is from Dostál (1965). Grain G 4-7-04 has an unindexed line at d = 7.5 Å, and grain G 4-11-05 has an unindexed line at d = 8 Å (Table 13). Raman spectra were obtained for grains G 4-7-04, G 4-8-05, and G 4-11-05 (Table 13), as well as for six other green grains. The Raman spectrum for grain G 4-7-04 (Table 13) shows a good match with an actinolite standard (Fig. 37). The Raman spectra for these nine green grains have 4-11 bands at wavenumbers 159, 177/187, 221/225, 368/371, 391/395, 414/416, 531/548, 662/672

(strong-to-very strong intensity), 744, 1029, 1047, and 1058/1065 cm⁻¹, and the Raman spectral data support the XRD identification of these grains as actinolite.

Table 13: XRD data for four actinolite grains from Carawine spherule layer sample W85-2 and actinolite and tremolite standards. Lines with intensities ≤2 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain G 4-7 | ID: '-04 | Grain G 3-20 | ID: 0-05 | Grain G 4-8 | ID: 3-05 | Grain G 4-1 | ID: 1-05 | Actino | olite | Tremo 13-4 | Tremolite 13-437 | |
|----------------|------------------|-----------------|------------------|----------------|------------------|----------------|------------------|--------|------------------|---------------|---------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| | | | | 9.0 | 7.5 | 9 | 8 | 9.120 | 6 | 8.98 | 1.6 | |
| 8.5 | 6 | ~8.5 | 9 | 8.4 | 9 | | | 8.470 | 7 | 8.38 | 10 | |
| 7.5 | 4 | | | | | 8 | 8 | | | | | |
| | | | | | | | | 5.130 | 4 | 5.07 | 1.6 | |
| | | 4.9 | 2.5 | | | | | 4.910 | 7 | 4.87 | 1 | |
| | | | | | | 4.8 | 4 | 4.780 | 1 | 4.76 | 2 | |
| | | | | 4.52 | 3 | | | 4.540 | 6 | 4.51 | 2 | |
| | | 4.4 | 1 | | | 4.4 | 1 | 4.460 | 1 | | | |
| | | | | | | | | 4.230 | 3 | 4.20 | 3.5 | |
| | | 3.85 | 1 | 3.85 | 1 | | | 3.892 | 6 | 3.87 | 1.6 | |
| 3.39 | 6 | 3.4 | 7 | 3.4 | 4 | 3.4 | 5.5 | 3.401 | 8 | 3.38 | 4 | |
| 3.3 | 3 | | | | | 3.3 | 5.5 | 3.290 | 5 | | | |
| | | | | 3.27 | 2.5 | 3.25 | 3 | | | 3.27 | 7.5 | |
| 3.13 | 5 | | | 3.12 | 4 | 3.15 | 5.5 | 3.143 | 7 | 3.12 | 10 | |
| | | 3.05 | 3 | | | | | | | 3.03 | 1 | |

Table 13: continued

| Grain G 4-7 | Grain ID: G 4-7-04 | | ID: 0-05 | Grain G 4-8 | ID: 3-05 | Grain ID: G 4-11-05 | | Actinolite | | Actinolite | | Tremolite 13-437 | |
|----------------|-----------------------|-------|------------------|----------------|------------------|------------------------|------------------|------------|------------------|------------|------------------|---------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | | |
| 2.94 | 5 | 2.95 | 2.5 | 2.94 | 3.5 | 2.9 | 5 | 2.959 | 7 | 2.938 | 4 | | |
| | | | | 2.83 | <1 | | | 2.823 | 3 | 2.805 | 4.5 | | |
| | | | | | | | | 2.744 | 4 | 2.730 | 1.6 | | |
| 2.71 | 10 | 2.7 | 10 | 2.7 | 10 | 2.72 | 8 | 2.719 | 10 | 2.705 | 9 | | |
| | | 2.65 | 4 | | | | | 2.644 | 6 | | | | |
| 2.6 | 4 | 2.6 | 4 | 2.6 | 4 | | | 2.568 | 3 | 2.592 | 3 | | |
| 2.55 | 4 | 2.55 | 9.5 | | | 2.55 | 10 | 2.543 | 10 | 2.529 | 4 | | |
| 2.5 | 6 | 2.5 | 3 | | | | | 2.505 | 1 | | | | |
| | | | | | | | | 2.392 | 2 | 2.380 | 3 | | |
| | | | | | | | | 2.344 | 5 | 2.335 | 3 | | |
| | | | | 2.33 | 2.5 | | | 2.330 | 3 | 2.321 | 4 | | |
| | | 2.3 | 2 | | | | | 2.308 | 4 | 2.298 | 1.2 | | |
| 2.28 | 4 | | | | | | | 2.288 | 5 | 2.273 | 1.6 | | |
| 2.25 | 4 | | | | | | | 2.220 | 5 | 2.206 | 0.6 | | |
| | | | | | | | | 2.191 | 3 | 2.181 | 0.6 | | |
| 2.175 | 7 | 2.17 | 3.5 | 2.17 | 8 | | | 2.171 | 5 | 2.163 | 3.5 | | |
| 2.055 | 6 | | | 2.05 | 7 | | | 2.051 | 6 | 2.042 | 1.8 | | |
| | | | | | | | | 2.022 | 6 | 2.015 | 4.5 | | |
| 2.0 | 5 | 2.0 | 2.5 | | | | | 2.008 | 3 | 2.002 | 1.6 | | |
| | | | | 1.97 | 1 | | | 1.971 | 3 | 1.963 | 0.6 | | |
| | | | | | | | | 1.945 | 3 | 1.929 | 0.6 | | |
Table 13: continued

| Grain G 4-7 | ID: 7-04 | Grain G 3-20 | ID: 0-05 | Grain G 4-8 | ID: -05 | Grain G 4-1 | ID: 1-05 | Actinolite | | Tremolite 13-437 | |
|----------------|------------------|-----------------|------------------|----------------|------------------|----------------|------------------|------------|------------------|---------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | | | | | 1.897 | 3 | 1.892 | 5 |
| 1.87 | 4 | | | 1.87 | 1 | | | 1.872 | 5 | 1.864 | 1.6 |
| | | 1.85 | 1 | | | | | 1.851 | 3 | | |
| 1.8 | 3 | | | 1.81 | 1 | | | 1.814 | 1 | 1.814 | 1.6 |
| | | | | | | | | 1.749 | 3 | 1.746 | 0.6 |
| | | | | | | | | 1.689 | 6 | 1.686 | 1 |
| 1.68 | 4 | | | | | | | 1.677 | 4 | | |
| 1.64 | 5 | 1.65 | 3 | 1.65 | 1.5 | | | 1.652 | 7 | 1.649 | 4 |
| | | | | | | | | | | 1.639 | 1 |
| | | 1.59 | 3 | | | | | | | | |
| | | 1.5 | 2.5 | | | | | End | of | Plus | 9 to |
| | | 1.43 | 2.5 | | | | | data | | 1.439 |) Å |
| | | | | | | | | | | on ca | ard |
| | | | | | | | | | | | |



Figure 37: Raman spectra of actinolite grain G 4-7-04 (Table 13) from Carawine spherule layer sample W85-2, and an actinolite standard from the RRUFF Raman spectral database.

Two colorless transparent grains have similar Raman spectra, and the Raman spectrum for one of the grains shows a good match with an almandine standard (Fig. 38).



Figure 38: Raman spectra of an almandine grain from Carawine spherule layer sample W85-2, and an almandine standard from the RRUFF Raman spectral database.

XRD patterns for two light gray opaque grains contain lines that match those of anatase (Table 14). Grain G 4-8-04 has unindexed lines at d-spacings of 1.63, 1.72, 1.79, 1.83, 2.58, and 3.35 Å that have typically weak intensities (Table 14). Grain G 3-28-05 has unindexed lines at d-spacings of 1.43, 1.52, 2.12, 2.21, and 3.28 Å (Table 14). For each of the five unindexed lines, the intensity is one.

| Grain G 4-8 | ID: -04 | Grain G 3-28 | ID: 8-05 | Ana 21-1 | tase 272 |
|----------------|------------------|-----------------|---------------------------------------|-------------|------------------|
| d (Å) | I/I _o | d (Å) | $d(\text{\AA}) I/I_o d(\text{\AA})$ | | I/I _o |
| 3.53 | 10 | 3.5 | 10 | 3.52 | 10 |
| 3.35 | 4 | | | | |
| | | 3.28 | 1 | | |
| 2.58 | 3 | | | | |
| 2.38 | 7 | 2.36 | 3 | 2.378 | 2 |
| | | 2.21 | 1 | | |
| | | 2.12 | 1 | | |
| 1.89 | 8 | 1.9 | 7 | 1.892 | 3.5 |
| 1.83 | 2 | | | | |
| 1.79 | 2 | | | | |
| 1.72 | 3 | | | | |
| | | 1.7 | 3 | 1.6999 | 2 |
| 1.665 | 3 | 1.66 | 3 | 1.6665 | 2 |
| 1.63 | 2 | | | | |
| | | 1.52 | 1 | | |
| | | 1.48 | 2 | 1.4808 | 1.4 |
| | | 1.43 | 1 | | |

Table 14:XRD data for two anatase grains from Carawine spherule layer sample
W85-2 and an anatase standard. Lines with intensities ≤ 1 in the standard that
were not observed in the patterns for the grains are not listed in the table.

Raman spectra for 41 varicolored grains have 4-5 bands at wavenumbers that clearly match those of anatase. For nine of the anatase grains, the Raman spectra have 1-3 additional bands at wavenumbers 265/267, 355, and 463/468 cm⁻¹ (e.g., Fig. 39) that match those of quartz. The unnormalized Raman spectrum for the grain shown in Figure 39 is shown in Figure 40. Since bands attributed to quartz occur in Raman spectra for several heavy mineral phases in many of the samples in this study, an unnormalized Raman spectrum of quartz standard R040031 (RRUFF Project, 2014) is shown in Figure 41.



Figure 39: Raman spectra of an anatase (A) + quartz (Q) grain from Carawine spherule layer sample W85-2, and anatase and quartz standards from the RRUFF Raman spectral database. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 40: Unnormalized Raman spectrum of an anatase (A) + quartz (Q) grain from Carawine spherule layer sample W85-2. A normalized Raman spectrum for this grain is shown in Figure 39.



Figure 41: Unnormalized Raman spectrum of a quartz standard (RRUFF Project, 2014).

The Raman spectrum for one anatase grain has two additional bands at wavenumbers 284 and 477 cm⁻¹ that are attributed to K-feldspar (Fig. 42), and the band at wavenumber 514 cm⁻¹ probably consists of both anatase and K-feldspar components. Since bands attributed to K-feldspar occur in Raman spectra for several grains in many of the samples in this study, an unnormalized Raman spectrum of orthoclase standard R070001 (RRUFF Project, 2014) is shown in Figure 43.



Figure 42: Raman spectra of an anatase (A) + K-feldspar (K) grain from Carawine spherule layer sample W85-2, and anatase and orthoclase (K-feldspar) standards from the RRUFF Raman spectral database. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 43: Unnormalized Raman spectrum of an orthoclase standard (RRUFF Project, 2014).

XRD patterns for two colorless-to-white, translucent-to-opaque grains contain lines that match those of anglesite (Table 15). Grain G 4-1-04 has unindexed lines at d-spacings of 2.96 and 4.1 Å, and grain D-S 4-8-04 has an unindexed line at d = 3.55 Å (Table 15). The latter unindexed line may represent the strongest line (d = 3.52 Å) for anatase (see pattern 21-1272 in Berry, 1974). Raman spectra (e.g., Fig. 44) for these two grains, as well as two additional white opaque grains, have 4-7 bands at wavenumbers 438/439, 449/450, 607, 641, 976/978, 1060, and 1156 cm⁻¹, and the Raman spectral data support the XRD identification of these grains as anglesite. Table 15: XRD data for two anglesite grains from Carawine spherule layer sample W85-2 and an anglesite standard. Lines with intensities ≤1.6 in the standard that were not observed in the patterns for the grains are not listed in the table.

| Grain G 4-1 | ID: -04 | Grain D-S 4- | ID: 8-04 | Angle 5-05 | site 77 |
|----------------|------------------|-----------------|------------------|---------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 4.25 | 9 | 4.25 | 6 | 4.26 | 8.7 |
| 4.1 | 3 | | | | |
| 3.85 | 6 | ~3.8 | 4 | 3.813 | 5.7 |
| | | ~3.63 | 4 | 3.622 | 2.3 |
| | | 3.55 | 5 | | |
| 3.49 | 5 | | | 3.479 | 3.3 |
| 3.39 | 5 | 3.33 | 10 | 3.333 | 8.6 |
| 3.20 | 8 | | | 3.220 | 7.1 |
| 3.06 | 4 | 3.0 | 8 | 3.001 | 10 |
| 2.96 | 4 | | | | |
| 2.75 | 3 | | | 2.773 | 3.5 |
| 2.68 | 6 | 2.69 | 8 | 2.699 | 4.6 |
| | | 2.62 | 3 | 2.618 | 0.8 |
| 2.46 | 4 | | | 2.406 | 1.7 |
| 2.26 | 4 | 2.28 | 5 | 2.276 | 2 |
| 2.15 | 4 | 2.16 | 5 | 2.164 | 2.6 |
| 2.07 | 8 | | | 2.067 | 7.6 |
| 2.04 | 10 | | | 2.031 | 3.4 |
| 2.0 | 4 | 2.02 | 9 | 2.028 | 4.8 |
| 1.95 | 4 | 1.96 | 8 | 1.973 | 2.1 |

Table 15: continued

| Grain ID: G 4-1-04 | | Grain D-S 4- | ID: 8-04 | Anglesite 5-0577 | | |
|-----------------------|------------------|------------------------|-------------|---------------------|------------------|--|
| d (Å) | I/I _o | d (Å) I/I _o | | d (Å) | I/I _o | |
| | | 1.87 | 5 | 1.879 | 0.6 | |
| 1.78 | 4 | | | 1.793 | 1.5 | |
| 1.75 | 3 | | | 1.741 | 0.8 | |
| 1.72 | 4 | | | 1.716 | 0.3 | |
| 1.64 | 4 | 1.66 | 5 | 1.656 | 0.7 | |
| | | 1.619 | 7 | 1.621 | 1.9 | |
| 1.615 | 3 | | | 1.611 | 1 | |
| | | 1.58 | 5 | 1.571 | 0.6 | |
| 1.46 | 3 | | | 1.467 | 0.7 | |



Figure 44: Raman spectra of anglesite grain D-S 4-8-04 (Table 15) from Carawine spherule layer sample W85-2, and an anglesite standard from the RRUFF Raman spectral database.

An XRD pattern for a black opaque octahedral grain contains lines that match those of ferroan magnesiochromite, and there are unindexed lines of weak intensities (\leq 3) at d-spacings of 1.9, 1.95, 2.4, and 3.5 Å (Table 16). The unindexed lines at d-spacings of 1.9, 2.4, and 3.5 Å are close to lines for anatase (see Table 14), so it is possible that this chrome spinel grain may have a small amount of anatase matrix material on its surface.

| Grain G 4-6 | ID: -05 | Magnesiochromite, ferroan 9-353 | | | |
|----------------|------------------|---------------------------------------|------------------|--|--|
| d (Å) | I/I _o | d (Å) | I/I _o | | |
| | | 4.76 | 2 | | |
| 3.5 | 3 | | | | |
| 2.95 | 4 | 2.92 | 2 | | |
| 2.46 | 10 | 2.49 | 10 | | |
| 2.4 | 1 | | | | |
| 2.08 | 2 | 2.07 | 5 | | |
| 1.95 | 1 | | | | |
| 1.9 | 1 | | | | |
| | | 1.687 | 0.5 | | |
| 1.59 | 5 | 1.593 | 6 | | |
| 1.46 | 8 | 1.466 | 7 | | |

Table 16:XRD data for a chrome spinel grain from Carawine spherule layer
sample W85-2 and a ferroan magnesiochromite standard.

A Raman spectrum for a light peach grain shows a good match with a rutile standard (Fig. 45), and a Raman spectrum for a light brown amber grain shows a reasonably good match with a dravite standard (Fig. 46).



Figure 45: Raman spectra of a rutile grain from Carawine spherule layer sample W85-2, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 46: Raman spectra of a tourmaline grain from Carawine spherule layer sample W85-2, and a dravite standard from the RRUFF Raman spectral database.

XRD patterns for two grains that resemble zircons have lines that match those of a zircon standard (Table 17), and the D-S patterns for both grains show arcs. The XRD pattern for grain D-S 7-26-04 has an unindexed line at d = 4.6 Å (Table 17). The Raman spectrum for grain D-S 7-26-04 shows a fairly good match with a zircon standard, except that several bands are shifted to lower frequency wavenumbers (Fig. 47). For zircon grain G 12-11-04/D-S 8-29-05, the Gandolfi and D-S patterns have unindexed lines at d-spacings of 1.98 and 2.43 Å, and 1.95 and 4.65 Å, respectively, and these four lines have weak (≤ 1) intensities (Table 17).

| Grain | ID: | | Gra | in ID: | | Zirc | con |
|---------|------------------|--------|------------------|---------|------------------|-------|------------------|
| D-S 7-2 | 26-04 | G 12-1 | 1-04 | D-S 8-2 | 9-05 | 6-02 | 266 |
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | 4.95(s) | 3 | | |
| 4.6 | 6 | | | 4.65 | 1 | | |
| | | 4.48 | 8 | 4.5 | 8 | 4.43 | 4.5 |
| | | | | 3.69(s) | 4 | | |
| | | | | 3.45(s) | 2 | | |
| 3.3 | 10 | 3.32 | 10 | 3.32 | 10 | 3.30 | 10 |
| | | | | 2.96(s) | 1 | | |
| | | | | 2.8(s) | 2.5 | | |
| | | 2.69 | 2 | 2.66 | 2 | 2.650 | 0.8 |
| 2.55 | 10 | 2.54 | 9 | 2.54 | 4.5 | 2.518 | 4.5 |
| | | 2.43 | 1 | | | | |
| | | 2.36 | 3.5 | 2.36 | 2 | 2.336 | 1 |
| | | 2.22 | 3 | 2.22 | 2.5 | 2.217 | 0.8 |
| 2.08 | 5 | 2.08 | 5 | 2.07 | 3 | 2.066 | 2 |
| | | 1.98 | 1 | 1.95 | <1 | | |
| 1.92 | 4 | 1.91 | 1 | 1.91 | 2.5 | 1.908 | 1.4 |
| | | 1.77 | 3 | 1.76 | 2.5 | 1.751 | 1.2 |
| 1.72 | 6 | 1.73 | 7 | 1.725 | 5 | 1.712 | 4 |

Table 17:XRD data for two zircon grains from Carawine spherule layer sample
W85-2 and a zircon standard. Lines with intensities <1 in the standard that
were not observed in the patterns for the grains are not listed in the table.

Table 17: continued

| Grain ID: | | | Grai | | Zircon | | |
|-----------|------------------|------------|------------------|---------|------------------|--------|------------------|
| D-S 7-2 | 26-04 | G 12-11-04 | | D-S 8-2 | 9-05 | 6-0266 | |
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 1.66 | 6 | 1.67 | 4 | 1.66 | 2.5 | 1.651 | 1.4 |
| | | | | 1.53 | 1 | 1.547 | 0.4 |
| | | 1.48 | 3 | 1.48 | 1 | 1.477 | 0.8 |
| 1.37 | 3 | 1.38 | 3 | 1.39 | 2.5 | 1.381 | 1 |
| 1.27 | 3 | 1.27 | 2 | | | 1.259 | 0.8 |
| 1.19 | 1 | 1.2 | 2 | 1.185 | 1 | 1.1883 | 1.2 |
| | | 1.13 | 1 | | | 1.1079 | 0.6 |
| 1.1 | 1 | | | | | 1.1006 | 0.6 |
| | | 1.06 | 1 | 1.06 | 1 | 1.0590 | 0.8 |

Notes: (s) = A spurious line that is the result of the absence of the nickel filter. Grain D-S 7-26-04 is pale pink and translucent. Grain G 12-11-04/D-S 8-29-05 is white and translucent-to-opaque.



Figure 47: Raman spectra of pale pink translucent zircon grain D-S 7-26-04 (Table 17) from Carawine spherule layer sample W85-2, and a zircon standard from the RRUFF Raman spectral database.

Anatase (n = 4) and corundum (n = 2) comprise the 125-250 µm size fraction. Raman spectra for three beige opaque grains have bands at wavenumbers that match those of an anatase standard. XRD patterns for two golden brown grains contain lines that match those of corundum (Table 18). The Raman spectra for these two grains show flat curves with no bands. It is possible that the corundum grains are contaminants.

| Grain D-S 7-2 | ID: 27-04 | Grain G 7-8 | ID: -05 | Corune 10-1 | dum 73 |
|------------------|------------------|----------------|------------------|----------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 3.48 | 7 | 3.5 | 10 | 3.479 | 7.5 |
| 2.51 | 9 | 2.55 | 10 | 2.552 | 9 |
| 2.37 | 6 | 2.39 | 8 | 2.379 | 4 |
| 2.15 | 1 | | | 2.165 | <0.1 |
| 2.09 | 10 | 2.09 | 10 | 2.085 | 10 |
| | | 1.955 | 3 | 1.964 | 0.2 |
| 1.75 | 9 | 1.73 | 10 | 1.740 | 4.5 |
| 1.6 | 8 | 1.6 | 9 | 1.601 | 8 |
| 1.58 | 6 | | | 1.546 | 0.4 |
| 1.52 | 3 | | | 1.514 | 0.6 |
| 1.50 | 3 | 1.51 | 3 | 1.510 | 0.8 |
| | | 1.41 | 5 | 1.404 | 3 |
| 1.39 | 4 | 1.38 | 5 | 1.374 | 5 |
| | | | | 1.337 | 0.2 |
| | | 1.27 | 1 | 1.276 | 0.4 |
| | | | | 1.239 | 1.6 |
| 1.23 | 2 | 1.24 | 4.5 | 1.2343 | 0.8 |

Table 18:XRD data for two corundum grains from the 125-250 µm size fraction
of Carawine spherule layer sample W85-2 and a corundum standard.

4.2.2.3 Sample X24-1

Subsamples 290.4 g, 293.7 g, and 888.5 g ($\Sigma = 1,472.6$ g) were used to characterize the 63-125 µm size fraction, and subsamples 290.4 g and 293.7 g ($\Sigma = 584.1$ g) were used to characterize the 125-250 µm size fraction of Carawine spherule layer sample X24-1. Very small dark particles (oxidized sulfide crystals?) were observed in hand sample. Brassy grains that resemble pyrite were observed in the HCl-insoluble heavy mineral separates using a binocular microscope. The heavy mineral separates for the 63-125 µm size fractions went through warm HNO₃ baths in order to dissolve the putative sulfide grains, and after the HNO₃ digestion, only one brassy grain remained in subsample 290.4 g. About nine brassy grains are present in the 125-250 µm size fraction.

For a brassy grain from the 125-250 μ m size fraction, an XRD pattern contains lines that match those for pyrite, and the pattern has an unindexed line of weak intensity at d = 1.67 Å (Table 19). A Raman spectrum for this grain has three bands at wavenumbers that match those of pyrite, and two additional bands that are attributed to hematite, but the match with the hematite standard is not very good (Fig. 48). The XRD and micro-Raman spectral data suggest that the very small dark particles that were observed in hand sample are partly oxidized pyrite crystals.

| Grain G 7-1: | ID: 5-05 | Pyrite 6-0710 | | | |
|-----------------|------------------|------------------|------------------|--|--|
| d (Å) | I/I _o | d (Å) | I/I _o | | |
| 3.15 | 1 | 3.128 | 3.5 | | |
| 2.72 | 10 | 2.709 | 8.5 | | |
| 2.42 | 8 | 2.423 | 6.5 | | |
| 2.22 | 6 | 2.2118 | 5 | | |
| 1.91 | 5 | 1.9155 | 4 | | |
| 1.67 | 1 | | | | |
| 1.63 | 9 | 1.6332 | 10 | | |
| 1.57 | 2 | 1.5640 | 1.4 | | |
| 1.51 | 3 | 1.5025 | 2 | | |
| 1.45 | 2 | 1.4448 | 2.5 | | |

Table 19:XRD data for a pyrite grain from the 125-250 µm size fraction
of Carawine spherule layer sample X24-1 and a pyrite standard.



Figure 48: Raman spectra of pyrite grain G 7-15-05 (Table 19) from Carawine spherule layer sample X24-1, and hematite and pyrite standards from the RRUFF Raman spectral database. The bands at wavenumbers 221 and 286 cm⁻¹ are attributed to hematite. No baseline correction was made for the sample spectrum.

The heavy mineral grains are described in Appendix S. Since the total weight (1,472.6 g) of the subsamples that were used to characterize the 63-125 μ m size fraction is different from that (584.1 g) of the subsamples that were used to characterize the 125-250 μ m size fraction, the heavy mineral abundance for the 63-125 μ m size fraction is shown on one column graph, and that for the 125-250 μ m size fraction is shown on a different column graph. For the 63-125 μ m size fraction (Fig. 49), anatase (± quartz, ± K-feldspar; n = 479) comprises 87.6% of the total grains (n = 547), a value that is quite

similar to those for Carawine spherule layer samples 84-1 (86.4%) and W85-2 (85.6%). Actinolite (n = 7), clinozoisite/epidote (n = 16), rutile \pm anatase (n = 14), tourmaline (n = 7) and zircon (n = 20) are minor components, and almandine (n = 1), chrome spinel (n = 1) and clinopyroxene (n = 2) occur in trace amounts. The grains are typically subrounded-to-subangular, and the colors of the phases are similar to those for Carawine spherule layer samples 84-1 and W85-2.



Figure 49: Heavy mineral abundance for the 63-125 µm size fraction of Carawine spherule layer sample X24-1.

XRD patterns for two green prismatic grains contain lines that suggest that the grains are actinolite (Table 20). In Table 20, the pattern for grain G 7-25-05 has an unindexed line at d = 9.5 Å, and the actinolite pattern that is used in lieu of a standard is from Dostál (1965).

Table 20: XRD data for two actinolite grains from Carawine spherule layer sample X24-1 and actinolite and tremolite standards. Lines with intensities ≤1.6 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain G 7-2: | ID: 5-05 | Grain ID: G 8-25-05 | | Actino | olite | Tremolite 13-437 | | |
|-----------------|------------------|------------------------|------------------|--------|------------------|---------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| 9.5 | 7 | | | | | | | |
| | | ~9 | 6 | 9.120 | 6 | 8.98 | 1.6 | |
| 8.5 | 7 | 8.4 | 6 | 8.470 | 7 | 8.38 | 10 | |
| 5.2 | 2 | 5.1 | 4 | 5.130 | 4 | 5.07 | 1.6 | |
| 5.0 | 6 | | | 4.910 | 7 | 4.87 | 1 | |
| | | | | 4.780 | 1 | 4.76 | 2 | |
| 4.5 | 7 | 4.5 | 4 | 4.540 | 6 | 4.51 | 2 | |
| | | 4? | 2 | 4.230 | 3 | 4.2 | 3.5 | |
| 3.9 | 3 | 3.85 | 2 | 3.892 | 6 | 3.87 | 1.6 | |
| 3.4 | 6 | 3.4 | 3 | 3.401 | 8 | 3.38 | 4 | |
| 3.25 | 4 | 3.3 | 3 | 3.290 | 5 | 3.27 | 7.5 | |
| 3.1 | 6 | 3.1 | 10 | 3.143 | 7 | 3.12 | 10 | |
| 2.91 | 5 | 2.95 | 3 | 2.959 | 7 | 2.938 | 4 | |

Table 20: continued

| Grain G 7-2: | ID: 5-05 | Grain G 8-25 | ID: 5-05 | Actino | olite | Tremolite 13-437 | |
|-----------------|------------------|-----------------|------------------|--------|------------------|---------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | 2.8 | 1 | 2.823 | 3 | 2.805 | 4.5 |
| | | | | 2.744 | 4 | 2.730 | 1.6 |
| 2.7 | 10 | 2.72 | 9 | 2.719 | 10 | 2.705 | 9 |
| 2.6 | 8 | 2.6 | 6 | 2.644 | 6 | 2.592 | 3 |
| | | | | 2.568 | 3 | | |
| | | | | 2.543 | 10 | 2.529 | 4 |
| | | | | 2.452 | 2 | | |
| | | | | 2.424 | 2 | 2.407 | 0.8 |
| 2.38 | 2 | 2.37 | 2 | 2.392 | 2 | 2.380 | 3 |
| | | | | 2.344 | 5 | | |
| | | | | 2.330 | 3 | 2.335 | 3 |
| 2.31 | 5 | 2.32 | 5 | 2.308 | 4 | 2.321 | 4 |
| | | | | 2.288 | 5 | | |
| 2.24 | 4.5 | | | 2.220 | 5 | | |
| | | | | 2.191 | 3 | 2.206 | 0.6 |
| 2.17 | 4.5 | 2.175 | 4 | 2.171 | 5 | 2.163 | 3.5 |
| | | | | 2.159 | 2 | | |
| | | | | 2.139 | 2 | | |
| 2.05 | 3 | | | 2.051 | 6 | 2.042 | 1.8 |
| | | | | 2.022 | 6 | 2.015 | 4.5 |

Table 20: continued

| Grain G 7-2: | ID: 5-05 | Grain G 8-2: | ID: 5-05 | Actino | olite | Tremolite 13-437 | |
|-----------------|------------------|-----------------|------------------|-------------------|------------------|---------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | 2.0 | 3 | 2.008 | 3 | 2.002 | 1.6 |
| | | | | 1.971 | 3 | 1.963 | 0.6 |
| | | | | 1.945 | 3 | | |
| 1.92 | 1.5 | | | | | 1.929 | 0.6 |
| | | | | 1.897 | 3 | 1.892 | 5 |
| | | 1.88 | 3 | 1.872 | 5 | | |
| 1.84 | 1.5 | | | 1.851 | 3 | 1.864 | 1.6 |
| | | 1.81 | 1 | 1.814 | 1 | 1.814 | 1.6 |
| | | | | 1.749 | 3 | 1.746 | 0.6 |
| 1.72 | 1 | 1.72 | 2 | 1.707 | 2 | | |
| 1.7 | 2.5 | | | 1.689 | 6 | 1.686 | 1 |
| | | | | 1.677 | 4 | | |
| 1.65 | 3.5 | 1.65 | 4 | 1.652 | 7 | 1.649 | 4 |
| | | | | | | 1.639 | 1 |
| | | 1.58 | 2 | End of data | | End | d |
| | | 1.51 | 1 | aut | | of dat | a |
| | | 1.47 | 4 | | | | |

A Raman spectrum for grain G 7-25-05 (Table 20) shows a good match with an actinolite standard (Fig. 50). Raman spectra for grain G 8-25-05 (Table 20) and a third green grain are similar to the Raman spectrum shown in Figure 50. For two other green grains, the Raman spectra each show one band of weak intensity at wavenumber 670/672 cm⁻¹ that is close to the strongest band (673 cm⁻¹) for actinolite (see Fig. 50).



Figure 50: Raman spectra of actinolite grain G 7-25-05 (Table 20) from Carawine spherule layer sample X24-1, and an actinolite standard from the RRUFF Raman spectral database.

A Raman spectrum for a transparent grain that is clear with a light greenish yellow tint shows a good match with an almandine standard (Fig. 51).



Figure 51: Raman spectra of an almandine grain from Carawine spherule layer sample X24-1, and an almandine standard from the RRUFF Raman spectral database.

XRD patterns for two grains that are light gray and clear with a very light yellow tint contain lines that match those of anatase (Table 21). Grain G 8-22-05 has an unindexed line of weak intensity at d = 1.62 Å (Table 21). Grain G 8-22-05 has four additional lines that match those for quartz, but a Raman spectrum for this grain has bands at wavenumbers that match only those of anatase (Fig. 52).

Table 21: XRD data for two anatase grains from Carawine spherule layer sample X24-1 and anatase and quartz standards. Lines with intensities ≤1.7 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain ID: G 8-22-05 | | Grain ID: G 9-8-05 | | Anatase 21-1272 | | Quartz 5-0490 | |
|------------------------|------------------|-----------------------|------------------|--------------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | | | 4.26 | 3.5 |
| 3.51 | 10 | ~3.5 | 10 | 3.52 | 10 | | |
| 3.35 | 1 | | | | | 3.343 | 10 |
| 2.38 | 2.5 | ~2.38 | 5 | 2.378 | 2 | | |
| 1.89 | 4.5 | ~1.9 | 6 | 1.892 | 1.5 | | |
| | | | | 1.6999 | 2 | | |
| | | ~1.68 | 3 | 1.6665 | 2 | | |
| 1.62 | 1 | | | | | | |
| 1.6 | 3 | | | | | 1.608 | <0.1 |
| 1.56 | 3 | | | | | 1.541 | 1.5 |
| 1.48 | 2.5 | ~1.48 | 4 | 1.4808 | 1.4 | | |
| 1.37 | 1 | | | | | 1.372 | 0.9 |
| 1.33 | 1.5 | | | 1.3378 | 0.6 | | |
| 1.265 | 1 | ~1.265 | 2 | 1.2649 | 1 | | |
| 1.165 | 1 | | | 1.1664 | 0.6 | | |



Figure 52: Raman spectra of anatase grain G 8-22-05 (Table 21) from Carawine spherule layer sample X24-1, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.

Raman spectra for 24 additional varicolored grains have bands at wavenumbers that match those of anatase, and for four of the grains, the Raman spectra each have an additional band of low intensity at wavenumber 464/466 cm⁻¹ that is interpreted as the strongest band for quartz (see Fig. 41). For eight varicolored grains, the Raman spectra (e.g., Fig. 53) have 3-5 bands at wavenumbers that match those for anatase, and 1-5 bands at wavenumbers 155/157, 179, 280/291, 365/370, 473/476, and 513 cm⁻¹ that match those for a K-feldspar standard (see Fig. 43). The band at wavenumber 513 cm⁻¹

(Fig. 53), relative to the bands at wavenumbers 395 and 635 cm⁻¹, has a much higher intensity than is normally observed for the anatase band near this wavenumber (cf., Fig. 52), supporting the identification of K-feldspar (see Fig. 43).



Figure 53: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from Carawine spherule layer sample X24-1 (cf., Figs. 42 and 43).

An XRD pattern for a black octahedral grain contains lines that match those of chromite and/or ferroan magnesiochromite (Table 22). A Raman spectrum for this grain supports the XRD identification (Fig. 54), although the match to the chromite and magnesiochromite standards is not very good.

Table 22:XRD data for a chrome spinel grain from Carawine spherule layer sample
X24-1 and chromite and ferroan magnesiochromite standards. Lines with
intensities ≤ 1 in the standards that were not observed in the pattern for the
grain are not listed in the table.

| Grain G 8-29 | ID: 9-05 | Chror 3-08 | nite 73 | Magnesiochromite, ferroan 9-353 | | |
|-----------------|------------------|---------------|------------------|---------------------------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| | | 4.82 | 5 | 4.76 | 2 | |
| 2.92 | 8 | 2.95 | 6 | 2.92 | 2 | |
| 2.52 | 10 | 2.52 | 10 | 2.49 | 10 | |
| 2.42 | 1 | 2.40 | 1 | | | |
| 2.07 | 9 | 2.07 | 7 | 2.07 | 0.5 | |
| 1.69 | 2 | 1.69 | 4 | 1.687 | 0.5 | |
| 1.6 | 6 | 1.6 | 9 | 1.593 | 6 | |
| 1.47 | 5 | 1.46 | 9 | 1.466 | 7 | |
| | | 1.31 | 2 | | | |
| 1.27 | 1 | 1.26 | 5 | 1.265 | 10 | |
| | | 1.20 | 3 | | | |
| | | 1.16 | 2 | | | |
| | | 1.11 | 3 | | | |
| | | 1.10 | 6 | | | |
| 1.08 | 1 | | | 1.081 | 5 | |



Figure 54: Raman spectra of chrome spinel grain G 8-29-05 (Table 22) from Carawine spherule layer sample X24-1, and chromite and magnesiochromite standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Two clinopyroxene grains were identified using micro-Raman spectroscopy. The Raman spectrum for the colorless grain shows a good match with an augite standard (Fig. 55), and the Raman spectrum for the other grain shows a very good match with a diopside standard (Fig. 56).



Figure 55: Raman spectra of a clinopyroxene grain from Carawine spherule layer sample X24-1, and an augite standard from the RRUFF Raman spectral database.



Figure 56: Raman spectra of a clinopyroxene grain from Carawine spherule layer sample X24-1, and a diopside standard from the RRUFF Raman spectral database.

XRD patterns for four grains contain lines that match those for clinozoisite and/or epidote (Table 23). For grains G 9-1-05 and G 9-4-05 (Table 23), all the lines are faint, and the patterns are difficult to read. The unindexed lines at d-spacings of 3.25-3.33 Å (Table 23) may represent the strongest line (d = 3.343 Å) for quartz (see quartz pattern 5-0490 in Table 21). The Raman spectra for grains G 7-23-05 and G 9-4-05 (Table 23) have 4-5 bands of very low intensities at wavenumbers 175, 435, 455/460, 565/568, 598, and 915/917 cm⁻¹. Clinozoisite standard R060284 (RRUFF Project, 2014) has bands of moderate to strong intensities at wavenumbers 169, 430, and 454 cm⁻¹, and epidote has

bands of strong intensities at wavenumbers 451, 563/567, 596/599, and 913/917 cm⁻¹ (see Fig. 24). The Raman spectral data support the XRD identification of grains G 7-23-05 and G 9-4-05 (Table 23) as clinozoisite/epidote. The Raman spectrum for grain G 7-24-05 (Table 23) shows no distinct bands.
Table 23: XRD data for four clinozoisite/epidote grains from Carawine spherule layer sample X24-1 and clinozoisite and epidote standards. Lines with intensities ≤2 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain G 7-23 | ID: 3-05 | Grain G 7-24 | ID: 4-05 | Grain G 9-1- | ID: -05 | Grain II G 9-4-0 | D: 15 | Clinoz 21-1 | oisite 28 | Epid 17-5 | ote 14 |
|-----------------|------------------|-----------------|------------------|-----------------|------------------|---------------------|------------------|----------------|------------------|--------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | | | | | 8.01 | 4 | 8.04 | 1 |
| | | | | | | 7.3? | <1 | | | | |
| | | | | 5.18? | <1 | | | | | | |
| 5.0 | 3 | 5.0 | 6 | | | 5.0 | 2 | 5.03 | 5 | 5.05 | 2.5 |
| | | | | | | | | 4.77 | 3 | 4.79 | 1 |
| 4.0 | 3 | 4.0 | 8 | 4.0 | 3 | | | 4.00 | 4 | 4.02 | 5 |
| | | | | ~3.95? | 1 | | | 3.98 | 4 | 3.99 | 1 |
| | | | | | | | | 3.75 | 3 | 3.77 | 2 |
| 3.45 | 3 | 3.45 | 6 | 3.5 | 5 | | | 3.47 | 5 | 3.49 | 3 |
| | | | | | | 3.425 | 3 | 3.40 | 3 | 3.40 | 4 |
| 3.3 | 2 | 3.25 | 4 | 3.33 | 10 | | | | | | |
| | | | | | | | | 3.19 | 3 | 3.21 | 2 |
| | | | | 3.1? | 1 | | | 3.05 | 2 | 3.06 | 2 |
| | | | | | | | | | | 2.930 | 1 |
| | | | | ~2.95? | 3 | 2.92 | 10 | 2.92 | 4 | 2.920 | 2.5 |
| 2.9 | 10 | 2.9 | 10 | | | 2.82-2.88 | 10 | 2.89 | 10 | 2.900 | 10 |
| | | | | | | | | | | 2.817 | 4 |
| 2.8 | 3 | 2.8 | 2 | 2.8 | 3 | | | 2.79 | 8 | 2.786 | 1.5 |
| | | | | | | | | 2.78 | 3 | | |

Table 23: continued

| Grain G 7-2 | ID: 3-05 | Grain G 7-24 | ID: 4-05 | Grain II G 9-1-0 | D: 5 | Grain G 9-4 | ID: -05 | Clinoz 21-1 | oisite 28 | Epide 17-5 | ote 14 |
|----------------|------------------|-----------------|------------------|---------------------|------------------|----------------|------------------|----------------|------------------|---------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 2.7 | 7 | 2.7 | 8 | | | 2.7 | 7 | 2.68 | 6 | 2.688 | 7 |
| | | | | ~2.64-2.7 | 3 | | | 2.67 | 6 | 2.679 | 10 |
| | | | | | | | | 2.64 | 5 | 2.656 | 3 |
| 2.59 | 5 | 2.6 | 7 | | | 2.575 | <1 | 2.59 | 7 | 2.599 | 5 |
| | | | | | | | | 2.53 | 3 | 2.531 | 3 |
| | | | | | | | | 2.44 | 5 | 2.460 | 5 |
| 2.4 | 4 | 2.4 | 5 | 2.4 | 4 | 2.41 | 7 | 2.40 | 6 | 2.409 | 4 |
| | | | | | | | | 2.39 | 5 | 2.401 | 4 |
| | | | | | | | | 2.36 | 3 | | |
| 2.3 | 2.5 | | | ~2.28 | 2 | 2.3 | 3 | 2.29 | 6 | 2.294 | 3 |
| | | 2.2 | 8 | | | 2.19 | 2 | 2.16 | 4 | 2.166 | 3 |
| | | | | | | | | 2.15 | 3 | 2.163 | 3 |
| 2.12 | 4 | 2.13 | 4 | | | 2.12? | 1 | 2.12 | 1 | 2.117 | 2.5 |
| | | | | ~2.1 | 2 | | | 2.10 | 6 | 2.109 | 2.5 |
| | | 2.08 | 3 | | | 2.08 | 4 | 2.09 | 6 | | |
| 2.07 | 2 | | | | | | | | | 2.072 | 1.5 |
| | | | | | | | | 2.06 | 5 | | |
| | | | | | | | | 2.04 | 3 | 2.048 | 2 |
| | | | | | | | | 2.01 | 3 | 2.01 | 1.5 |
| | | 2.0 | 4 | | | | | 2.00 | 3 | End dat | of a |

Table 23: continued

| Grain G 7-2 | ID: 3-05 | Grain G 7-24 | ID: 4-05 | Grain II G 9-1-0 | D: 95 | Grain G 9-4 | ID: -05 | Clinozo 21-1 | oisite 28 | Epid 17-5 | ote 14 |
|----------------|------------------|-----------------|------------------|---------------------|------------------|----------------|------------------|-----------------|------------------|--------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 1.95 | 2 | 1.92 | 1 | ~1.9? | <1 | | | 1.949 | 2 | | |
| 1.88 | 3 | 1.87 | 4.5 | ~1.89 | <1 | 1.88 | 5 | 1.873 | 3 | | |
| | | | | 1.83? | 1 | | | 1.866 | 5 | | |
| 1.79 | 1 | 1.77 | 4.5 | | | | | 1.766 | 2 | | |
| | | | | | | 1.7 | 1.5 | 1.701 | 4 | | |
| 1.68 | 1 | | | | | | | 1.683 | 3 | | |
| 1.64 | 3.5 | | | ~1.64 | 2 | 1.645 | 8 | 1.629 | 6 | | |
| | | 1.62 | 4.5 | | | | | 1.618 | 5 | | |
| | | | | ~1.59-1.6 | 1 | | | 1.606 | 2 | | |
| 1.58 | 3 | | | | | 1.58 | 2 | 1.584 | 5 | | |
| | | | | | | | | 1.570 | 5 | | |
| | | | | | | | | 1.535 | 3 | | |
| | | | | | | | | 1.522 | 3 | | |
| 1.45 | 3 | | | ~1.465 | 3 | 1.455 | 1 | 1.450 | 4 | | |
| 1.42 | 3 | | | ~1.425? | <1 | 1.415 | 10 | 1.432 | 4 | | |
| | | | | | | | | 1.394 | 6 | | |
| | | | | | | | | 1.386 | 4 | | |
| | | | | | | | | End dat | of a | | |

Raman spectra for seven other grains suggest that they too are

clinozoisite/epidote. For each of the seven grains, the Raman spectra always have bands at wavenumbers 564/572 and 914/917 cm⁻¹, and additional bands are typically present at one or more of the following wavenumbers: 349/353, 426/434, 451/460, and 598/604 cm⁻¹. For most of these seven grains, the Raman spectral bands have low intensities. However, for one of the seven grains, the Raman spectrum has well-developed bands at wavenumbers that show an excellent match with an epidote standard (Fig. 57). For four of these seven grains, 1-5 additional bands are present at wavenumbers 141/148, 202, 397/399, 515/516, 637/642 cm⁻¹ (attributed to anatase), and 462/465 cm⁻¹ (attributed to quartz). Therefore, both the micro-Raman spectroscopic and XRD results (Table 23) suggest that quartz may be associated with some of the clinozoisite/epidote grains.



Figure 57: Raman spectra of an epidote grain from Carawine spherule layer sample X24-1, and an epidote standard from the RRUFF Raman spectral database.

XRD patterns for two amber grains and a peach-colored grain (G 8-3-05) contain lines that match those of rutile (Table 24). The pattern for the latter grain (G 8-3-05) has five additional lines that match those of anatase.

| Grain G 8-9 | ID: -05 | Grain G 8-10 | ID: 0-05 | Grain G 8-3 | ID: -05 | Rutil 21-12 | e 76 | Anata 21-12 | se 72 |
|----------------|------------------|-----------------|------------------|----------------|------------------|----------------|------------------|----------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | 3.5 | 10 | | | 3.52 | 10 |
| 3.25 | 10 | 3.25 | 10 | 3.25 | 5 | 3.25 | 10 | | |
| 2.5 | 5 | 2.49 | 7 | 2.48 | 3 | 2.487 | 5 | | |
| | | | | 2.4 | 3 | | | 2.378 | 2 |
| ~2.31 | 2 | 2.29 | 3 | | | 2.297 | 0.8 | | |
| 2.2 | 3 | 2.2 | 4 | 2.2 | 2.5 | 2.188 | 2.5 | | |
| ~2.1? | 1 | 2.06 | 1 | | | 2.054 | 1 | | |
| | | | | 1.9 | 2.5 | | | 1.892 | 1.5 |
| | | | | 1.7 | 3.5 | | | 1.6999 | 2 |
| 1.695 | 6 | 1.69 | 6 | 1.68 | 3.5 | 1.6874 | 6 | | |
| | | | | 1.66 | 3 | | | 1.6665 | 2 |
| 1.625 | 3 | | | | | 1.6237 | 2 | | |
| ~1.47 | <1 | 1.48 | 1 | 1.47 | 4 | 1.4797 | 1 | 1.4808 | 1.4 |
| | | 1.45 | 1 | | | 1.4528 | 1 | | |
| | | | | | | 1.4243 | 0.2 | | |
| | | 1.37 | 2.5 | | | 1.3598 | 2 | | |
| ~1.36? | <1 | 1.35 | 2.5 | 1.35 | 1 | 1.3465 | 1.2 | | |

Table 24:XRD data for three rutile grains from Carawine spherule layer sample
X24-1 and rutile and anatase standards.

A Raman spectrum for grain G 8-10-05 (Table 24) has bands at wavenumbers that match those for a rutile standard (Fig. 58), and this Raman spectrum confirms the XRD identification of the grain. For 11 other peach, brownish peach, reddish amber, and amber grains, the Raman spectra have bands at wavenumbers that clearly match those for rutile. For two of the grains, the Raman spectra have 4-5 additional bands at wavenumbers that match those for anatase.



Figure 58: Raman spectra of rutile grain G 8-10-05 (Table 24) from Carawine spherule layer sample X24-1, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

XRD patterns for four green grains contain lines that match those of ferrian

dravite (Table 25). The patterns for grains G 7-28-05 and G 7-29-05 are difficult to read.

| Grain G 7-2 | ID: 7-05 | Grain I G 7-28- | D: 05 | Grain I G 7-29 | ID: -05 | Grain G 8-2 | ID: -05 | Dravite, 1 19-13 | ferrian 72 |
|----------------|------------------|--------------------|------------------|-------------------|------------------|----------------|------------------|---------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 6.5 | 4 | 6.4 | 5 | 6.0-6.6 | 4 | 6.5 | 5 | 6.44 | 6 |
| 5.0 | 2 | ~5.0 | 1 | ~5.0 | 1 | 5.0 | 1 | 5.01 | 4 |
| | | | | | | | | 4.62 | 4 |
| 4.25 | 3.5 | ~4.3-4.4 | 8 | ~4.25 | 6 | 4.25 | 3 | 4.25 | 9 |
| 4.1 | 7 | ~4 | 8? | ~4.0 | 6 | 4.0 | 5 | 4.00 | 9 |
| 3.5 | 3 | 3.485 | 8 | ~3.6 | 8 | 3.5 | 3 | 3.51 | 9 |
| | | | | ~3.4 | 8 | | | 3.40 | 1 |
| | | | | 3.0 | 9? | | | 3.03 | 1 |
| 2.95 | 3.5 | 2.95 | 8 | 2.95 | 9? | 3.0 | 4 | 2.979 | 9 |
| 2.6 | 10 | 2.585 | 10 | 2.59 | 10 | 2.6 | 10 | 2.586 | 10 |
| | | | | ~2.45? | 1 | | | 2.461 | 1 |
| | | | | | | | | 2.390 | 1 |

Table 25:XRD data for four tourmaline grains from Carawine spherule layer sample
X24-1 and a ferrian dravite standard. Lines with an intensity of 1 in the
standard that were not observed in the patterns for the grains are not listed
in the table.

Table 25: continued

| Grain G 7-2 | ID: 7-05 | Grain ID G 7-28-0 |): 5 | Grain II G 7-29-0 | D:)5 | Grain G 8-2 | ID: -05 | Dravite, 19-13 | ferrian 72 |
|----------------|------------------|----------------------|------------------|----------------------|------------------|----------------|------------------|----------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 2.35 | 3 | 2.35-2.40 | 3 | 2.35-2.4 | 2 | 2.35 | 1 | 2.356 | 1 |
| | | | | | | | | 2.308 | 1 |
| | | 2.2 | 4 | 2.2-2.3 | 2 | | | 2.200 | 1 |
| 2.18 | 2 | | | | | | | 2.172 | 1 |
| | | ~2.12-2.15 | 1 | | | | | 2.141 | 1 |
| | | | | | | 2.1 | <1 | 2.120 | 1 |
| | | | | | | | | 2.066 | 1 |
| 2.05 | 4 | ~2.04 | 6 | | | | | 2.052 | 3 |
| | | | | 2.02-2.08 | 3 | 2.03 | 4 | 2.027 | 1 |
| 1.91 | 3.5 | 1.92 | 2 | 1.92 | 3 | 1.91 | 4 | 1.932 | 2 |
| 1.86 | 2 | ~1.87 | <1 | | | | | 1.889 | 1 |
| 1.84 | 2 | | | | | | | 1.858 | 1 |
| 1.76 | 1 | | | | | | | 1.793 | 1 |
| 1.73 | 1 | ~1.73-1.77 | <1 | | | | | 1.757 | 1 |
| | | | | | | 1.665 | 1 | 1.671 | 1 |
| 1.65 | 3.5 | 1.65 | 2.5 | 1.64-1.66 | 4 | 1.645 | 2 | 1.650 | 1 |
| 1.60 | 1 | 1.595 | 2 | 1.6 | 3 | 1.595 | 2 | 1.603 | 2 |
| | | 1.56 | 1 | | | | | 1.553 | 1 |

Table 25: continued

| Grain G 7-2 | ID: 7-05 | Grain II G 7-28-0 | D: 05 | Grain II G 7-29-(| D: 05 | Grain G 8-2 | ID: -05 | Dravite, 19-13 | ferrian 72 |
|----------------|------------------|----------------------|------------------|----------------------|------------------|----------------|------------------|----------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | 1.51 | 3 | 1.50-1.51 | 5 | | | 1.519 | 2 |
| 1.5 | 2 | | | | | 1.505 | 1 | 1.491 | 1 |
| | | | | | | | | 1.467 | 1 |
| 1.45 | 2 | 1.45-1.46 | 4 | 1.44-1.46 | 5 | 1.455 | 1 | 1.441 | 1 |
| | | 1.43 | 1.5 | | | | | 1.427 | 1 |
| | | 1.41 | 1.5 | 1.40 | 3 | 1.415 | 1 | 1.416 | 1 |
| | | 1.36 | 2.5 | | | 1.38 | <1 | 1.360 | 1 |
| | | | | | | 1.355 | 1 | 1.347 | 1 |
| | | 1.33 | 1 | | | 1.33 | 1 | 1.335 | 1 |
| | | 1.31 | 1 | | | 1.31 | 1 | 1.315 | 1 |
| | | 1.275 | 2.5 | | | | | 1.283 | 2 |
| | | | | | | 1.27 | 1 | 1.267 | 1 |
| | | | | | | 1.24 | 1 | 1.242 | 1 |
| | | ~1.198? | 1 | | | | | 1.208 | 1 |
| | | 1.196 | 1.5 | | | | | 1.195 | 1 |

The Raman spectra for grains G 7-28-05 (Fig. 59) and G 8-2-05 (Fig. 60) support the identification of these grains as tournalines that was made on the basis of the XRD results (Table 25). For two olive green grains that were not X-rayed, the Raman spectra have ~3-9 bands at wavenumbers that show a fairly good match with those of a dravite standard (e.g., Fig. 61).



Figure 59: Raman spectra of tourmaline grain G 7-28-05 (Table 25) from Carawine spherule layer sample X24-1, and a dravite standard from the RRUFF Raman spectral database. A cosmic spike at wavenumber ~1188 cm⁻¹ was manually removed from the sample spectrum. The Raman spectrum for the dravite standard was acquired using a 514-nm laser.



Figure 60: Raman spectra of tourmaline grain G 8-2-05 (Table 25) from Carawine spherule layer sample X24-1, and a dravite standard from the RRUFF Raman spectral database. Cosmic spikes at wavenumbers ~859 and 870 cm⁻¹ were manually removed from the sample spectrum. The Raman spectrum for the dravite standard was acquired using a 514-nm laser.



Figure 61: Raman spectra of a tourmaline grain from Carawine spherule layer sample X24-1, and a dravite standard from the RRUFF Raman spectral database.

XRD Gandolfi patterns for seven grains that are clear with a very light yellow tint contain lines that match those of zircon, and the data for two of the grains are given in Table 26.

| Grain G 8-8 | ID: -05 | Grain I G 9-5- | ID: •05 | Zirc 6-02 | on 66 |
|----------------|------------------|-------------------|------------------|--------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 4.45 | 8 | 4.43 | 6 | 4.43 | 4.5 |
| 3.33 | 10 | ~3.3 | 8 | 3.30 | 10 |
| | | ~2.65 | 1 | 2.650 | 0.8 |
| 2.53 | 7 | 2.53 | 10 | 2.518 | 4.5 |
| 2.35 | 5 | 2.34 | 4 | 2.336 | 1 |
| 2.22 | 2 | 2.22 | 2 | 2.217 | 0.8 |
| 2.08 | 5 | 2.062 | 3 | 2.066 | 2 |
| 1.91 | 3 | 1.91 | 5 | 1.908 | 1.4 |
| 1.76 | 3 | 1.73 | 6 | 1.751 | 1.2 |
| 1.71 | 4 | 1.71 | 8 | 1.712 | 4 |
| 1.66 | 4 | 1.65 | 3 | 1.651 | 1.4 |
| | | | | 1.547 | 0.4 |
| | | 1.50 | 2 | 1.495 | 0.4 |
| 1.48 | 2.5 | 1.48 | 2 | 1.477 | 0.8 |
| 1.38 | 1 | 1.39 | 8 | 1.381 | 1 |
| | | 1.37 | 8 | 1.362 | 0.8 |
| | | 1.29 | 1 | 1.290 | 0.6 |
| | | ~1.260 | 3 | 1.259 | 0.8 |

Table 26:XRD data for two zircon grains from Carawine spherule layer sample
X24-1 and a zircon standard.

Raman spectra for 12 grains that are champagne or clear with a very light-to-light yellow tint have 5-25 bands at wavenumbers 202/205, 210/214, 221/225, 267, 327/329, 333, 350/356, 392/397, 409/417, 437/439, 443/446, 465/470, 482, 497/501, 505/508, 525, 544, 583, 596, 619/626, 632, 639/643, 693, 703/710, 754, 810/812, 819/827, 864/874, 965/974, 986, 997/1007, 1062, 1172/1185, 1317, and 1465 cm⁻¹ that clearly match those of zircon (e.g., Fig. 62). Most of these bands have very low intensities, but bands of moderate-to-strong intensities typically occur at wavenumbers 202/205, 210/214, 221/225, 350/356, 437/439, 965/974, and 997/1007 cm⁻¹. A Raman spectrum for a grain that is probably a zircon has two bands of low intensity at wavenumbers 351 and 1001 cm⁻¹. A Raman spectrum for a white, translucent-to-opaque grain has no distinct bands.



Figure 62: Raman spectra of a zircon grain from Carawine spherule layer sample X24-1, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

For the 125-250 μ m size fraction that was characterized by subsamples 290.4 g and 293.7 g ($\Sigma = 584.1$ g), anatase (n = 40), anatase + K-feldspar (n = 22) and tourmaline (n = 1) comprise 63.5%, 34.9%, and 1.6%, respectively, of the total grains (n = 63; Fig. 63).



Figure 63: Heavy mineral abundance for the 125-250 µm size fraction of Carawine spherule layer sample X24-1.

A Raman spectrum for a beige grain has bands at wavenumbers that clearly match those of anatase, and Raman spectra for five colorless-to-white, translucent-to-opaque grains have 5-9 bands at wavenumbers that match those of anatase and K-feldspar (e.g., Fig. 64; cf., Figs. 42 and 43). An XRD pattern for a very light bluish green grain contains lines that show a good match with those of a ferrian dravite standard, and the pattern has unindexed lines of weak intensity at d-spacings of 3.75 and 5.4 Å (Table 27).



Figure 64: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from Carawine spherule layer sample X24-1 (cf., Figs. 42 and 43). The band of moderate intensity at wavenumber 465 cm⁻¹ may represent the band of strongest intensity for quartz (Q). A Raman spectrum of a quartz standard is shown in Figure 41.

Table 27: XRD data for a tourmaline grain from the 125-250 µm size fraction of Carawine spherule layer sample X24-1 and a ferrian dravite standard. Lines with intensities of 1 in the standard that were not observed in the pattern for the grain are not listed in the table.

| Grain G 7-20 | ID:)-05 | Dravite, 1 19-13 | ferrian 72 |
|-----------------|------------------|---------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o |
| 6.4 | 5 | 6.44 | 6 |
| 5.4 | 1 | | |
| 5.0 | 4 | 5.01 | 4 |
| 4.6 | 2 | 4.62 | 4 |
| 4.25 | 3 | 4.25 | 9 |
| 4.0 | 5 | 4.00 | 9 |
| 3.75 | 1 | | |
| 3.5 | 4 | 3.51 | 9 |
| 3.3 | 1.5 | 3.40 | 1 |
| 3.1 | 1.5 | 3.03 | 1 |
| 2.98 | 4.5 | 2.979 | 9 |
| 2.58 | 10 | 2.586 | 10 |
| 2.38 | 2.5 | 2.390 | 1 |
| 2.2 | 1.5 | 2.200 | 1 |
| 2.12 | 1.5 | 2.120 | 1 |
| 2.05 | 4.5 | 2.052 | 3 |
| 1.92 | 2 | 1.932 | 2 |

Table 27: continued

| Grain G 7-20 | ID:)-05 | Dravite, 1 19-13 | ferrian 72 |
|-----------------|------------------|---------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o |
| 1.86 | 1 | 1.858 | 1 |
| 1.78 | 1 | 1.793 | 1 |
| 1.65 | 2.5 | 1.650 | 1 |
| 1.6 | 2.5 | 1.603 | 2 |
| 1.51 | 2 | 1.519 | 2 |
| 1.46 | 2 | 1.467 | 1 |
| 1.42 | 2 | 1.427 | 1 |

4.2.2.4 Sample 43-1

Subsamples 283.8 g, 495.5 g, 535.3 g, 819.5 g, 893.3 g, 1,046.2 g, and 1,078.1 g ($\Sigma = 5,151.7$ g) were used to characterize Carawine spherule layer sample 43-1. For the 63-125 µm and 125-250 µm size fractions, there are ~145 and ~5 grains, respectively, of brownish red and reddish amber secondary iron oxide/oxyhydroxide. Pyrite was not observed in hand sample, but brassy grains resembling pyrite were observed in the first heavy mineral separate using a binocular microscope. The HCl-insoluble material in the 63-125 µm and 125-250 µm size fractions went through warm HNO₃ baths in order to dissolve the putative sulfide grains, and after the HNO₃ digestion, there are only 8 remnant brassy grains in the 63-125 µm size fraction. Two of the brassy grains are octahedral. Raman spectra for two brassy grains are each similar to the Raman spectrum for pyrite from Carawine spherule layer sample W85-2 (see Fig. 35).

The heavy mineral grains are described in Appendix S, and their abundance is shown in Figure 65. For the 63-125 μ m size fraction, anatase (n = 651) comprises 90.4% of the total grains (n = 720), a value that is comparable to those for Carawine spherule layer samples 84-1, W85-2, and X24-1. Rutile ± anatase (n = 14) and zircon (n = 44) are minor components, and the other phases occur in trace amounts. The grains are typically subrounded-to-subangular.



Figure 65: Heavy mineral abundance for Carawine spherule layer sample 43-1.

A Raman spectrum for a light forest green grain shows a fairly good match with an actinolite standard (Fig. 66).



Figure 66: Raman spectra of an actinolite grain from Carawine spherule layer sample 43-1, and an actinolite standard from the RRUFF Raman spectral database.

XRD patterns for seven grains contain lines that match those of anatase, and the data for three of the grains are given in Table 28. For grain D-S 3-27-03 (Table 28), the line at d = 1.375 Å of weak intensity matches a line of similar intensity for quartz. However, the second and third strongest (intensity) lines for quartz at d-spacings of 4.26 and 1.817 Å, respectively, are not present in the pattern for grain D-S 3-27-03 (Table 28), so the origin of the line at d = 1.375 Å that occurs in this pattern is not clear. For grain G 8-6-03 (Table 28), the XRD pattern contains two or three lines that have similar d-spacings to those of quartz. A Raman spectrum (Fig. 67) for this grain has bands at wavenumbers that match those of anatase, and an additional band of very low intensity at

wavenumber 464 cm⁻¹ suggests that quartz is present. This grain appears to consist of light medium gray, opaque anatase with colorless vitreous matrix material on its surface that is probably the quartz. The XRD pattern for grain G 8-7-03 (Table 28) definitely contains lines for both anatase and quartz.

| Table 28: | XRD data for three anatase grains from Carawine spherule layer sample |
|-----------|--|
| | 43-1 and anatase and quartz standards. Lines with intensities <1 in the |
| | standards that were not observed in the patterns for the grains are not listed |
| | in the table. |

| Grain D-S 3-2 | ID: 27-03 | Grain G 8-6- | ID: -03 | Grain G 8-7 | ID: -03 | Anat 21-12 | ase 272 | Quar 5-04 | rtz 90 |
|------------------|------------------|-----------------|------------------|----------------|------------------|---------------|------------------|--------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | ~4.25? | <1 | 4.26 | 3 | | | 4.26 | 3.5 |
| 3.52 | 10 | 3.51 | 10 | 3.515 | 8 | 3.52 | 10 | | |
| | | 3.33 | 3 | 3.34 | 10 | | | 3.343 | 10 |
| | | | | 2.45 | 2 | | | 2.458 | 1.2 |
| 2.43 | 1 | | | | | 2.431 | 1 | | |
| 2.385 | 4 | 2.375 | 4 | 2.375 | 1.5 | 2.378 | 2 | | |
| 2.335 | 1 | 2.335 | <1 | | | 2.332 | 1 | | |
| | | | | 2.28 | 2 | | | 2.282 | 1.2 |
| | | | | 2.24 | 1 | | | 2.237 | 0.6 |
| | | | | 2.13 | 2 | | | 2.128 | 0.9 |
| | | | | 1.98 | 1 | | | 1.980 | 0.6 |
| 1.895 | ~5 | 1.892 | 6 | 1.89 | 3 | 1.892 | 3.5 | | |
| | | | | 1.818 | 5 | | | 1.817 | 1.7 |

Table 28: continued

| Grain ID: D-S 3-27-03 | | Grain ID: G 8-6-03 | | Grain I G 8-7- | Grain ID: G 8-7-03 | | Anatase 21-1272 | | Quartz 5-0490 | |
|--------------------------|------------------|-----------------------|------------------|-------------------|-----------------------|--------|--------------------|--------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| | | ~1.81 | <1 | | | | | 1.801 | <0.1 | |
| 1.705 | 4 | 1.705 | 2 | 1.7 | 2 | 1.6999 | 2 | | | |
| 1.67 | 4 | 1.67 | 2 | 1.67 | 2 | 1.6665 | 2 | | | |
| | | | | 1.545 | 2.5 | | | 1.541 | 1.5 | |
| 1.49 | 1 | | | | | 1.4930 | 0.4 | | | |
| 1.485 | 4 | 1.484 | 1 | 1.482 | 1 | 1.4808 | 1.4 | | | |
| | | | | 1.382 | 1 | | | 1.382 | 0.7 | |
| 1.375 | 2 | | | 1.374 | 2 | | | 1.375 | 1.1 | |
| | | 1.365 | <1 | | | 1.3641 | 0.6 | | | |
| 1.340 | 2 | 1.34 | <1 | | | 1.3378 | 0.6 | | | |
| | | | | 1.285 | <1 | | | 1.288 | 0.3 | |
| 1.266 | 4 | 1.266 | 1 | 1.27 | <1 | 1.2649 | 1 | | | |
| | | | | 1.258 | <1 | | | 1.256 | 0.4 | |
| 1.24? | 1 | | | | | 1.2509 | 0.4 | | | |
| | | | | 1.228 | <1 | | | 1.228 | 0.2 | |
| | | | | 1.2 | 1 | | | 1.1997 | 0.5 | |
| | | | | 1.183 | 1.5 | | | 1.1838 | 0.4 | |
| | | | | ~1.165 | <1 | 1.1664 | 0.6 | | | |
| | | | | 1.083 | 1 | | | 1.0816 | 0.4 | |
| | | | | 1.047 | <1 | | | 1.0477 | 0.2 | |



Figure 67: Unnormalized Raman spectrum of anatase (A) + quartz (Q) grain G 8-6-03 (Table 28) from Carawine spherule layer sample 43-1 (cf., Figs. 39 and 40). A quartz standard is shown in Figure 41. No baseline correction was made for the sample spectrum.

Raman spectra for 36 additional varicolored grains have bands at wavenumbers that clearly match those of anatase, and for two of the grains, the Raman spectra have additional bands at wavenumbers 208/209, 261/263, 351/355, and 463/464 cm⁻¹ that match those of quartz (see Fig. 41). The colors of the anatase grains are similar to those for the anatase grains in Carawine spherule layer samples 84-1, W85-2, and X24-1. A Raman spectrum for a peach, opaque grain has ~13 bands with wavenumbers and intensities that show a very good match with a brookite standard (Fig. 68).



Figure 68: Raman spectra of a brookite grain from Carawine spherule layer sample 43-1, and a brookite standard from the RRUFF Raman spectral database.

For a black, octahedral, opaque grain, an XRD pattern contains lines that match those of chromite and/or ferroan magnesiochromite (Table 29). A Raman spectrum for this grain is similar to the Raman spectrum (see Fig. 54) for chrome spinel grain G 8-29-05 (Table 22) from Carawine spherule layer sample X24-1, and the grains are similar in appearance. For three other black opaque grains, the Raman spectra have 1-3 bands at wavenumbers 564/568, 696, and 723/741 cm⁻¹, and these Raman spectra are similar to those (see Figs. 23 and 54) for chrome spinel grains.

| Grain I D-S 3-9 | Chromite 3-0873 | | Magnesiochromite, ferroan 9-353 | | |
|--------------------|--------------------|------------------------|---------------------------------------|-------|------------------|
| d (Å) | I/I _o | d (Å) I/I _o | | d (Å) | I/I _o |
| ~4.8-4.9 | 4 | 4.82 | 5 | | |
| | | | | 4.76 | 2 |
| ~2.95 | 7 | 2.95 | 6 | 2.92 | 2 |
| 2.5 9 | | 2.52 | 10 | 2.49 | 10 |
| | | 2.40 | 1 | | |
| ~2.06 | 10 | 2.07 | 7 | 2.07 | 0.5 |
| ~1.69 | 2 | 1.69 | 4 | 1.687 | 0.5 |
| 1.595 | 7 | 1.6 | 9 | 1.593 | 6 |
| ~1.47 | 5 | 1.46 | 9 | 1.466 | 7 |

Table 29:XRD data for a chrome spinel grain from Carawine spherule layer sample
43-1 and chromite and ferroan magnesiochromite standards.

An XRD pattern for a white opaque, well-rounded grain contains lines that match those of hemimorphite, and there may be a line of very weak intensity at a d-spacing of \sim 2.75 Å (Table 30). If this line is present, it is unindexed.

Table 30:XRD data for a hemimorphite grain from Carawine spherule layer sample43-1 and a hemimorphite standard. Lines with intensities <1 in the standard</td>that were not observed in the pattern for the grain are not listed in the table.

| Grain G 7-29 | ID: -03 | Hemimorphite 5-0555 | | | |
|-----------------|------------------|------------------------|------------------|--|--|
| d (Å) | I/I _o | d (Å) | I/I _o | | |
| 6.6 | 6 | 6.60 | 8.6 | | |
| 5.39 | 3 | 5.36 | 5.5 | | |
| 4.61 | 3 | 4.62 | 4.1 | | |
| 4.2 | 3 | 4.18 | 3.8 | | |
| 3.3 | 9 | 3.296 | 7.3 | | |
| | | 3.288 | 7.5 | | |
| 3.1 | 10 | 3.104 | 10 | | |
| 2.925 | 3 | 2.929 | 4 | | |
| ~2.75? | <1 | | | | |
| ~2.69 | <1 | 2.698 | 1 | | |
| 2.56 | 8 | 2.559 | 5.1 | | |
| 2.455 | 3 | 2.450 | 3.2 | | |
| 2.4 | 8 | 2.400 | 5.4 | | |
| 2.235 | 1 | 2.229 | 1.1 | | |

Table 30: continued

| Grain G 7-29 | ID: 9-03 | Hemimorphite 5-0555 | | | |
|-----------------|------------------|------------------------|------------------|--|--|
| d (Å) | I/I _o | d (Å) | I/I _o | | |
| 2.195 | 2 | 2.198 | 1.9 | | |
| | | 2.183 | 1.6 | | |
| 2.10 | 1 | 2.092 | 1 | | |
| 2.03 | 2 | 2.020 | 1.3 | | |
| 1.85 | 1 | 1.851 | 0.7 | | |
| 1.81 | 2 | 1.808 | 1.7 | | |
| 1.785 | 2 | 1.786 | 1.6 | | |
| ~1.67 | <1 | 1.668 | 1 | | |
| 1.565 | <1 | 1.563 | 0.8 | | |
| 1.518 | 1 | 1.516 | 1.4 | | |

Raman spectra for six grains have bands at wavenumbers that clearly match those of rutile, and for two of the grains, the Raman spectra each show two additional bands at wavenumbers that are attributed to quartz. A Raman spectrum (Fig. 69) for a light peach grain has bands at wavenumbers that match those for rutile and anatase (cf., Figs. 27 and 28), and it has a shoulder at wavenumber 462 cm⁻¹ that is attributed to quartz (see Fig. 41).



Figure 69: Unnormalized Raman spectrum of a rutile (R) + anatase (A) + quartz (Q) grain from Carawine spherule layer sample 43-1 (cf., Figs. 27, 28, and 41). No baseline correction was made for the sample spectrum.

An XRD pattern for a light gray-to-white, opaque grain has four lines that match those of rutile, and an unindexed line of strong intensity at a d-spacing of \sim 7 Å (Table 31). This grain is similar in appearance to the two "rutile + unidentified" grains in Carawine spherule layer sample 84-1 (see section 4.2.2.1).

| Grain D-S 8- | ID: 7-03 | Rutile 21-1276 | | |
|-----------------|------------------|-------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | |
| ~7 | 10 | | | |
| 3.24 | 10 | 3.25 | 10 | |
| ~2.48 | 2 | 2.487 | 5 | |
| | | 2.297 | 0.8 | |
| | | 2.188 | 2.5 | |
| | | 2.054 | 1 | |
| 1.685 | 2 | 1.6874 | 6 | |
| | | | 2 | |
| ~1.49 <1 | | 1.4797 | 1 | |

Table 31:XRD data for a "rutile + unidentified" grain from Carawine
spherule layer sample 43-1 and a rutile standard.

XRD patterns for six grains contain lines that match those of zircon, and the data for five of the grains are given in Table 32. For the pink transparent grain (G 2-18-05), the Gandolfi pattern has an unindexed line of weak intensity at d = 2.14 Å (Table 32). The D-S pattern for this grain consists of dots. For the very light pink-to-white grain (G 12-16-04) and the white translucent-to-opaque grains (G 12-20-04 and G 12-22-04) (Table 32), the D-S patterns show arcs. The white translucent grain (G 12-21-04; Table 32) was lost after its analysis with the Gandolfi camera.

| Grain ID: G 2-18-05 | | Grain G 12-1 | ID: 6-04 | Grain ID: G 12-20-04 | | Grain ID: G 12-21-04 | | Grain ID: G 12-22-04 | | Zircon 6-0266 | |
|------------------------|------------------|-----------------|------------------|-------------------------|------------------|-------------------------|------------------|-------------------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 4.45 | 9 | 4.48 | 8 | 4.5 | 7 | 4.45 | 3 | 4.5 | 8 | 4.43 | 4.5 |
| 3.33 | 10 | 3.32 | 10 | 3.31 | 10 | 3.35 | 10 | 3.31 | 10 | 3.30 | 10 |
| | | 2.65 | 1 | | | 2.68 | 1 | 2.69 | 1 | 2.650 | 0.8 |
| 2.54 | 9 | 2.54 | 9 | 2.54 | 7.5 | 2.53 | 3 | 2.53 | 7 | 2.518 | 4.5 |
| 2.35 | 4 | 2.35 | 2 | 2.36 | 2 | 2.375 | 2 | 2.36 | 2 | 2.336 | 1 |
| 2.22 | 2 | 2.22 | 2 | 2.21 | 1 | 2.225 | 1 | 2.22 | 1 | 2.217 | 0.8 |
| 2.14 | 1 | | | | | | | | | | |
| 2.07 | 5 | 2.08 | 5 | 2.09 | 2 | 2.08 | 2 | 2.09 | 5 | 2.066 | 2 |
| 1.92 | 6 | 1.93 | 3 | 1.93 | 4 | 1.91 | 1 | 1.92 | 3.5 | 1.908 | 1.4 |
| 1.76 | 3 | 1.77 | 2 | 1.77 | 1 | 1.77 | 2 | 1.77 | 6 | 1.751 | 1.2 |
| 1.72 | 5.5 | 1.75 | 8.5 | 1.73 | 3.5 | 1.735 | 3 | | | 1.712 | 4 |
| 1.66 | 5 | 1.67 | 6 | 1.67 | 3 | 1.665 | 3 | 1.69 | 3 | 1.651 | 1.4 |
| | | | | | | ~1.56 | <1 | | | 1.547 | 0.4 |
| 1.50 | 2 | | | | | 1.495 | 1 | 1.5 | 1 | 1.495 | 0.4 |
| 1.48 | 3 | 1.49 | 2 | 1.48 | 1 | | | | | 1.477 | 0.8 |
| 1.38 | 3 | 1.38 | 2 | 1.38 | 1 | 1.40 | 1 | 1.38 | 1 | 1.381 | 1 |

Table 32:XRD data for five zircon grains from Carawine spherule layer
sample 43-1 and a zircon standard.

The Raman spectrum (Fig. 70) for grain G 12-16-04 (Table 32) has bands that show a fairly good match with a zircon standard, and this Raman spectrum confirms the XRD identification of the grain. The Raman spectrum for white opaque grain G 12-22-04 (Table 32) has no distinct bands. Raman spectra were obtained for three other grains that appear to be zircons. For one of the grains, the Raman spectrum shows bands at wavenumbers 353 and 1006 cm⁻¹ that suggest that it is a zircon. For the other two grains, the Raman spectra show 10-13 bands at wavenumbers 202/203, 223/224, 351/353, 412/413, 438, 469, 502/503, 630/633, 707, 817/818, 969/970, 1000/1003, and 1178 cm⁻¹ that clearly match those of zircon.

A Raman spectrum for a colorless, transparent grain has two distinct bands at wavenumbers 981 and 1053 cm⁻¹ (Fig. 71). This grain is possibly anglesite, but it is considered as an unidentified grain (see Fig. 65).



Figure 70: Raman spectra of zircon grain G 12-16-04 (Table 32) from Carawine spherule layer sample 43-1, and a zircon standard from the RRUFF Raman spectral database.



Figure 71: Raman spectra of an unidentified grain (possibly anglesite) from Carawine spherule layer sample 43-1, and an anglesite standard from the RRUFF Raman spectral database.

For the 125-250 μ m size fraction, a black opaque grain was not analyzed, but it has a similar appearance to the chrome spinel grains in the 63-125 μ m size fraction. Four grains are similar in appearance to the zircon grains in the 63-125 μ m size fraction. One of these grains is pink and translucent. The XRD pattern for this grain contains lines that match those of zircon (Table 33). A Raman spectrum for grain G 7-26-04 (Table 33) shows ~13 bands at wavenumbers that match those of a zircon standard (Fig. 72). The Raman spectrum therefore confirms the XRD identification of the grain. Table 33: XRD data for a zircon grain from the 125-250 µm size fraction of Carawine spherule layer sample 43-1 and a zircon standard. Lines with intensities <1 in the standard that were not observed in the pattern for the grain are not listed in the table.

| Grain G 7-20 | ID: 5-04 | Zircon 6-0266 | | |
|-----------------|------------------|------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | |
| 4.45 | 9 | 4.43 | 4.5 | |
| 3.33 | 10 | 3.30 | 10 | |
| 2.65 | 1 | 2.650 | 0.8 | |
| 2.54 | 10 | 2.518 | 4.5 | |
| 2.35 | 5 | 2.336 | 1 | |
| 2.24 | 3 | 2.217 | 0.8 | |
| 2.08 | 3 | 2.066 | 2 | |
| 1.92 | 9 | 1.908 | 1.4 | |
| 1.76 | 3 | 1.751 | 1.2 | |
| 1.72 | 9 | 1.712 | 4 | |
| 1.66 | 2 | 1.651 | 1.4 | |
| 1.485 | 2 | 1.477 | 0.8 | |
| 1.4 | 7 | 1.381 | 1 | |
| 1.37 | 7 | 1.362 | 0.8 | |
| 1.3 | 2 | 1.290 | 0.6 | |
| 1.27 | 2 | 1.259 | 0.8 | |


Figure 72: Raman spectra of zircon grain G 7-26-04 (Table 33) from Carawine spherule layer sample 43-1, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

4.2.2.5 Sample 42-1A

Subsamples 216.1 g and 341.4 g ($\Sigma = 557.5$ g) were used to characterize Carawine spherule layer sample 42-1A. The bulk of the heavy mineral separates consist of pale brown (5YR 5/2), moderate reddish orange (10R 6/6), medium dark gray (N4), and dark gray (N3) grains that appear to consist of secondary iron and manganese oxide/oxyhydroxide phases. By visual estimate, there are >10,000 secondary grains in the 63-125 µm size fraction, and there are several thousand secondary grains in the 125-250 µm size fraction. A few of the grains have a cubic habit, and they may be pseudomorphs after pyrite. No brassy pyrite grains were observed in hand sample.

Grains that did not appear to be secondary iron or manganese oxide/oxyhydroxide phases were handpicked from the heavy mineral separates, and the phases were identified by micro-Raman spectroscopy. The heavy mineral grains are described in Appendix S, and their abundance is shown in Figure 73.



Figure 73: Heavy mineral abundance for Carawine spherule layer sample 42-1A.

For the 63-125 μ m size fraction, anatase (n = 517) comprises 88.4% of the total grains (n = 585), a value that is comparable to those for the Carawine spherule layer samples that are described above. Chrome spinel (n = 8), rutile ± anatase (n = 20), rutile + unidentified (n = 10), and zircon ± anatase (n = 29) are minor components, and there is a single grain of tourmaline. Most of the grains are subrounded-to-subangular. As compared to Carawine spherule layer samples 84-1, W85-2, X24-1, and 43-1, anatase shows about twice as many colors/hues, and there are no amber or reddish amber rutile grains. Eighty percent of the rutile ± anatase grains are light buff-to-buff in color.

Raman spectra for 49 varicolored grains have bands at wavenumbers that clearly match those of anatase (e.g., Fig. 74), and for two of the grains, the Raman spectra have

1-2 additional bands at wavenumbers 265 and 464 cm⁻¹ that are attributed to quartz (see Fig. 41). For a third grain, the Raman spectrum has two additional bands at wavenumbers 285 and 476 cm⁻¹ that are attributed to K-feldspar (see Fig. 43).



Figure 74: Raman spectra of an anatase grain from Carawine spherule layer sample 42-1A, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.

Raman spectra that are similar to each other were obtained for two of the black opaque grains (e.g., Fig. 75). These Raman spectra are similar to the Raman spectrum (see Fig. 54) for chrome spinel grain G 8-29-05 (Table 22) from Carawine spherule layer sample X24-1.



Figure 75: Raman spectra of a chrome spinel grain from Carawine spherule layer sample 42-1A, and chromite and magnesiochromite standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for four grains have bands at wavenumbers that clearly match those of rutile. For nine other grains, the Raman spectra each have 5-8 bands at wavenumbers that match those of rutile and anatase (e.g., Fig. 76; cf., Figs. 27 and 28), and for one of the grains, the Raman spectrum has an additional band at wavenumber 464 cm⁻¹ that is attributed to quartz (see Fig. 41).



Figure 76: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Carawine spherule layer sample 42-1A (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum.

For five white opaque grains, the Raman spectra each have 3-4 bands at wavenumbers that match those of rutile, and 4-5 unindexed bands at wavenumbers 636, 860/864, 1151/1153, 1181/1183, and 1313/1320 cm⁻¹ (e.g., Fig. 77). This Raman spectrum is very similar to that for a similar-looking grain from Carawine spherule layer sample 84-1 (see Fig. 29). These grains are referred to as "rutile + unidentified" in Figure 73.



Figure 77: Raman spectra of a white opaque rutile grain with unindexed (U) bands ("rutile + unidentified") from Carawine spherule layer sample 42-1A, and a rutile standard from the RRUFF Raman spectral database (cf., Fig. 29).

A Raman spectrum for an olive green grain has bands at wavenumbers that appear to match those of a tourmaline standard (Fig. 78).



Figure 78: Raman spectra of a tourmaline grain from Carawine spherule layer sample 42-1A, and a tourmaline standard from the RRUFF Raman spectral database.

Raman spectra for two pale pink grains and four varicolored opaque grains have eight and 3-6 bands, respectively, at wavenumbers 200/202, 224/227, 347/355, 410/413, 435/442, 628, 810/820, 968, and 1000/1004 cm⁻¹ that match those of zircon. Raman spectra for two grains that are clear with a light yellow tint and transparent-to-translucent have 3-5 bands at wavenumbers 223, 354/359, 409, 439, 963, and 1000/1004 cm⁻¹ that match those of zircon. Raman spectra for a light reddish peach opaque grain and a light gray-to-white opaque grain each have only 1-2 bands at wavenumbers 351 and 999/1007 cm⁻¹, and the grains are probably zircon grains.

A Raman spectrum (Fig. 79; cf., Figs. 32 and 33) of a translucent grain that is clear with a light yellow tint has bands at wavenumbers that are attributed to zircon and anatase. This grain appears to be a zircon with a small amount of colorless, vitreous matrix material on its surface. The anatase probably comprises the matrix material. Translucent-to-opaque and opaque zircon grains (n = 10) comprise 34.5% of the total zircon grains (n = 29) in the 63-125 μ m size fraction, and they show three basic colors: peach, clear with a (very) light yellow tint, and light gray-to-white.



Figure 79: Unnormalized Raman spectrum of a zircon (Z) + anatase (A) grain from Carawine spherule layer sample 42-1A (cf., Figs. 32 and 33).

For the 125-250 μ m size fraction, anatase (n = 83) comprises 83.0% of the total grains (Fig. 73). There is a single grain of clinopyroxene, and rutile ± anatase (n = 9) and zircon (n = 7) are minor components. Raman spectra for four grains each have five bands at wavenumbers that clearly match those for anatase. A Raman spectrum for a very light yellow-to-olive green elongate grain shows a good match with an augite standard (Fig. 80).



Figure 80: Raman spectra of a clinopyroxene grain from Carawine spherule layer sample 42-1A, and an augite standard from the RRUFF Raman spectral database.

A Raman spectrum for a buff grain has bands at wavenumbers that clearly match those of a rutile standard (Fig. 81). Raman spectra for four light buff-to-buff grains have 5-8 bands at wavenumbers that show the grains to consist of rutile + anatase. In this size fraction (125-250 μ m), all the rutile ± anatase grains are very light buff-to-buff, and almost all of them are subangular-to-angular.



Figure 81: Raman spectra of a buff rutile grain from Carawine spherule layer sample 42-1A, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for an amber translucent grain (Fig. 82) and a red-peach, opaque, well-rounded grain, each have 6 bands at wavenumbers 201/206, 224/226, 347/349, 413/414, 437/438, and 996/1001 cm⁻¹ that match those of a zircon standard.



Figure 82: Raman spectra of an amber translucent zircon grain from Carawine spherule layer sample 42-1A, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

4.2.2.6 Sample X38-2

Subsamples 85.0879 g and 144.3 g ($\Sigma \approx 229.4$ g) were used to characterize Carawine spherule layer sample X38-2 that is from the TTT locality (see Fig. 4). About a dozen dark red, reddish brown, amber, and ochre grains of secondary iron oxide/oxyhydroxide are present in the heavy mineral separates. No brassy pyrite crystals were observed in hand sample, or in the heavy mineral separates using a binocular microscope. XRD analysis, micro-Raman spectroscopy, and SEM/EDX analysis were used to identify the phases.

The heavy mineral grains are described in Appendix S, and their abundance is shown in Figure 83. For the 63-125 μ m size fraction, anatase (n = 1,069), rutile ± anatase ± TiO₂ II (n = 296), and zircon (n = 200) comprise 64.1%, 17.7%, and 12.0%, respectively, of the total grains (n = 1,667). Chrome spinel (n = 57) and tourmaline ± anatase (n = 36) are minor components, and the other phases occur in trace amounts. The grains are mostly subrounded-to-subangular, and the colors and hues of the phases are similar to those for the Carawine spherule layer samples described above that are from the Ripon Hills area (see Fig. 4).



Figure 83: Heavy mineral abundance for Carawine spherule layer sample X38-2.

Three light olive green, blocky-to-prismatic grains were not analyzed, but they are identified as actinolite on the basis of their similar appearance to actinolite grains in the other Carawine spherule layer samples (see Appendix S). XRD patterns for five white opaque and two gray opaque grains contain lines that match those of anatase, and the data for three of the grains are given in Table 34. The anatase grains appear polycrystalline when viewed with both a binocular microscope and the Raman imaging system. For two of the white opaque grains, lines on their D-S patterns support this interpretation. Raman spectra for 34 varicolored grains have bands at wavenumbers that match those of anatase

(e.g., Fig. 84), and for six of the grains, the Raman spectra each show a band of low intensity at wavenumber 463/465 cm⁻¹ that is attributed to quartz (see Fig. 41).

| Grain D-S 8-1 | ID: 10-04 | Grain G 10-2 | ID: 0-04 | Grain G 12-2 | ID: 2-04 | Anata 21-12 | se 72 |
|------------------|------------------|-----------------|------------------|-----------------|------------------|----------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 3.54 | 10 | 3.51 | 10 | 3.5 | 10 | 3.52 | 10 |
| 2.44 | 1 | 2.40 | 1 | | | 2.431 | 1 |
| 2.38 | 4 | 2.39 | 3.5 | 2.35 | 3 | 2.378 | 2 |
| 2.33 | 1 | 2.33 | 1 | | | 2.332 | 1 |
| 1.89 | 5 | 1.89 | 6 | 1.88 | 6 | 1.892 | 3.5 |
| 1.71 | 3 | 1.71 | 3.5 | 1.7 | 4 | 1.6999 | 2 |
| 1.67 | 3 | 1.67 | 3 | 1.65 | 4 | 1.6665 | 2 |
| 1.48 | 2 | 1.48 | 4 | 1.48 | 4 | 1.4808 | 1.4 |
| 1.37 | 1 | 1.37 | 2 | | | 1.3641 | 0.6 |
| 1.35 | 1 | 1.34 | 2 | 1.33 | 2 | 1.3378 | 0.6 |
| 1.27 | 2 | 1.27 | 2 | 1.26 | 2 | 1.2649 | 1 |

Table 34:XRD data for three anatase grains from Carawine spherule layer sample
X38-2 and an anatase standard. Lines with intensities <1 in the standard that
were not observed in the patterns for the grains are not listed in the table.



Figure 84: Raman spectra of an anatase grain from Carawine spherule layer sample X38-2, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.

XRD patterns for four grains contain lines that match those of anglesite, and the data for two of the grains are given in Table 35. The pattern for grain G 11-22-04 (Table 35) was difficult to read. A Raman spectrum for grain G 9-20-04 (Table 35) has bands at wavenumbers that show a good match with an anglesite standard (Fig. 85), and this Raman spectrum provides confirmation of the XRD identification of this grain.

Table 35:XRD data for two anglesite grains from Carawine spherule layer sample
X38-2 and an anglesite standard. Lines with intensities ≤2.3 in the standard
that were not observed in the patterns for the grains are not listed in the
table.

| Grain G 9-20 | ID: 0-04 | Grain G 11-2 | ID: 2-04 | Angle 5-05 | site 77 |
|-----------------|------------------|-----------------|------------------|---------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 4.3 | 5 | 4.25 | 4 | 4.26 | 8.7 |
| | | 3.84 | 2 | 3.813 | 5.7 |
| 3.39 | 6 | ~3.5 | 1 | 3.479 | 3.3 |
| 3.3 | 10 | 3.3 | 5 | 3.333 | 8.6 |
| 3.1 | 5 | | | 3.220 | 7.1 |
| 2.95 | 3 | 3.0 | 9 | 3.001 | 10 |
| | | 2.75 | 6 | 2.773 | 3.5 |
| 2.7 | 5 | | | 2.699 | 4.6 |
| | | 2.65? | 1 | 2.618 | 0.8 |
| | | 2.41 | 1 | 2.406 | 1.7 |
| | | ~2.3 | 2 | 2.276 | 2 |
| | | ~2.2 | 1 | 2.193 | 0.7 |
| 2.17 | 2 | | | 2.164 | 2.6 |
| 2.07 | 6 | 2.1 | 10 | 2.067 | 7.6 |
| | | 2.05 | 10 | 2.031 | 3.4 |
| | | 2.0 | 9 | 2.028 | 4.8 |
| | | 1.98 | 6 | 1.973 | 2.1 |
| | | ~1.9 | 3 | 1.905 | 0.3 |
| 1.8 | 1 | | | 1.793 | 1.5 |
| 1.7 | 1 | ~1.72 | 2 | 1.703 | 1.6 |

Table 35: continued

| Grain G 9-20 | ID: 0-04 | Grain G 11-2 | ID: 2-04 | Anglesite 5-0577 | | |
|-----------------|------------------|-----------------|------------------|---------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| 1.62 | 1 | 1.62 | 4 | 1.621 | 1.9 | |
| | | 1.5 | 1 | 1.493 | 1.5 | |
| | | 1.41 | 1 | 1.406 | 0.3 | |



Figure 85: Raman spectra of anglesite grain G 9-20-04 (Table 35) from Carawine spherule layer sample X38-2, and an anglesite standard from the RRUFF Raman spectral database.

A Raman spectrum for a light yellow peach opaque grain has ~13 bands at wavenumbers that clearly match those of a brookite standard (Fig. 86). This Raman spectrum shows a very good match with the Raman spectrum (see Fig. 68) for the brookite grain from Carawine spherule layer sample 43-1.



Figure 86: Raman spectra of a brookite grain from Carawine spherule layer sample X38-2, and a brookite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

There are 44 black opaque grains, and five of the grains have an octahedral shape. XRD patterns for three of the grains, two of which are octahedral, contain lines that match those of chromite and/or ferroan magnesiochromite (Table 36), and the D-S patterns (octahedral grains) show dots. No Raman spectra are available for these three grains, but a Raman spectrum for another black opaque grain has bands that suggest that it is a chrome spinel (Fig. 87; cf., Figs. 54 and 75).

Table 36: XRD data for three chrome spinel grains from Carawine spherule layer sample X38-2 and chromite and ferroan magnesiochromite standards. Lines with intensities ≤1 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain ID: G 8-4-04 | | Grain ID: G 10-28-04 | | Grain ID: G 3-1-05 | | Chromite 3-0873 | | Magnesiochromite, ferroan 9-353 | |
|-----------------------|------------------|-------------------------|------------------|-----------------------|------------------|-----------------|------------------|---------------------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | | | 4.82 | 5 | 4.76 | 2 |
| | | | | 4.2(s) | 3 | | | | |
| | | | | 2.98 | 1 | 2.95 | 6 | | |
| 2.92 | 3 | 2.92 | 2 | | | | | 2.92 | 2 |
| | | | | 2.51 | 10 | 2.52 | 10 | | |
| ~2.49 | 10 | 2.5 | 10 | | | | | 2.49 | 10 |
| 2.05 | 4 | 2.07 | 1 | 2.08 | 7 | 2.07 | 7 | 2.07 | 0.5 |
| | | | | 1.95(s) | 1 | | | | |
| | | | | 1.72(s) | 1 | | | | |

Table 36: continued

| Grain G 8-4 | ID: -04 | Grain ID: G 10-28-04 | | Grain ID: G 3-1-05 | | Chromite 3-0873 | | Magnesiochromite, ferroan 9-353 | |
|----------------|------------------|-------------------------|------------------|-----------------------|------------------|--------------------|------------------|---------------------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | | | 1.69 | 4 | 1.687 | 0.5 |
| 1.592 | 6 | 1.59 | 6 | 1.61 | 9 | 1.6 | 9 | 1.593 | 6 |
| 1.465 | 7 | 1.465 | 9 | 1.48 | 8 | 1.46 | 9 | 1.466 | 7 |
| | | | | 1.38 | 1 | 1.40 | 1 | | |
| | | | | | | 1.31 | 2 | | |
| | | | | 1.27 | 3 | 1.26 | 5 | 1.265 | 10 |
| | | | | | | 1.20 | 3 | 1.197 | 0.5 |
| | | | | 1.18 | 1 | 1.16 | 2 | | |
| | | | | | | 1.11 | 3 | 1.108 | 0.5 |
| | | | | | | 1.10 | 6 | | |
| | | | | 1.08 | 4 | | | 1.081 | 5 |

Note: (s) = A probable spurious line that is the result of the absence of the nickel filter.



Figure 87: Raman spectra of a chrome spinel grain from Carawine spherule layer sample X38-2, and chromite and magnesiochromite standards from the RRUFF Raman spectral database (cf., Figs. 54 and 75). No baseline correction was made for the sample spectrum. A cosmic spike at wavenumber ~1240 cm⁻¹ was manually removed from the sample spectrum.

There are 13 medium dark gray-to-dark steel gray opaque grains that have colorless-to-emerald green matrix material on their surfaces, and XRD data for two of the grains are given in Table 37. As observed with a binocular microscope, grain G 10-27-04 (Table 37) has a very minor amount of emerald green matrix material on its surface, and the XRD pattern for this grain contains lines that match those of chromite and/or ferroan magnesiochromite. Grain D-S 10-20-05 (Table 37) has emerald green matrix material on its surface, and the XRD pattern for this grain contains lines that match those of chromite and/or ferroan magnesiochromite. Grain D-S 10-20-05 (Table 37) has emerald green matrix material on its surface, and the XRD pattern for this grain contains lines that match those of chromite, material on its surface, and the XRD pattern for this grain contains lines that match those of chromite, material on its surface, and the XRD pattern for this grain contains lines that match those of chromite, material on its surface, and the XRD pattern for this grain contains lines that match those of chromite, material on its surface, and the XRD pattern for this grain contains lines that match those of chromite, material on its surface, and the XRD pattern for this grain contains lines that match those of chromite, material on its surface.

ferroan magnesiochromite, and muscovite, with an unindexed line at d = 3.65 Å. The XRD data suggest that these 13 dark gray opaque grains are chrome spinels with muscovite matrix material on their surfaces.

Table 37: XRD data for two chrome spinel grains with matrix material on their surfaces from Carawine spherule layer sample X38-2, and chromite, ferroan magnesiochromite, and muscovite standards. Lines with intensities ≤ 1.2 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain G 10-2 | ID: 27-04 | Grain D-S 10-2 | ID: 20-05 | Chror 3-08 | nite 73 | Magnesioc ferro 9-35 | hromite, an 53 | Muscov 7-4 | ite 3T 2 |
|-----------------|------------------|-------------------|------------------|---------------|------------------|----------------------------|----------------------|---------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | ~10 | 9 | | | | | 9.97 | >10 |
| | | ~4.9? | <1 | | | | | 4.99 | 5.5 |
| ~4.8 | 2 | | | 4.82 | 5 | 4.76 | 2 | | |
| | | 4.5 | 9 | | | | | 4.49 | 2 |
| | | | | | | | | 4.46 | 2 |
| | | 3.65 | 8 | | | | | | |
| | | 3.35 | 8 | | | | | 3.331 | >10 |
| | | ~3.1 | 2 | | | | | 3.110 | 1 |
| 2.92 | 5 | 2.9 | 4 | 2.95 | 6 | 2.92 | 2 | | |
| | | | | | | | | 2.884 | 1.6 |
| | | 2.59 | 10 | | | | | 2.589 | 1.6 |
| | | | | | | | | 2.564 | 2.5 |

Table 37: continued

| Grain G 10-2 | ID: 7-04 | Grain D-S 10-2 | ID: 20-05 | Chror 3-08 | nite 73 | Magnesioch ferroa 9-35 | nromite, an 3 | Muscov 7-42 | ite 3T 2 |
|-----------------|------------------|-------------------|------------------|---------------|------------------|------------------------------|---------------------|----------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 2.5 | 10 | 2.5 | 9 | 2.52 | 10 | 2.49 | 10 | | |
| | | 2.4 | 1 | 2.40 | 1 | | | 2.384 | 0.8 |
| 2.07 | 6 | | | 2.07 | 7 | 2.07 | 0.5 | | |
| | | | | | | | | 1.999 | 4.5 |
| | | | | 1.69 | 4 | 1.687 | 0.5 | | |
| 1.6 | 8 | 1.6 | 1 | 1.60 | 9 | 1.593 | 6 | | |
| | | 1.508 | 7 | | | | | 1.502 | 1.2 |
| 1.465 | 9 | 1.47 | 7 | 1.46 | 9 | 1.466 | 7 | | |
| | | 1.433 | 4 | 1.40 | 1 | | | | |
| | | | | 1.31 | 2 | | | | |
| | | | | 1.26 | 5 | 1.265 | 10 | | |
| 1.2 | 3 | | | 1.20 | 3 | 1.197 | 0.5 | | |

An XRD pattern for a translucent grain that is clear with a light yellow tint contains lines that match those of clinozoisite and/or epidote (Table 38). In the pattern for grain G 11-28-04 (Table 38), the lines at d-spacings of 4.25, 3.36, and 1.82 Å match the three strongest lines for quartz, and the unindexed line at d = 3.51 Å is close to the strongest line (d = 3.52 Å) for anatase (see pattern 21-1272 in Table 34).

Table 38: XRD data for a clinozoisite/epidote grain from Carawine spherule layer sample X38-2, and clinozoisite, epidote, and quartz standards. For the quartz standard, only the three strongest lines are listed in the table. Lines with intensities ≤2 in the standards that were not observed in the pattern for the grain are not listed in the table.

| Grain G 11-2 | ID: 8-04 | Clinozoisite 21-128 | | Epide 17-5 | ote 14 | Quartz 5-0490 | |
|-----------------|------------------|------------------------|------------------|---------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | 8.01 | 4 | 8.04 | 1 | | |
| 5.0 | 6 | 5.03 | 5 | 5.05 | 2.5 | | |
| | | 4.77 | 3 | 4.79 | 1 | | |
| 4.25? | <1 | | | | | 4.26 | 3.5 |
| 4.0 | 4 | 4.00 | 4 | 4.02 | 5 | | |
| | | 3.98 | 4 | 3.99 | 1 | | |
| | | 3.75 | 3 | 3.77 | 2 | | |
| 3.51 | 1 | | | | | | |
| 3.45 | 1 | 3.47 | 5 | 3.49 | 3 | | |
| | | 3.40 | 3 | 3.40 | 4 | | |
| 3.36 | 5 | | | | | 3.343 | 10 |
| 3.21 | <1 | 3.19 | 3 | 3.21 | 2 | | |
| 3.1? | <1 | 3.05 | 2 | 3.06 | 2 | | |
| | | 2.92 | 4 | 2.920 | 2.5 | | |
| 2.89 | 10 | 2.89 | 10 | 2.900 | 10 | | |
| | | | | 2.817 | 4 | | |
| 2.8 | 2 | 2.79 | 8 | 2.786 | 1.5 | | |

Table 38: continued

| Grain G 11-2 | ID: 8-04 | Clinoz 21-1 | oisite 28 | Epide 17-5 | ote 14 | Quai 5-04 | rtz 90 |
|-----------------|------------------|----------------|------------------|---------------|------------------|--------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | 2.78 | 3 | | | | |
| 2.69 | 2 | 2.68 | 6 | 2.688 | 7 | | |
| | | 2.67 | 6 | 2.679 | 10 | | |
| | | 2.64 | 5 | 2.656 | 3 | | |
| | | 2.59 | 7 | 2.599 | 5 | | |
| | | 2.53 | 3 | 2.531 | 3 | | |
| 2.52 | 1 | 2.51 | 2 | | | | |
| | | 2.44 | 5 | 2.460 | 5 | | |
| 2.4 | 3 | 2.40 | 6 | 2.409 | 4 | | |
| | | 2.39 | 5 | 2.401 | 4 | | |
| | | 2.36 | 3 | | | | |
| 2.3 | 2 | | | 2.301 | 1 | | |
| | | 2.29 | 6 | 2.294 | 3 | | |
| 2.16 | 1 | 2.16 | 4 | 2.166 | 3 | | |
| | | 2.15 | 3 | 2.163 | 3 | | |
| 2.12 | 3 | 2.12 | 1 | 2.117 | 2.5 | | |
| 2.10 | 3 | 2.10 | 6 | 2.109 | 2.5 | | |
| | | 2.09 | 6 | | | | |
| | | 2.06 | 5 | 2.072 | 1.5 | | |
| 2.05 | 1 | 2.04 | 3 | 2.048 | 2 | | |
| 2.01 | <1 | 2.01 | 3 | 2.010 | 1.5 | | |

Table 38: continued

| Grain G 11-2 | ID: 8-04 | Clinozoisite 21-128 | | Epidote 17-514 | | Quartz 5-0490 | |
|-----------------|------------------|------------------------|------------------|------------------------|--|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) I/I _o | | d (Å) | I/I _o |
| | | 2.00 | 3 | End of data | | | |
| | | 1.873 | 3 | | | | |
| ~1.86 | 4 | 1.866 | 5 | | | | |
| 1.82 | 1 | | | | | 1.817 | 1.7 |
| 1.77 | <1 | 1.766 | 2 | | | | |
| 1.7 | 1 | 1.701 | 4 | | | | |
| | | 1.683 | 3 | | | | |
| 1.635 | 5 | 1.629 | 6 | | | | |
| 1.62 | 3 | 1.618 | 5 | | | | |

XRD patterns for four grains contain lines that match those of rutile, and the data for two of the grains are given in Table 39. A Raman spectrum (Fig. 88) for grain G 10-21-04 (Table 39) has bands at wavenumbers that clearly match those of a rutile standard, and this Raman spectrum confirms the XRD identification of this grain.

| Grain G 10-1 | ID: 8-04 | Grain G 10-2 | Grain ID: G 10-21-04 | | le 76 | |
|-----------------|------------------|-----------------|-------------------------|--------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| 3.25 | 10 | 3.25 | 10 | 3.25 | 10 | |
| 2.48 | 8 | 2.49 | 7 | 2.487 | 5 | |
| | | 2.3 | 2 | 2.297 | 0.8 | |
| 2.2 | 1 | 2.19 | 4 | 2.188 | 2.5 | |
| | | 2.05 | 0.5 | 2.054 | 1 | |
| 1.69 | 8 | 1.69 | 6.5 | 1.6874 | 6 | |
| | | 1.63 | 3.5 | 1.6237 | 2 | |
| | | 1.49 | 2 | 1.4797 | 1 | |
| | | 1.46 | 1 | 1.4528 | 1 | |
| 1.36 | 2 | 1.36 | 3 | 1.3598 | 2 | |
| | | 1.1 | 1 | 1.0936 | 0.8 | |

Table 39: XRD data for two rutile grains from Carawine spherule layer sample X38-2 and a rutile standard. Lines with intensities ≤ 1.2 in the standard that were not observed in the patterns for the grains are not listed in the table.



Figure 88: Raman spectra of rutile grain G 10-21-04 (Table 39) from Carawine spherule layer sample X38-2, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for another 144 grains have bands at wavenumbers that match those of rutile, so 50% (n = 148) of the estimated total number of rutile grains in the 63-125 μ m size fraction (n = 296) were analyzed by micro-Raman spectroscopy and/or XRD. For 32 of the rutile grains, the Raman spectra also have several, or all, of the characteristic bands for anatase. For twenty rutile ± anatase grains, the Raman spectra each show a band of low intensity at wavenumber 461/464 cm⁻¹ (Fig. 89; cf., Figs. 27, 28, and 41), and a few of the Raman spectra that show this band also have an additional band of low intensity at wavenumber 262/263 cm⁻¹. The bands at wavenumbers 461/464 and 262/263 cm⁻¹ are attributed to quartz.



Figure 89: Unnormalized Raman spectrum of a rutile (R) + anatase (A) + quartz (Q) grain from Carawine spherule layer sample X38-2 (cf., Figs. 27 and 28). A quartz standard is shown in Figure 41. No baseline correction was made for the sample spectrum.

The high-pressure α -PbO₂-structured polymorph of TiO₂ (TiO₂ II) was identified in nine rutile grains from the 63-125 µm size fraction, and in one rutile grain (#3) from the 125-250 µm size fraction (Table 40) by micro-Raman spectroscopy. For each of the ten grains (Table 40), the date of analysis is given to facilitate the retrieval of the raw Raman spectral data for that grain.

| Grain Identification Number//Date of Analysis | Description of Grain (Color, Diaphaneity, Shape, Size (µm), Angularity) | Number of spots analyzed/Number of spots with TiO ₂ II | Phases Present |
|---|---|---|--|
| 9//10-16-09 | Buff, Opaque, Blocky, ~60 x 90, Subangular | 4/4 | Rutile TiO ₂ II |
| 10//11-13-09 | Light buff, Opaque, Blocky, ~50 x 70, Subrounded | 4/4 | Rutile TiO ₂ II (Anatase) (Quartz) |
| 26//11-13-09 | Buff, Opaque, Blocky, ~80 x 110, Subrounded | 4/4 | Rutile TiO ₂ II (Quartz) |
| 28//11-13-09 | Buff, Opaque, Blocky, ~80 x 100, Subangular | 2/2 | Rutile TiO ₂ II |
| 5//11-15-09 | Buff, Opaque, Blocky, ~60 x 90, Subrounded | 3/3 | Rutile TiO ₂ II Anatase |
| 11//11-18-09 | Light buff, Opaque, Blocky, ~100 x 100, Subrounded | 4/4 | Rutile TiO ₂ II (Anatase) Quartz |

Table 40:Description of and micro-Raman analytical data for rutile + TiO_2 II
grains from Carawine spherule layer sample X38-2.

Table 40: continued

| Grain Identification Number//Date of Analysis | Description of Grain (Color, Diaphaneity, Shape, Size (µm), Angularity) | Number of spots analyzed/Number of spots with TiO ₂ II | Phases Present |
|---|---|---|---|
| 12//11-18-09 | Very light peach-to-buff, Opaque, Subequant, ~80 x 90, Subrounded | 1/1 | Rutile TiO ₂ II |
| 19//11-18-09 | Very light peach-to-buff, Opaque, Blocky, ~60 x 70, Subrounded | 3/3 | Rutile TiO ₂ II (Quartz) |
| 21//11-18-09 | Light peach-to-buff, Opaque, Blocky, ~90 x 90, Subrounded | 1/1 | Rutile TiO ₂ II Quartz |
| 3//11-28-09 | Buff, Opaque, Blocky, ~120 x 160, Subangular | 4/3 | Rutile (TiO ₂ II) (Quartz) |

Note: The phases in parentheses were not identified at every probed spot on the grain.

The Raman spectrum for grain #28 (Table 40) is shown in Figure 90, along with the Raman spectra of rutile standard R050031 (RRUFF Project, 2014) and of synthetic TiO₂ II from El Goresy et al. (2001, their Fig. 2).



Figure 90: Raman spectra of TiO₂ II + rutile (R) grain #28 (Table 40) from Carawine spherule layer sample X38-2, a rutile standard (RRUFF Project, 2014), and synthetic TiO₂ II from El Goresy et al. (2001, their Fig. 2). For the Raman spectrum of grain #28 (Table 40), the bands at wavenumbers 150, 174, 286, 314, 339, 356, 428, 532, and 570 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum. ID = identification number; SL = spherule layer.

The quality of the Raman spectra for the ten rutile + TiO₂ II grains (Table 40) is generally good-to-excellent. For each of the Raman spectra, rutile is indicated by the three characteristic bands at wavenumbers 237/246, 438/445, and 608/610 cm⁻¹. For about half of the Raman spectra, there is a band of very low intensity at wavenumber 142/145 cm⁻¹ that is also attributed to rutile (see Fig. 26). The Raman spectra for each of the ten grains (Table 40) contain 5-9 bands at wavenumbers 149/150, 172/175, 279/286, 313/317, 339/340, 355/359, 426/430, 531/534, and 568/580 cm⁻¹ (e.g., Fig. 90) that match those for TiO₂ II. These nine bands are in excellent agreement with those for the natural high-pressure α -PbO₂-structured polymorph of TiO₂ (TiO₂ II) from the Ries (see El Goresy et al., 2001, their Fig. 2) and Chesapeake Bay (see Jackson et al., 2006, their Fig. 3) impact structures, and the Australasian microtektite layer (see Glass and Fries, 2008, their Fig. 8), as well as for synthetic TiO₂ II (Fig. 90). The band at wavenumber 149/150 cm⁻¹ attributed to the TiO₂ II phase may appear as a shoulder on the rutile band of low intensity at wavenumber 142/145 cm⁻¹ (e.g., Fig. 91), or it is absent (e.g., Fig. 92).



Figure 91: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #10 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). The bands at wavenumbers 174, 279, 315, 339, 357, and 531 cm⁻¹, and the shoulders at wavenumbers 150, 428, and 576 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001).


Figure 92: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #26 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). The bands at wavenumbers 173, 315, 340, 357, and 533 cm⁻¹, and the shoulder at wavenumber 282 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the spectrum.

The TiO₂ II band at wavenumber 568/580 cm⁻¹ is sometimes absent (e.g., Fig. 92), and the TiO₂ II band at wavenumber 426/430 cm⁻¹ commonly appears as a shoulder on the strongest rutile band that occurs at wavenumber 438/445 cm⁻¹ (e.g., Fig. 93). The Raman spectrum (Fig. 93) for grain #21 (Table 40) has shoulders at wavenumbers 205, 264, and 462 cm⁻¹ that match bands for quartz, and this Raman spectrum has an unindexed band at wavenumber 514 cm⁻¹. This unindexed band possibly represents the band of strongest intensity for K-feldspar (see Fig. 43).



Figure 93: Unnormalized Raman spectrum of rutile (R) + TiO₂ II + quartz (Q) grain #21 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). A Raman spectrum of a quartz standard is shown in Figure 41. The bands at wavenumbers 174, 282, 314, 339, 355, and 531 cm⁻¹, and the shoulders at wavenumbers 150 and 428 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). The band at wavenumber 514 cm⁻¹ is unindexed (U).

The three Raman spectra (e.g., Fig. 94) for grain #5 (Table 40) have additional bands at wavenumbers that match those of anatase, and some of the Raman spectra for grains #10 and #11 (Table 40; Appendix AA, Fig. 300) also have bands that match those of anatase. Raman spectra for grains #12, #19, and #9 (Table 40) are given in Appendix AA (Figs. 301, 302, and 303, respectively). A band or shoulder at wavenumber 462/464

cm⁻¹ that is attributed to quartz (see Fig. 41) occurs in 1-3 of the Raman spectra for grains #10, #19, and #26 (Table 40).



Figure 94: Unnormalized Raman spectrum of rutile (R) + TiO₂ II + anatase (A) grain #5 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). A Raman spectrum of an anatase standard is shown in Figure 21. The bands at wavenumbers 173, 317, 340, and 359 cm⁻¹, and the shoulders at wavenumbers 284 and 429 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001).

XRD patterns for five green-to-olive green grains contain lines that match those of tourmaline, and the data for three of the grains are given in Table 41. Grain D-S 7-17-04 has an unindexed line of weak intensity at a d-spacing of ~ 8 Å, and grain D-S 9-8-05 has unindexed lines at d-spacings of 4.4, 6.2, and 7.3 Å (Table 41). A Raman spectrum (Fig. 95) for grain D-S 9-8-05 (Table 41) has bands at wavenumbers that show a reasonably good match with those of a dravite standard.

Table 41: XRD data for three tourmaline grains from Carawine spherule layer sample X38-2 and dravite and ferrian dravite standards. Lines with intensities ≤2 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain ID: D-S 7-17-04 | | Grain ID: G 3-21-05 | | Grain ID: D-S 9-8-05 | | Dravite 14-76 | | Dravite, ferrian 19-1372 | |
|--------------------------|------------------|------------------------|------------------|-------------------------|------------------|------------------|------------------|-----------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| ~8 | 1 | | | | | | | | |
| | | | | 7.3 | 3 | | | | |
| ~6.5 | 5 | | | | | | | 6.44 | 6 |
| | | 6.4 | 6 | | | 6.38 | 3 | | |
| | | | | 6.2 | 7 | | | | |
| ~5 | 4 | | | 5.0 | 3 | 4.98 | 2.5 | 5.01 | 4 |
| | | | | | | | | 4.62 | 4 |
| ~4.6 | 3 | | | 4.6 | 3 | 4.60 | 1.8 | | |
| | | | | 4.4 | 2.5 | | | | |
| | | | | 4.3 | 5 | | | 4.25 | 9 |
| ~4.2 | 5 | 4.22 | 3 | 4.2 | 4 | 4.22 | 6.5 | | |
| ~4 | 7 | 4.0 | 6 | 4.0 | 10 | 3.99 | 8.5 | 4.00 | 9 |
| ~3.5 | 10 | 3.5 | 5 | | | 3.48 | 6 | 3.51 | 9 |
| ~3.4 | 1 | | | | | | | 3.40 | 1 |
| | | 3.33 | 1 | 3.35 | 1 | 3.38 | 1.6 | | |
| | | | | 3.0 | 2 | 3.01 | 1.2 | 2.979 | 9 |
| ~2.95 | 9 | 2.95 | 3.5 | | | 2.961 | 8.5 | | |

Table 41: continued

| Grain ID: D-S 7-17-04 | | Grain ID: G 3-21-05 | | Grain ID: D-S 9-8-05 | | Dravite 14-76 | | Dravite, ferrian 19-1372 | |
|--------------------------|------------------|------------------------|------------------|-------------------------|------------------|------------------|------------------|-----------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | 2.86 | 2.5 | 2.897 | 1 | | |
| ~2.58 | 10 | 2.59 | 10 | 2.58 | 9 | 2.576 | 10 | 2.586 | 10 |
| ~2.375 | 5 | 2.38 | 1 | | | 2.376 | 2 | | |
| | | | | 2.32 | 2.5 | 2.342 | 2 | | |
| | | | | 2.24 | 1 | | | 2.200 | 1 |
| ~2.17 | 2 | | | | | | | 2.172 | 1 |
| | | | | 2.16 | 2 | 2.163 | 1.4 | | |
| | | 2.14 | 1 | | | | | 2.141 | 1 |
| ~2.125 | 2 | | | | | 2.127 | 1.6 | | |
| | | | | 2.1 | 1 | 2.112 | 1 | | |
| | | | | | | 2.054 | 2 | 2.052 | 3 |
| ~2.04 | 4 | 2.04 | 4.5 | 2.03 | 3.5 | 2.040 | 4.5 | | |
| ~1.98 | 1 | | | 1.99 | 1 | 1.991 | 0.6 | | |
| ~1.92 | 3 | 1.92 | 4 | | | 1.920 | 3.5 | | |
| | | | | 1.905 | 3 | 1.901 | 0.6 | | |
| ~1.87 | 1 | | | | | 1.877 | 0.8 | | |
| | | | | 1.85 | 1 | 1.849 | 0.8 | | |
| 1.78 | 1 | | | | | 1.781 | 0.8 | | |

Table 41: continued

| Grain ID: D-S 7-17-04 | | Grain ID: G 3-21-05 | | Grain ID: D-S 9-8-05 | | Dravite 14-76 | | Dravite, ferrian 19-1372 | |
|--------------------------|------------------|------------------------|------------------|-------------------------|------------------|------------------|------------------|-----------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | 1.76 | 0.5 | | | 1.757 | 1 |
| ~1.66 | 3 | 1.66 | 2 | | | 1.660 | 2.5 | | |
| | | | | 1.64 | 2 | 1.641 | 1.6 | | |
| | | 1.61 | 1 | | | | | 1.603 | 2 |
| | | | | 1.59 | 3.5 | 1.592 | 2 | | |
| ~1.585 | 3 | | | | | 1.586 | < 0.1 | | |
| | | | | 1.55 | 0.5 | | | 1.553 | 1 |
| | | 1.51 | 1 | | | | | 1.519 | 2 |
| ~1.5 | 3 | | | | | 1.5056 | 1.6 | | |
| | | | | 1.42 | 0.5 | 1.4178 | 0.8 | | |
| ~1.415 | 1 | | | | | | | 1.416 | 1 |



Figure 95: Raman spectra of tourmaline grain D-S 9-8-05 (Table 41) from Carawine spherule layer sample X38-2, and a dravite standard from the RRUFF Raman spectral database.

A Raman spectrum for a pale green grain has one band of low intensity at wavenumber 374 cm^{-1} that is close to the strongest band for tourmaline. Raman spectra for five additional grains have ~5-12 bands at wavenumbers 142/143, 169/170, 178, 207/209, 215, 238/243, 261/264, 366/374 (strong), 603, 646, 663/670, 700/703, 714, 723, 749/758, 764/768, and $781/791 \text{ cm}^{-1}$ that suggest that the grains are tourmalines. For one of these grains, the Raman spectrum has additional bands at wavenumbers 153, 284, 475, and 514 (strong) cm⁻¹ that are attributed to K-feldspar (see Fig. 43), as well as a band at wavenumber 464 cm^{-1} (strong) that is attributed to quartz (see Fig. 41). For another one

of these grains, the Raman spectrum has four additional bands at wavenumbers that match those of anatase, as well as a band at wavenumber 464 cm⁻¹ that is attributed to quartz. K-feldspar, quartz, and anatase probably comprise minor amounts of matrix material on the surfaces of the tourmaline grains.

The zircon grains have similar colors to those for the zircon grains in the other Carawine spherule layer samples (Appendix S). However, for the 63-125 μ m size fraction of sample X38-2, the abundance (872 grains/kg) of zircon grains is 1-2 orders of magnitude higher than the values for the other Carawine spherule layer samples. Of the total number (n = 200) of zircon grains in the 63-125 μ m size fraction, 84 (42%) are transparent, 31 (15.5%) are translucent, 28 (14%) are translucent-to-opaque, 56 (28%) are opaque, and there are no data for one (0.5%) grain.

XRD analysis was done on 86 varicolored grains that appear to be single crystals of zircon on the basis of their shape and color as observed using a binocular microscope. XRD analysis focused on the translucent-to-opaque and opaque zircon grains in order to search for shock-produced baddeleyite (ZrO₂) and/or reidite (e.g., see Glass and Liu, 2001; Glass et al., 2002). Of the 86 zircon grains that were analyzed by XRD, three are transparent, one is translucent, 28 are translucent-to-opaque, 53 are opaque, and there are no data for one grain. Therefore, 81 of the 84 (96.4%) zircon grains that are translucentto-opaque or opaque were analyzed by XRD. Seventy-one grains were run on both the G and D-S cameras. Seven grains were run on just the D-S camera, and eight grains were run on just the G camera.

The XRD patterns for all 86 grains contain lines that match those of zircon. The data for four of the zircon grains are given in Table 42. The pattern for grain D-S 7-14-04 has an unindexed line of weak intensity at d = 4.15 Å (Table 42). Grain D-S 7-14-04 is

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pinkish white and there are no data for its diaphaneity. Grain D-S 8-3-04 is white and grain D-S 8-21-04 is pale pink-to-white, and both grains (Table 42) are translucent-to-opaque. Grain D-S 8-22-04 (Table 42) is white-to-very light peach and opaque.

| Grain D-S 7-1 | Grain ID: D-S 7-14-04 | | Grain ID: D-S 8-3-04 | | Grain ID: D-S 8-21-04 | | Grain ID: D-S 8-22-04 | | Zircon 6-0266 | |
|------------------|--------------------------|-------|-------------------------|-------|--------------------------|-------|--------------------------|-------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| 4.45 | 8 | 4.45 | 8 | 4.5 | 6 | 4.45 | 8 | 4.43 | 4.5 | |
| 4.15 | 1 | | | | | | | | | |
| ~3.3 | 10 | 3.3 | 10 | 3.34 | 10 | 3.3 | 10 | 3.30 | 10 | |
| 2.54 | 8 | 2.53 | 9 | | | 2.54 | 8 | 2.518 | 4.5 | |
| | | | | ~2.33 | 1 | 2.35 | 3 | 2.336 | 1 | |
| | | 2.23 | 1 | | | 2.23 | 1 | 2.217 | 0.8 | |
| 2.08 | 2 | 2.1 | 4 | ~2.07 | 4 | 2.08 | 5 | 2.066 | 2 | |
| 1.92 | 2 | 1.92 | 2 | | | 1.92 | 5 | 1.908 | 1.4 | |
| | | | | | | 1.78 | 4 | 1.751 | 1.2 | |
| 1.72 | 4 | 1.73 | 5 | 1.73 | 3 | 1.72 | 6 | 1.712 | 4 | |
| | | | | 1.69 | 2 | | | 1.651 | 1.4 | |
| | | 1.48 | 0.5 | | | | | 1.477 | 0.8 | |
| | | 1.38 | 0.5 | 1.39 | 2 | 1.39 | 1 | 1.381 | 1 | |
| | | | | | | 1.37 | 1 | 1.362 | 0.8 | |
| | | 1.27 | 0.5 | | | | | 1.259 | 0.8 | |

Table 42:XRD data for four zircon grains from Carawine spherule layer sample
X38-2 and a zircon standard. Lines with intensities <1 in the standard that
were not observed in the patterns of the grains are not listed in the table.

XRD patterns for about a dozen of the zircon grains have one or two unindexed ("extra") lines that are not present for the zircon standard (6-0266) in Berry (1974). None of the unindexed lines correspond to any of the lines of moderate or strong intensity for reidite (scheelite-type $ZrSiO_4$) that are reported in Glass et al. (2002) and Liu (1979). The patterns for two of the grains each show a line of weak-to-moderate intensity at a d-spacing of ~3.1 Å. This line is close to the line (d = 3.16 Å) of strongest intensity for baddeleyite (see pattern 13-307 in Berry, 1974). However, none of the other unindexed lines in these two grains correspond to any of the lines of moderate intensity for

Most of the D-S patterns for the zircon grains show varying degrees of streakiness (for a discussion of streakiness, see Hörz and Quaide, 1973): four grains show dots, one grain shows dash-dots, one grain shows possible arcs, 67 grains show small-to-large arcs, one grain shows arcs-lines, and four grains show lines. Of the 67 grains that show arcs, 43 are opaque, 23 are translucent-to-opaque, and there are no data for one grain. The five grains that show arcs-lines or lines are opaque. Therefore, at least 98.6% of the zircon grains that show arcs-to-lines on their D-S patterns are translucent-to-opaque or opaque. The XRD data suggest that the translucent-to-opaque and opaque zircon grains are not perfectly single crystals, but instead, they have varying degrees of internal disorder that results in a polycrystalline structure (see Hörz and Quaide, 1973). Transmission electron microscope (TEM) analysis of a white opaque zircon grain to be strongly metamict with asterism at the micron-scale, but there is no evidence for shock metamorphism (H. Leroux, personal communication, 2010).

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Raman spectra for six transparent and translucent grains that were not analyzed by XRD have ~5-14 bands at wavenumbers that match those of zircon. A Raman spectrum for a transparent grain (Fig. 96) has ~14 bands at wavenumbers that show a good match with a zircon standard. A Raman spectrum (Fig. 97) for a translucent grain has ~8 bands at wavenumbers that match those of zircon, but a few of the bands show a decrease in intensity as compared to the Raman spectrum for the transparent grain (Fig. 96).



Figure 96: Raman spectra of a transparent zircon grain from Carawine spherule layer sample X38-2, and a zircon standard from the RRUFF Raman spectral database.



Figure 97: Raman spectra of a translucent zircon grain from Carawine spherule layer sample X38-2, and a zircon standard from the RRUFF Raman spectral database.

Raman spectra were obtained for 10 zircon grains that were first identified by XRD, including the four grains that are listed in Table 42. These 10 zircon grains are typically pinkish white-to-white, translucent-to-opaque or opaque, and they all show arcs or arcs/lines on their D-S patterns. The Raman spectra for the translucent-to-opaque grains typically have 5-8 bands at wavenumbers that support the XRD identification of these grains as zircons (e.g., Fig. 98).



Figure 98: Raman spectra of white translucent-to-opaque zircon grain D-S 3-19-05 (see Appendix S) from Carawine spherule layer sample X38-2, and a zircon standard from the RRUFF Raman spectral database.

As compared with the bands for the transparent (Fig. 96) and translucent (Fig. 97) zircon grains, the bands for the translucent-to-opaque zircon grains are typically broader and they have lower intensities. Furthermore, the bands of strong intensities at wavenumbers ~353/355, 437/441, and 1001/1004 cm⁻¹ (Figs. 96 and 97) typically shift to lower frequency wavenumbers at ~346/350, ~429/437, and 998/999 cm⁻¹, respectively, for the translucent-to-opaque zircon grains (e.g., Fig. 98). For the opaque zircon grains, the Raman spectra typically have ~0-3 bands of very low-to-low intensity (e.g., Figs. 99 and 100).



Figure 99: Raman spectra of white opaque zircon grain D-S 8-19-04 (see Appendix S) from Carawine spherule layer sample X38-2, and a zircon standard from the RRUFF Raman spectral database. The band at wavenumber 915 cm⁻¹ is unindexed (U), but it may represent a strong intensity band for epidote (see Fig. 24).



Figure 100: Raman spectra of very light yellow-pink opaque zircon grain D-S 8-24-04 (see Appendix S) from Carawine spherule layer sample X38-2, and a zircon standard from the RRUFF Raman spectral database.

The broadening, decrease in intensity, and shift to lower frequency wavenumbers for several of the bands in the Raman spectra for these 10 zircon grains are similar to changes that have been observed for bands in the Raman spectra for metamict zircons (e.g., Nasdala et al., 1995). For five of these 10 zircon grains, the Raman spectra each show a band of varying intensity at wavenumber 914/917 cm⁻¹ (e.g., Fig. 99). This band remains unindexed, but it may represent a band of strong intensity for clinozoisite/epidote (see Fig. 24). No lines for clinozoisite/epidote were observed on the XRD patterns for these five zircon grains, but the clinozoisite/epidote, if present, may possibly occur in

trace amounts on the surfaces of the zircon grains. For the 16 zircon grains that were analyzed by micro-Raman spectroscopy, none of the Raman spectra show any bands at wavenumbers that match those of baddeleyite or three other polymorphs of ZrO_2 as given in Wittmann et al. (2006), or reidite as given in Knittle and Williams (1993), van Westrenen et al. (2004), and Wittmann et al. (2006). Therefore, XRD analysis and/or micro-Raman spectroscopy of 46% (n = 92) of the total zircon grains (n = 200) in the 63-125 µm size fraction show no evidence for baddeleyite or reidite.

SEM/EDX analyses were obtained for six zircon grains, all of which were analyzed by XRD, and five of which were analyzed by micro-Raman spectroscopy. Three of the zircon grains (D-S 7-14-04, D-S 8-3-04, and D-S 8-22-04) are included in Table 42. The zircon grains are typically pinkish white-to-white, translucent-to-opaque or opaque, and they all show arcs on their D-S patterns. A Raman spectrum for one grain has 6 bands at wavenumbers that match those of zircon, and this Raman spectrum confirms the XRD identification of the grain. Raman spectra for the other four grains have up to 3 bands at wavenumbers that suggest that the grains are zircons.

EDX analyses show that each of the six grains consists of Zr, Si, and O. The EDX analyses are only qualitative, but are consistent with the identification of the grains as zircons as determined by XRD and/or micro-Raman spectroscopy. SEM analysis shows a polygonal network of cracks on an equant subrounded grain (D-S 7-14-04; Table 42; Fig. 101) and on a white opaque, prismatic subrounded grain (D-S 8-19-04; Fig. 102; see Fig. 99 for a Raman spectrum), but it did not show any evidence of planar microstructures or granular texture, features that have been observed in shock-metamorphosed zircons (e.g., Bohor et al., 1993; Glass and Liu, 2001; Wittmann et al., 2006). Therefore, 46% (n = 92) of the total number of zircon grains (n = 200) that were recovered from the 63-125 μ m

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size fraction were analyzed by one or more methods (XRD, micro-Raman spectroscopy, TEM, and SEM/EDX), and the results revealed no obvious evidence for shock metamorphism.



Figure 101: Secondary electron image of pinkish white zircon grain D-S 7-14-04 (Table 42) from Carawine spherule layer sample X38-2 showing a polygonal network of cracks. The magenta-colored rectangle encloses the area of the EDX scan.



Figure 102: Secondary electron image of white opaque zircon grain D-S 8-19-04 from Carawine spherule layer sample X38-2 showing a polygonal network of cracks. A Raman spectrum for this grain is shown in Figure 99. The magenta-colored square encloses the area of the EDX scan.

Anatase (n = 14), rutile \pm anatase \pm TiO₂ II (n = 4), and zircon (n = 2) comprise the 125-250 µm size fraction (Fig. 83). Raman spectra for a light gray grain and a colorless-to-white grain have bands at wavenumbers that match those of anatase. Raman spectra for four grains have bands at wavenumbers that clearly match those of rutile, and for two of the grains, the Raman spectra have additional bands at wavenumbers that match those of anatase \pm quartz. For one of the rutile grains (see grain #3 in Table 40), three of the four Raman spectra have additional bands at wavenumbers that match those of TiO₂ II and quartz (Appendix AA, Fig. 304). XRD patterns for a pink translucent grain (G 7-14-04) and a white opaque grain (G 9-9-04) contain lines that match those of zircon (Table 43). The pattern for grain G 7-14-04 has an unindexed line at d = 2.57 Å (Table 43). On the D-S patterns, grain G 7-14-04 shows dots, and grain G 9-9-04 shows small arcs.

Table 43: XRD data for two zircon grains from the 125-250 μ m size fraction of Carawine spherule layer sample X38-2 and a zircon standard. Lines with intensities ≤ 1.4 in the standard that were not observed in the patterns for the grains are not listed in the table.

| Grain G 7-14 | ID: 4-04 | Grain G 9-9 | ID: -04 | Zircon 6-0266 | | | | | | |
|-----------------|------------------|------------------------|------------|------------------|------------------|--|--|--|--|--|
| d (Å) | I/I _o | d (Å) I/I _o | | d (Å) | I/I _o | | | | | |
| 4.45 | 8 | ~4.45 | 7 | 4.43 | 4.5 | | | | | |
| ~3.3 | 10 | ~3.32 | 10 | 3.30 | 10 | | | | | |
| 2.57 | 8 | | | | | | | | | |
| 2.52 | 8 | ~2.53 | 8 | 2.518 | 4.5 | | | | | |
| 2.32 | 1 | | | 2.336 | 1 | | | | | |
| 2.24 | 1 | | | 2.217 | 0.8 | | | | | |
| 2.08 | 3 | 2.08 | 1 | 2.066 | 2 | | | | | |
| 1.75 | 5 | 1.74 | 6 | 1.751 | 1.2 | | | | | |
| 1.73 | 5 | 1.71 | 6 | 1.712 | 4 | | | | | |
| | | 1.67 | 4 | 1.651 | 1.4 | | | | | |

For the estimated total number of rutile \pm anatase grains (n = 300) that were recovered from the 63-250 µm size fraction of Carawine spherule layer sample X38-2, four grains (~1.3%) were analyzed by XRD, and 149 grains (~49.7%), including one of the X-rayed grains, were analyzed by micro-Raman spectroscopy. Rutile \pm anatase grains that contain the TiO₂ II phase (n = 10) comprise ~6.7% of the grains that were analyzed by micro-Raman spectroscopy, and they comprise a minimum of ~3.3% of the estimated total number of rutile \pm anatase grains in the 63-250 µm size fraction of sample X38-2.

4.2.3 Carawine Context Samples

4.2.3.1 Sample 104141

Sample 104141 was collected ~5 m stratigraphically below the Carawine spherule layer (see Table 4). Subsample 357.2 g was used to characterize Carawine context sample 104141, and the phases were identified by micro-Raman spectroscopy. For the 63-125 μ m size fraction, there are ~223 secondary iron oxide/oxyhydroxide grains, and ~10 of these grains appear to be pseudomorphs after cubic crystals of pyrite. For three of the secondary grains, the Raman spectra show no bands, but for 10 secondary grains, the Raman spectra show one or more bands at wavenumbers 220/224, 244/245, 282/298, 389/394, 400, 547, and 683/685 cm⁻¹. The bands at wavenumbers 389/394, 547, and 683/685 cm⁻¹ are attributed to goethite (Fig. 103). Hematite can show a band of strong intensity at wavenumber 400 cm⁻¹ (Colomban et al., 2008), whereas bands at 220/224, 244/245, and 282/298 cm⁻¹ have been reported for both goethite (e.g., Fig. 103) and hematite (de Faria et al., 1997; Colomban et al., 2008).



Figure 103: Raman spectra of a goethite grain from Carawine context sample 104141, and a goethite standard from the RRUFF Raman spectral database. The sample was collected ~5 m stratigraphically below the Carawine spherule layer.

Grains that did not appear to be secondary iron oxide/oxyhydroxide phases were handpicked from the heavy mineral separate. The heavy mineral grains are described in Appendix T, and their abundance is shown in Figure 104. For the 63-125 μ m size fraction, anatase (n = 43) and chrome spinel (n = 35) comprise 48.3% and 39.3%, respectively, of the total grains (n = 89). Rutile + anatase (n = 2), tourmaline (n = 3), and zircon (n = 6) are minor components. Most of the grains are subrounded, but a few grains are subangular.



Figure 104: Heavy mineral abundance for Carawine context sample 104141. The sample was collected ~5 m stratigraphically below the Carawine spherule layer.

Raman spectra for 17 grains each have five bands with wavenumbers that match those of an anatase standard (e.g., Fig. 105). In contrast to the Carawine spherule layer samples, no buff, beige, or white anatase grains were recovered from Carawine context sample 104141.



Figure 105: Raman spectra of a very light peach anatase grain from Carawine context sample 104141, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser. The sample was collected ~5 m stratigraphically below the Carawine spherule layer.

The chrome spinel grains are black (n = 31), dark steel gray (n = 2), dark red (n = 1), and dark reddish brown (n = 1). The black and dark steel gray grains are opaque, and 30 (~91%) of these grains have light yellow-to-green matrix material on their surfaces. The dark red and dark reddish brown grains are translucent-to-opaque.

Raman spectra for nine grains typically have 1-2 bands of low intensities at wavenumbers 563/577 and 729/757 cm⁻¹. A Raman spectrum (Fig. 106) for a dark steel

gray grain that has green matrix material on its surface has bands at wavenumbers 570, 648, and 684 cm⁻¹ that are attributed to chrome spinel, and bands at wavenumbers 192, 265, and 410? cm⁻¹ that are attributed to muscovite. The bands at wavenumbers 704 and 743 cm⁻¹ probably have both chrome spinel and muscovite components (cf., Fig. 87). This grain is similar in appearance to the chrome spinel grains in Carawine spherule layer sample X38-2 that have muscovite in the green matrix material on their surfaces (see section 4.2.2.6).



Figure 106: Raman spectra of a chrome spinel (Chr) grain (cf., Fig. 87) with green muscovite (M) matrix material on its surface from Carawine context sample 104141, and magnesiochromite and muscovite standards from the RRUFF Raman spectral database. The sample was collected ~5 m stratigraphically below the Carawine spherule layer.

The Raman spectra for two light brown grains have bands at wavenumbers that match those of rutile and anatase, and the Raman spectrum for one of the grains is given in Figure 107.



Figure 107: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Carawine context sample 104141 (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum. The sample was collected ~5 m stratigraphically below the Carawine spherule layer.

For an olive green grain, the Raman spectrum (Fig. 108) has 3-4 bands of moderate-to-strong intensities at wavenumbers that appear to match those of a tourmaline standard. For another olive green grain, the Raman spectrum has bands at wavenumbers 223 and 370 cm⁻¹, and this grain is probably a tourmaline.



Figure 108: Raman spectra of an olive green tourmaline grain from Carawine context sample 104141, and a tourmaline standard from the RRUFF Raman spectral database. The sample was collected ~5 m stratigraphically below the Carawine spherule layer.

The zircon grains are light champagne or clear with a (very) light yellow tint, and they are typically prismatic in shape. In contrast to the Carawine spherule layer samples (see Appendix S), no pink, white, or opaque zircon grains were recovered from Carawine context sample 104141 (see Appendix T). Raman spectra for three of these grains have 3-13 bands at wavenumbers that clearly match those of a zircon standard (e.g., Fig. 109).



Figure 109: Raman spectra of a light champagne, transparent zircon grain from Carawine context sample 104141, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~5 m stratigraphically below the Carawine spherule layer.

The 125-250 μ m size fraction consists of two anatase grains and a light champagne zircon grain. The Raman spectra for the anatase grains each have the five characteristic bands at wavenumbers 142/143, 196, 395, 514, and 637 cm⁻¹. The zircon grain was not analyzed, but it is similar in appearance to the zircon grains in the 63-125 μ m size fraction.

4.2.3.2 Sample 104175

Sample 104175 was collected ~20 m stratigraphically above the Carawine spherule layer (see Table 4). Subsample 235.4 g was used to characterize Carawine context sample 104175, and almost all the grains in the heavy mineral separates consist of secondary phases. For the 63-125 μ m size fraction, there are 34 ochre, brown, reddish brown, and cherry red secondary iron oxide/oxyhydroxide grains, 29 dark steel gray opaque grains, and two lighter-colored grains (see below). A Raman spectrum for one of the iron oxide/oxyhydroxide grains has bands of low intensities at wavenumbers 297 and 395 cm⁻¹ that are close to bands of moderate-to-strong intensities for goethite (see Fig. 103). Several of the dark steel gray opaque grains appear to be pseudomorphs after aggregates of blocky crystals. The Raman spectra for these grains generally have no bands, but for one of the grains, the Raman spectrum has 5-6 bands of low intensities at wavenumbers that suggest a manganese oxide (Fig. 110).



Figure 110: Raman spectra of a possible manganese oxide grain from Carawine context sample 104175, and a hollandite standard from the RRUFF Raman spectral database. The sample was collected ~20 m stratigraphically above the Carawine spherule layer.

The descriptions of the two lighter-colored grains are given in Appendix T. For both grains, the Raman spectra (Figs. 111 and 112) remain unidentified. For the 63-125 µm size fraction, therefore, there are only 0-2 primary heavy mineral grains.



Figure 111: Unnormalized Raman spectrum of an unidentified light bluish gray opaque grain from Carawine context sample 104175. The sample was collected ~20 m stratigraphically above the Carawine spherule layer.



Figure 112: Unnormalized Raman spectrum of an unidentified white translucent-toopaque grain from Carawine context sample 104175. The sample was collected ~20 m stratigraphically above the Carawine spherule layer.

For the 125-250 μ m size fraction, there are only secondary grains: 7 ochre and 12 dark steel gray opaque grains that are similar in appearance to those in the 63-125 μ m size fraction.

4.2.3.3 Sample X68-1

Sample X68-1 was collected ~10-20 m stratigraphically below the Carawine spherule layer (see Table 4). Subsamples 300.0 g and 304.7 g ($\Sigma = 604.7$ g) were used to characterize Carawine context sample X68-1, and the phases were identified by micro-Raman spectroscopy. By visual estimate, there are >10,000 grains of secondary iron

oxide/oxyhydroxide and manganese oxide(s) in the 63-125 μm size fraction. Raman spectra for five grains that appear to be pseudomorphs after pyrite (striated cubes) have 4-9 bands at wavenumbers 213/222, 240, 285/295, 390/400, 470/475, 535/546, 594/596, 649, 679, 999, and 1310/1318 cm⁻¹. For one of these grains, the Raman spectrum (Fig. 113) has bands that suggest the grain is hematite, but the match is not very good. The band at wavenumber 1310/1318 cm⁻¹ in some of these Raman spectra may correspond to the band of very strong intensity at wavenumber 1314 cm⁻¹ that has been reported for hematite (e.g., see Ciobotă et al., 2012). The bands at wavenumbers 470/475, 535/546, 679, and 999 cm⁻¹ are close to bands that have been reported for goethite (see de Faria et al., 1997; Das and Hendry, 2011; Ciobotă et al., 2012; and references therein). It is not clear what phase(s) is (are) responsible for the bands at wavenumbers 594/596 and 649 cm⁻¹.



Figure 113: Raman spectra of a hematite grain from Carawine context sample X68-1, and a hematite standard from the RRUFF Raman spectral database. The sample was collected ~10-20 m stratigraphically below the Carawine spherule layer.

Raman spectra for ~30 (light) yellow, orange, and golden opaque grains typically have ~8-14 bands at wavenumbers attributed to goethite, hematite, and quartz (e.g., Fig. 114).



Figure 114: Raman spectra of a goethite (G) + quartz (Q) + hematite (H) grain from Carawine context sample X68-1, and goethite, hematite, and quartz standards from the RRUFF Raman spectral database. The sample was collected ~10-20 m stratigraphically below the Carawine spherule layer.
Raman spectra for two steel gray-to-dark steel gray opaque grains have 5-6 bands at wavenumbers 181, 270/287, 355, 490/494, 572/576, and 638/642 (strong) cm⁻¹ that suggest that they are manganese oxides (e.g., Fig. 115).



Figure 115: Raman spectra of a possible manganese oxide grain from Carawine context sample X68-1, and a hollandite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~10-20 m stratigraphically below the Carawine spherule layer.

Grains in the 63-125 μ m size fraction that did not appear to be secondary iron or manganese oxide/oxyhydroxide phases were handpicked from the heavy mineral separates. The heavy mineral grains are described in Appendix T, and their abundance is shown in Figure 116. Anatase (n = 5), rutile (n = 3), and tourmaline (n = 1) comprise 55.6%, 33.3%, and 11.1%, respectively, of the total grains (n = 9).



Figure 116: Heavy mineral abundance for Carawine context sample X68-1. The sample was collected ~10-20 m stratigraphically below the Carawine spherule layer.

Raman spectra for two grains have 4-5 bands at wavenumbers that match those of anatase, as well as 1-4 bands at wavenumbers that match those of quartz. The origin (detrital or secondary) of the anatase grains is not clear from their appearance as observed

using a binocular microscope. Raman spectra for three grains have bands at wavenumbers that clearly match those of a rutile standard (e.g., Fig. 117). Unlike Carawine spherule layer sample X38-2 (see Appendix S), no peach, buff, or amber rutile grains were recovered from Carawine context sample X68-1 (see Appendix T). On the basis of its appearance, a light yellow-green translucent grain is tentatively identified as tourmaline.



Figure 117: Raman spectra of a rutile grain from Carawine context sample X68-1, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~10-20 m stratigraphically below the Carawine spherule layer.

For the 125-250 μ m size fraction, there are ~20 secondary iron oxide/oxyhydroxide grains, and ~430 steel gray-to-dark steel gray opaque grains, many of which have yellow matrix material on them. A Raman spectrum for a steel gray grain has bands at wavenumbers 186, 511, 586, and 640 cm⁻¹ that suggest that the grain is a manganese oxide (see Figs. 110 and 115). A Raman spectrum for the yellow matrix material has bands at wavenumbers 203, 354, 396, and 463 (strongest) cm⁻¹ that match those in a quartz standard (see Fig. 41). Primary heavy minerals appear to be absent from the 125-250 μ m size fraction.

4.2.4 Jeerinah Spherule Layer Samples

4.2.4.1 Sample W94-1Q

Sample W94-1Q is a piece of float that was derived (B. M. Simonson, personal communication, 2013) from the basal thin-bedded zone of the Jeerinah spherule layer at the Hesta outcrop (see Hassler et al., 2005). Subsamples 10.3210 g, 13.0639 g, and 15.3415 g ($\Sigma \approx 38.73$ g) were used to characterize Jeerinah spherule layer sample W94-1Q. No brassy sulfide grains were observed in the heavy mineral separates. For the 63-125 µm size fraction, there are now ~30 secondary iron oxide/oxyhydroxide grains, but an unknown number of these grains were removed from the cavity slides before sample analysis.

The heavy mineral grains are described in Appendix U, and their abundance is shown in Figure 118. For the 63-125 μ m size fraction, anatase (n = 551) and anatase + K-feldspar (n = 183) comprise 71.6% and 23.8%, respectively, of the total grains (n = 769). Rutile ± anatase (n = 20) is a minor component, and the other phases occur in trace amounts. The grains are typically subrounded and subangular.



Figure 118: Heavy mineral abundance for Jeerinah spherule layer sample W94-1Q.

An XRD pattern for a beige grain contains lines that match those of anatase (Table 44). Raman spectra for 34 varicolored grains have bands at wavenumbers that clearly match those of anatase (e.g., Fig. 119), and the Raman spectrum for a white opaque anatase grain has three additional bands at wavenumbers that match those of quartz.

Table 44:XRD data for an anatase grain from Jeerinah spherule layer sample W94-1Qand an anatase standard. Lines with intensities ≤ 1 in the standard that werenot observed in the pattern for the grain are not listed in the table.

| Grain ID: G 10-3-05 | | Anatase 21-1272 | | |
|------------------------|------------------|--------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | |
| 3.53 | 10 | 3.52 | 10 | |
| 2.38 | 2 | 2.378 | 2 | |
| 1.895 | 5 | 1.892 | 3.5 | |
| 1.71 | 3.5 | 1.6999 | 2 | |
| 1.67 | 3.5 | 1.6665 | 2 | |
| 1.48 | 3.5 | 1.4808 | 1.4 | |
| 1.365 | 1 | 1.3641 | 0.6 | |
| 1.34 | 1.5 | 1.3378 | 0.6 | |
| 1.27 | 2.5 | 1.2649 | 1 | |
| 1.255 | 1 | 1.2509 | 0.4 | |
| 1.155 | 1.5 | 1.1608 | 0.4 | |



Figure 119: Raman spectra of an anatase grain from Jeerinah spherule layer sample W94-1Q, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.

Raman spectra for seven grains typically have 4 bands at wavenumbers that match those of anatase, 2-7 bands at wavenumbers 154, 262/269, 282/286, 370, 404/409, 453/457, 474/476, 754/759, and 1121 cm⁻¹ that match those of a K-feldspar (orthoclase) standard (see Fig. 43), and a band of moderate-to-strong intensity at wavenumber 513/514 cm⁻¹ that is attributed to both anatase and K-feldspar (e.g., Fig. 120; cf., Figs. 42 and 53). The anatase + K-feldspar grains are typically beige, white, or clear with a very light yellow tint, translucent-to-opaque, and subangular-to-angular. A Raman spectrum for a blocky grain has bands at wavenumbers that match those of K-feldspar, and a Raman spectrum for the white matrix material that is attached to its surface has bands that match those of anatase. More detailed work on these grains is necessary to determine the complete textural relationship(s) of the two phases and their mode(s) of origin.



Figure 120: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from Jeerinah spherule layer sample W94-1Q (cf., Figs. 42 and 53). No baseline correction was made for the sample spectrum.

For two dark gray-to-black opaque grains, the Raman spectra have bands that suggest that the grains are chrome spinels (e.g., Fig. 121; cf., Figs. 54 and 87), and for another black opaque grain, the Raman spectrum has bands at wavenumbers that show a fairly good match with those of an ilmenite standard (Fig. 122).



Figure 121: Raman spectra of a chrome spinel grain from Jeerinah spherule layer sample W94-1Q, and a magnesiochromite standard from the RRUFF Raman spectral database (cf., Figs. 54 and 87). No baseline correction was made for the sample spectrum.



Figure 122: Raman spectra of an ilmenite grain from Jeerinah spherule layer sample W94-1Q, and an ilmenite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

For 12 (light) buff and (golden) amber grains, Raman spectra for three of the grains have bands that match those of a rutile standard (e.g., Fig. 123), and Raman spectra for the other nine grains have bands at wavenumbers that match those of rutile and anatase (e.g., Fig. 124; cf., Figs. 27 and 28). For the grains identified by micro-Raman spectroscopy, the rutile \pm anatase grains have distinctively different colors than those for the anatase \pm K-feldspar grains (see Appendix U).



Figure 123: Raman spectra of a rutile grain from Jeerinah spherule layer sample W94-1Q, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 124: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Jeerinah spherule layer sample W94-1Q (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum.

A Raman spectrum for a light yellow olive grain that has a minor amount of white matrix material on its surface has four bands at wavenumbers that match those of a dravite standard, as well as five bands at wavenumbers that match those of an anatase standard (Fig. 125). This grain is interpreted as a tourmaline grain with white anatase matrix material on its surface. Raman spectra for two light yellow-green grains have 1-3 bands of low intensity at wavenumbers 230, 318, and 370/371 (strongest) cm⁻¹. The bands at wavenumbers 318 and 370/371 cm⁻¹ are close to bands in the dravite standard shown in Figure 95, and the the grains are probably tourmalines.



Figure 125: Raman spectra of a tourmaline (T) + anatase (A) grain from Jeerinah spherule layer sample W94-1Q, and anatase and dravite standards from the RRUFF Raman spectral database. There is an unindexed (U) band at wavenumber 341 cm⁻¹. The Raman spectra for the anatase and dravite standards were acquired using a 514-nm laser.

Raman spectra for five transparent or translucent grains that are pink or clear with a light yellow tint have ~2-15 bands at wavenumbers 202/204, 212/213, 219/224, 350/355 (strong), 390/391, 412/414, 438/440, 468/471, 504/505, 628/631, 707/709, 819/823, 869/873, 967/972, 999/1005 (strong), and 1184 cm⁻¹ that match those of a zircon standard (e.g., Fig. 126).



Figure 126: Raman spectra of a zircon grain from Jeerinah spherule layer sample W94-1Q, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

For the 125-250 μ m size fraction, anatase (n = 98) and anatase + K-feldspar (n = 23) comprise 77.8% and 18.2%, respectively, of the total grains (n = 126), values that are comparable to those for the 63-125 μ m size fraction (Fig. 118). Rutile + anatase (n = 3) is a minor component, and tourmaline and zircon are trace components. Raman spectra for four very light peach-to-light gray grains each have five bands at wavenumbers that match those of anatase. For a beige subrounded grain with a translucent angular crystal attached to it, a Raman spectrum for the beige grain has bands at wavenumbers that match those of anatase, and a Raman spectrum for the crystal has bands at wavenumbers that match those of K-feldspar. A Raman spectrum for a brownish peach, subrounded grain with light greenish gray matrix material attached to its surface has bands at wavenumbers that match those of rutile and anatase (Fig. 127). This grain is interpreted as a rutile grain with light greenish gray anatase matrix material on its surface.



Figure 127: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Jeerinah spherule layer sample W94-1Q (cf., Figs. 27 and 28).

An XRD pattern for a light apple green subrounded grain contains lines that mostly match those of dravite, with a few lines that match those of ferrian dravite (Table 45). A Raman spectrum for this grain has bands that appear to match those of a dravite standard (Fig. 128). A pink, transparent, prismatic grain was not analyzed, but it is similar in appearance to some of the zircon grains in the 63-125 µm size fraction. No white opaque zircon grains were recovered from Jeerinah spherule layer sample W94-1Q. Table 45: XRD data for a tourmaline grain from the 125-250 μ m size fraction of Jeerinah spherule layer sample W94-1Q and dravite and ferrian dravite standards. Lines with intensities ≤ 2 in the standards that were not observed in the pattern for the grain are not listed in the table.

| Grain G 10-: | ID: 5-05 | : Dravite 5 14-76 | | Dravite, ferrian 19-1372 | |
|-----------------|------------------|----------------------|------------------|-----------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | 6.44 | 6 |
| 6.35 | 4 | 6.38 | 3 | | |
| 4.95 | 2 | 4.98 | 2.5 | 5.01 | 4 |
| 4.6 | 2 | 4.60 | 1.8 | 4.62 | 4 |
| 4.2 | 4 | 4.22 | 6.5 | 4.25 | 9 |
| 4.0 | 10 | 3.99 | 8.5 | 4.00 | 9 |
| | | | | 3.51 | 9 |
| 3.45 | 3 | 3.48 | 6 | | |
| 3.35 | 1 | 3.38 | 1.6 | | |
| 3.1 | <1 | 3.11 | 0.6 | | |
| 3.0 | 1 | 3.01 | 1.2 | | |
| 2.95 | 3 | 2.961 | 8.5 | 2.979 | 9 |
| 2.58 | 10 | 2.576 | 10 | 2.586 | 10 |
| 2.45 | <1 | 2.451 | 0.2 | | |
| 2.35 | 2 | 2.342 | 2 | | |
| 2.18 | 2 | 2.189 | 1.8 | | |

Table 45: continued

| Grain ID: G 10-5-05 | | Dravite 14-76 | | Dravite, ferrian 19-1372 | |
|------------------------|------------------|------------------|------------------|-----------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 2.12 | 2 | 2.127 | 1.6 | | |
| 2.04 | 3.5 | 2.054 | 2 | 2.052 | 3 |
| 2.0 | 3 | 2.040 | 4.5 | | |
| 1.92 | 1 | 1.920 | 3.5 | | |
| 1.86 | 1 | | | 1.858 | 1 |
| 1.77 | 1 | 1.781 | 0.8 | | |
| 1.73 | 1 | 1.729 | 0.4 | | |
| 1.68 | 1 | | | 1.671 | 1 |
| | | 1.660 | 2.5 | | |
| 1.65 | 3 | | | 1.650 | 1 |
| 1.6 | 3 | | | 1.603 | 2 |
| 1.55 | <1 | | | 1.553 | 1 |
| 1.455 | 2 | 1.4555 | 2 | | |
| 1.44 | 1 | 1.4485 | 1.2 | 1.441 | 1 |
| 1.42 | 1 | | | 1.427 | 1 |



Figure 128: Raman spectra of tourmaline grain G 10-5-05 (Table 45) from Jeerinah spherule layer sample W94-1Q, and a dravite standard from the RRUFF Raman spectral database. The Raman spectrum for the dravite standard was acquired using a 514-nm laser.

4.2.4.2 Sample X21-1

Sample X21-1 is a piece of float that was derived (B. M. Simonson, personal communication, 2013) from the basal thin-bedded zone of the Jeerinah spherule layer at the Hesta outcrop (see Hassler et al., 2005). The 63-125 μ m size fractions of eleven subsamples (7.5830 g, 15.1772 g, 15.6521 g, 21.7690 g, 22.3758 g, 22.6439 g, 29.9445 g, 30.7247 g, 32.5125 g, 32.9150 g, and 34.2206 g; $\Sigma \approx 265.52$ g) were used to characterize Jeerinah spherule layer sample X21-1. No brassy sulfide grains were observed in the

heavy mineral separates. There are ~90 dark red, dark reddish brown, reddish orange, and ochre secondary iron oxide/oxyhydroxide grains.

The heavy mineral grains are described in Appendix U, and their abundance is shown in Figure 129. Anatase (n = 3,041) grains comprise 83.6% of the total number of grains (n = 3,639), and anatase + K-feldspar (n = 283), rutile \pm anatase \pm TiO₂ II (n = 196), and zircon (n = 60) are minor components. The other phases occur in trace amounts. The grains are typically subrounded and subangular.



Figure 129: Heavy mineral abundance for the 63-125 µm size fraction of Jeerinah spherule layer sample X21-1.

One of the Raman spectra for a very light green grain has bands at wavenumbers that show a very good match with an actinolite standard (Fig. 130).



Figure 130: Raman spectra of an actinolite grain from Jeerinah spherule layer sample X21-1, and an actinolite standard from the RRUFF Raman spectral database.

Raman spectra for 30 varicolored grains have bands at wavenumbers that match those of an anatase standard (e.g., Fig. 131), and the Raman spectra for two of the grains have bands at wavenumbers 263/264 and 464 cm⁻¹ that are attributed to quartz (see Fig. 41). Many of the anatase grains are similar in appearance to those in Jeerinah spherule layer sample W94-1Q. Raman spectra for eight translucent-to-opaque, subangular-toangular grains that are typically beige, white, or clear with a very light yellow tint have bands at wavenumbers that match those of anatase and K-feldspar (e.g., Fig. 132; cf., Figs. 42, 53, and 120). More work is necessary to determine the textural relationship(s) between anatase, K-feldspar, and quartz.



Figure 131: Raman spectra of an anatase grain from Jeerinah spherule layer sample X21-1, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 132: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from Jeerinah spherule layer sample X21-1 (cf., Figs. 42, 53, and 120). The bands at wavenumbers 866 and 1180 cm⁻¹ are unindexed (U).

A Raman spectrum for a colorless transparent grain has bands at wavenumbers that match those of an anglesite standard (Fig. 133), whereas a Raman spectrum for another grain has bands of very low intensity at wavenumbers 980 and 1052 cm⁻¹ that suggest that the grain is anglesite. Raman spectra for five colorless-to-white grains have \sim 4-8 bands at wavenumbers that have a good match with those of a baryte standard (Fig. 134).



Figure 133: Raman spectra of an anglesite grain from Jeerinah spherule layer sample X21-1, and an anglesite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 134: Raman spectra of a barite grain from Jeerinah spherule layer sample X21-1, and a baryte standard from the RRUFF Raman spectral database.

A Raman spectrum for a light golden orange grain has 13 bands at wavenumbers that show a very good match with those of a brookite standard (Fig. 135), and this Raman spectrum shows a very good match with those for the brookite grains in Carawine spherule layer samples 43-1 (Fig. 68) and X38-2 (Fig. 86).



Figure 135: Raman spectra of a brookite grain from Jeerinah spherule layer sample X21-1, and a brookite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for nine black and two dark steel gray opaque grains have bands that suggest that they are chrome spinels. The Raman spectra typically have a broad band of strong intensity at wavenumber $724/747 \text{ cm}^{-1}$ that can have a shoulder on it at wavenumber $683/712 \text{ cm}^{-1}$, and a broad band of very low intensity at wavenumber $540/570 \text{ cm}^{-1}$ (e.g., Fig. 136). An XRD pattern (Table 46) for a black opaque grain (G 10-14-05) contains lines that match those of chromite and ferroan magnesiochromite, and the pattern has an unindexed line of weak intensity at d = 1.54 Å. In this pattern, the lines at d-spacings of 1.27 Å and 1.6 Å have much lower intensities than the corresponding lines in the standards (Table 46). A Raman spectrum for grain G 10-14-05 (Table 46) is shown in Figure 137 (cf., Figs. 23, 54, and 121).

Several of the Raman spectra for the chrome spinel grains have additional broad bands of very low intensities at wavenumbers 445/452, 885/910, and 1433/1460 cm⁻¹. A band of low intensity at wavenumber ~447 cm⁻¹ was observed in a Raman spectrum of synthetic MgCr₂O₄ spinel at ambient conditions (Wang et al., 2002; Yong et al., 2012). The broad bands at wavenumbers 885/910 and 1433/1460 cm⁻¹ remain unindexed. A Raman spectrum for a black opaque grain with white matrix material on its surface has five bands at wavenumbers that match those of anatase, and bands at wavenumbers 708 and 739 cm⁻¹ that are attributed to chrome spinel (Fig. 138). The white matrix material is interpreted as anatase, and these data suggest that at least some of the anatase may be of secondary origin.



Figure 136: Raman spectra of a chrome spinel grain from Jeerinah spherule layer sample X21-1, and chromite and magnesiochromite standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

| Grain ID: G 10-14-05 | | Chromite 3-0873 | | Magnesiochromite, ferroan 9-353 | |
|-------------------------|------------------|--------------------|------------------|---------------------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | 4.82 | 5 | 4.76 | 2 |
| 2.95 | 3 | 2.95 | 6 | 2.92 | 2 |
| 2.5 | 10 | 2.52 | 10 | 2.49 | 10 |
| 2.4 | 2 | 2.40 | 1 | | |
| 2.08 | 1 | 2.07 | 7 | 2.07 | 0.5 |
| 1.7 | 1 | 1.69 | 4 | 1.687 | 0.5 |
| 1.6 | 1.5 | 1.6 | 9 | 1.593 | 6 |
| 1.54 | 1 | | | | |
| 1.47 | 7 | 1.46 | 9 | 1.466 | 7 |
| 1.38 | <1 | 1.40 | 1 | | |
| 1.33 | <1 | 1.31 | 2 | | |
| 1.27 | <1 | 1.26 | 5 | 1.265 | 10 |
| 1.23 | 1 | | | 1.249 | 0.5 |
| | | 1.20 | 3 | 1.197 | 0.5 |
| | | 1.16 | 2 | | |
| | | 1.11 | 3 | 1.108 | 0.5 |
| | | 1.10 | 6 | | |
| 1.08 | 1 | | | 1.081 | 5 |

Table 46:XRD data for a chrome spinel grain from Jeerinah spherule layer sample
X21-1 and chromite and ferroan magnesiochromite standards.



Figure 137: Raman spectra of chrome spinel grain G 10-14-05 (Table 46) from Jeerinah spherule layer sample X21-1 (cf., Figs. 23, 54, and 121), and chromite and magnesiochromite standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 138: Unnormalized Raman spectrum of a black opaque chrome spinel (Chr) grain with white anatase (A) matrix material on its surface from Jeerinah spherule layer sample X21-1 (cf., Figs. 131 and 136).

Raman spectra for three light yellow-green grains are similar, and they have bands at wavenumbers that show a good match with a clinopyroxene (diopside) standard (e.g., Fig. 139). A Raman spectrum for a black opaque grain shows a good match with a hematite standard (Fig. 140).



Figure 139: Raman spectra of a clinopyroxene grain from Jeerinah spherule layer sample X21-1, and a diopside standard from the RRUFF Raman spectral database.



Figure 140: Raman spectra of a black opaque hematite grain from Jeerinah spherule layer sample X21-1, and a hematite standard from the RRUFF Raman spectral database.

For 56 varicolored grains, most of which are (light) buff or shades of peach, Raman spectra for 12 of them have bands at wavenumbers that match those of rutile, whereas the Raman spectra for the other 44 grains have bands at wavenumbers that match those of rutile and anatase. Three of the grains have 1-3 bands at wavenumbers $205, 353/354, and 461/463 \text{ cm}^{-1}$ that are attributed to quartz (e.g., Fig. 141).



Figure 141: Raman spectra of a rutile (R) + quartz (Q) grain from Jeerinah spherule layer sample X21-1, and quartz and rutile standards from the RRUFF Raman spectral database.

For two light buff rutile \pm anatase grains (Table 47), the Raman spectra (Figs. 142 and 143) both have nine additional well-developed bands and a shoulder at wavenumbers that match those of the TiO₂ II phase (see Fig. 90). For grain #46 (Table 47), the Raman spectrum (Fig. 142) has a shoulder at wavenumber 143 cm⁻¹ that is attributed to rutile (see Fig. 26). The shoulder at wavenumber 412/413 cm⁻¹ was observed in synthetic TiO₂ II by Mammone et al. (1980). Grain #47 (Table 47) is >125 µm in size, but it was recovered from the 63-125 µm size fraction. Therefore, ~29% (n = 56) of the estimated total number of rutile \pm anatase grains (n = 196) that were recovered from the 63-125 µm size fraction of Jeerinah spherule layer sample X21-1 were analyzed by micro-Raman spectroscopy. Rutile \pm anatase grains that contain the TiO₂ II phase (n = 2) comprise ~3.6% of the analyzed grains, and they comprise a minimum of 1.0% of the estimated total number of rutile \pm anatase grains in the 63-125 µm size fraction.

Table 47:Description of and micro-Raman analytical data for rutile + TiO_2 II
grains from Jeerinah spherule layer sample X21-1.

| Grain Identification Number//Date of Analysis | Description of Grain (Color, Diaphaneity, Shape, Size (µm), Angularity) | Number of spots analyzed/Number of spots with TiO ₂ II | Phases Present |
|---|---|---|--|
| 46//12-17-09 | Light buff, Opaque, Subequant, 140 x 60, Subrounded | 4/4 | Rutile TiO ₂ II (Anatase) |
| 47//12-17-09 | Light buff, Opaque, Irregular, 200 x 125, Angular | 3/3 | Rutile TiO ₂ II |

Note: For grain #46, anatase is in parentheses to indicate that it was identified at only one of the four probed spots.



Figure 142: Unnormalized Raman spectrum of TiO₂ II + rutile (R) grain #46 (Table 47) from Jeerinah spherule layer sample X21-1 (cf., Fig. 90). The bands at wavenumbers 149, 173, 286, 315, 339, 355, 427, 531, and 571 cm⁻¹, and the shoulder at wavenumber 412 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.


Figure 143: Unnormalized Raman spectrum of TiO₂ II + rutile (R) grain #47 (Table 47) from Jeerinah spherule layer sample X21-1 (cf., Fig. 90). The bands at wavenumbers 150, 173, 284, 314, 339, 355, 427, 531, and 574 cm⁻¹, and the shoulder at wavenumber 413 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.

Raman spectra for two olive green grains have bands at wavenumbers that appear to match those of tourmaline, and one of the Raman spectra is given in Figure 144. In this Raman spectrum, the additional bands at wavenumbers 573, 915, and 939 cm⁻¹ may indicate clinozoisite, and if so, the clinozoisite may occur as very fine-grained matrix material on the surface of the tourmaline grain.



Figure 144: Raman spectra of an olive green tourmaline (T) + clinozoisite (C) (?) grain from Jeerinah spherule layer sample X21-1, and clinozoisite and tourmaline standards from the RRUFF Raman spectral database. The Raman spectrum for the clinozoisite standard was acquired using a 514-nm laser.

Raman spectra for 26 varicolored grains have ~2-14 bands at wavenumbers that match those of a zircon standard (e.g., Fig. 145).



Figure 145: Raman spectra of a champagne zircon grain from Jeerinah spherule layer sample X21-1, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

An XRD pattern for a pink grain contains lines that match those of zircon (Table 48). The zircon grains show similar colors to those in Jeerinah spherule layer sample W94-1Q (see Appendix U). Eight zircon grains are translucent-to-opaque (see Appendix U). For five of the zircon grains, the Raman spectra have 3-5 additional bands at wavenumbers that match those of anatase (Fig. 146; cf., Figs. 32 and 33). One of these zircon grains has some white matrix material on its surface, probably anatase. Table 48:XRD data for a pink zircon grain from Jeerinah spherule layer sample
X21-1 and a zircon standard. Lines with intensities <1 in the standard that
were not observed in the pattern for the grain are not listed in the table.

| Grain ID: G 10-16-05 | | Zircon 6-0266 | |
|-------------------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o |
| 4.45 | 4 | 4.43 | 4.5 |
| 3.3 | 10 | 3.30 | 10 |
| 2.63 | 1 | 2.650 | 0.8 |
| 2.53 | 4 | 2.518 | 4.5 |
| 2.34 | 2 | 2.336 | 1 |
| 2.23 | 1.5 | 2.217 | 0.8 |
| 2.07 | 3 | 2.066 | 2 |
| ~1.9? | <1 | 1.908 | 1.4 |
| 1.75 | 2 | 1.751 | 1.2 |
| 1.72 | 5 | 1.712 | 4 |
| 1.65 | 5 | 1.651 | 1.4 |
| 1.55 | 1 | 1.547 | 0.4 |
| 1.48 | 1.5 | 1.477 | 0.8 |
| 1.38 | 3.5 | 1.381 | 1 |
| 1.295 | 1 | 1.290 | 0.6 |
| 1.25 | 1 | 1.259 | 0.8 |



Figure 146: Unnormalized Raman spectrum of a zircon (Z) + anatase (A) grain from Jeerinah spherule layer sample X21-1 (cf., Figs. 32 and 33). No baseline correction was made for the sample spectrum.

The Raman spectra for six grains remain unidentified. For four of the grains, the Raman spectra have 1-3 bands at wavenumbers 520, 1050/1051, and 1130 cm⁻¹ (e.g., Fig. 147). Coesite has a band of very strong intensity at wavenumber 520/521 cm⁻¹, but it also has bands of moderate-to-strong intensities at wavenumbers 177/178 and 270/271 cm⁻¹ (Boyer et al., 1985). These latter two bands for coesite are not present in the Raman spectra for these four grains, so these four grains are not considered to be coesite. The remaining two unidentified grains consist of a light amber, translucent-to-opaque grain, and a beige opaque grain. A Raman spectrum for the light amber grain shows bands of

low intensity at wavenumbers 856 and 1002 cm⁻¹, and a Raman spectrum for the beige grain shows a single band of low intensity at wavenumber 223 cm⁻¹.



Figure 147: Unnormalized Raman spectrum of an unidentified grain from Jeerinah spherule layer sample X21-1. The grain is colorless, transparent, blocky, and subangular.

4.2.5 Bee Gorge Spherule Layer and Context Samples

4.2.5.1 Introduction

The heavy mineral fraction results for the Bee Gorge spherule layer and context samples are given in the same section (4.2.5) for the following reasons. Bee Gorge sample BB consists of a thin spherule layer sandwiched between two carbonate lutite context layers (Appendix D). There is no stratigraphic "up" arrow on the sample, so the relative age of the three layers is unknown, but the heavy mineral assemblage for the spherule layer can be compared with those for carbonate lutite context layers that are in direct contact with the spherule layer. Bee Gorge samples 96714A and 96714B are mirror-image slabs from the same rock, and there are stratigraphic "up" arrows on the samples. Each sample consists of a basal carbonate lutite context layer that is in direct contact with the overlying (younger) spherule layer (Appendix D). Therefore, for Bee Gorge samples 96714A and 96714B, the heavy mineral assemblage for the spherule layer can be compared with that for the immediately subjacent basal carbonate lutite context layer. Bee Gorge context sample 92058 was collected ~1 m above the Bee Gorge spherule layer (see Table 6) at a different locale than those for Bee Gorge samples BB, 96714A, and 96714B (see Fig. 4). The heavy mineral fraction results for context sample 92058 are reported in section 4.2.5 since this section contains the results for the other context layers.

4.2.5.2 Sample BB

The spherule layer is ~8-14 mm thick (Appendix D, Fig. 285), and it is referred to as "BB (sl)" in this dissertation. The thinner context layer, typically <7 mm thick, is named "context layer #1", and it is referred to as "BB (#1)" in this dissertation. The other

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context layer (~6-11 mm thick) is named "context layer #2", and it is referred to as "BB (#2)" in this dissertation.

4.2.5.2.1 Spherule Layer (BB (sl))

Subsamples 9.8364 g, 10.6019 g, and 10.7999 g ($\Sigma \approx 31.24$ g) were used to characterize the Bee Gorge spherule layer in sample BB. No brassy sulfide grains were observed in the heavy mineral separates. For the 63-125 µm size fraction, there are ~10 dark-to-cherry red grains, and ~60 dark brown-to-black opaque grains that appear to be secondary phases. Some of the dark brown-to-black grains are pseudomorphs of aggregates of very small cubic crystals.

The dark brown-to-black grains are typically subangular-to-angular, and they have sharp irregular margins. About 20 of these grains have a clear-to-white matrix material on their surfaces. Raman spectra for four of these grains consistently have bands at wavenumbers 224/225 (moderate), 244/245, 290/292 (moderate), 407/410 (moderate), 499/504, 607/611, 820/834, 1067/1078, and 1310/1315 (strong) cm⁻¹. These bands are similar in wavenumbers and intensities to those for hematite as given in de Faria et al. (1997) and Das and Hendry (2011). A Raman spectrum for the white matrix material has a band of low intensity at wavenumber 465 cm⁻¹ that is interpreted as the strongest band for quartz (see Fig. 41).

The heavy mineral grains are described in Appendix V, and their abundance is shown in Figure 148. For the 63-125 μ m size fraction, anatase (n = 27), anatase + K-feldspar (n = 10), and rutile ± anatase (n = 20) comprise 39.1%, 14.5%, and 29.0%, respectively, of the total grains (n = 69), and the other phases are minor components. The grains are typically subrounded and subangular.



Figure 148: Heavy mineral abundance for the Bee Gorge spherule layer in sample BB.

The Raman spectra for two grains that are clear with a very light green tint exhibit some variability in the wavenumbers of some of the bands. The Raman spectrum for one of the grains shows a good match with an actinolite standard (Fig. 149), and the Raman spectrum for the second grain is suggestive of actinolite (Appendix BB, Fig. 305).



Figure 149: Raman spectra of an actinolite grain from the Bee Gorge spherule layer in sample BB, and an actinolite standard from the RRUFF Raman spectral database.

The Raman spectra for 13 varicolored grains each have five bands at wavenumbers that match those of an anatase standard (e.g., Fig. 150), and in one of the Raman spectra, a band at wavenumber 464 cm^{-1} is attributed to quartz (see Fig. 41).



Figure 150: Raman spectra of an anatase grain from the Bee Gorge spherule layer in sample BB, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.

The Raman spectra for six grains that are typically white or clear with a light yellow tint have 2-4 bands at wavenumbers that match those of anatase, and 2-6 bands at wavenumbers that match those of K-feldspar (e.g., Fig. 151; cf., Figs. 42, 43, and 53). For three of the anatase + K-feldspar grains, the Raman spectra have 1-3 additional bands at wavenumbers 207, 263, and 464 cm⁻¹ that are attributed to quartz (see Fig. 41).



Figure 151: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from the Bee Gorge spherule layer in sample BB (cf., Figs. 42, 43, and 53).

A Raman spectrum for a dark brownish black, opaque grain shows a reasonably good match with a magnesiochromite standard (Fig. 152).



Figure 152: Raman spectra of a chrome spinel grain from the Bee Gorge spherule layer in sample BB, and a magnesiochromite standard from the RRUFF Raman spectral database.

A Raman spectrum for a transparent grain that is clear with a light yellow tint shows a good match with a clinozoisite standard (Fig. 153). Raman spectra for two transparent grains that are clear with a light golden or yellow tint are very similar, and they show a good match with a monazite standard (e.g., Fig. 154).



Figure 153: Raman spectra of a clinozoisite grain from the Bee Gorge spherule layer in sample BB, and a clinozoisite standard from the RRUFF Raman spectral database.



Figure 154: Raman spectra of a monazite grain from the Bee Gorge spherule layer in sample BB, and a monazite standard from the RRUFF Raman spectral database.

For 19 grains that are mostly buff or shades of peach, Raman spectra for 10 of them have bands at wavenumbers that match those of rutile (e.g., Appendix BB, Fig. 306), and Raman spectra for nine of them have bands at wavenumbers that match those of rutile and anatase (e.g., Fig. 155). In addition to these 19 grains, another grain that was not analyzed is similar in appearance to some of the rutile \pm anatase grains, and it is therefore considered to be rutile \pm anatase. Therefore, 19 of the 20 (95%) rutile \pm anatase grains in the 63-125 µm size fraction were analyzed by micro-Raman spectroscopy, and none of the Raman spectra show any evidence for the TiO₂ II phase.



Figure 155: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from the Bee Gorge spherule layer in sample BB (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum.

Raman spectra for three light brownish-to-olive green, prismatic grains have bands at wavenumbers and intensities that show a reasonably good match with tourmaline standards (e.g., Fig. 156). For one of the grains, the Raman spectrum shows a band of strong intensity at wavenumber 143 cm⁻¹ that is attributed to anatase (see Fig. 21). There is no obvious matrix material on this tourmaline grain, so the anatase must be very fine-grained. For the three tourmaline grains, the Raman spectra show some variability in the wavenumbers of the bands of lower intensities, but these bands are present in either the Raman spectra for tourmaline standards R070563 or R060123

(RRUFF Project, 2014), or the Raman spectra for some tourmalines that are reported in Gasharova et al. (1997).



Figure 156: Raman spectra of a tourmaline grain from the Bee Gorge spherule layer in sample BB, and a dravite standard from the RRUFF Raman spectral database. The Raman spectrum for the dravite standard was acquired using a 514-nm laser.

Raman spectra for three transparent grains that are clear with a light yellow-togreen tint have ~15 bands with wavenumbers that show a very good match with a zircon standard (e.g., Fig. 157). The Raman spectra for the zircon grains typically show sharp, well-developed peaks. There are no white opaque zircon grains. In contrast to the Carawine and Jeerinah spherule layer samples, no (pale) pink or champagne zircon grains were recovered from the Bee Gorge spherule layer in sample BB (see Appendix V).



Figure 157: Raman spectra of a zircon grain from the Bee Gorge spherule layer in sample BB, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

For the 125-250 µm size fraction, there are 10 dark red, reddish brown, and black grains that resemble the secondary iron oxide/oxyhydroxide grains in the 63-125 µm size fraction. A Raman spectrum for a translucent grain that is clear with a light yellow-green tint has bands at wavenumbers that show a reasonably good match with those for actinolite standard R050025 (RRUFF Project, 2014). Raman spectra for two beige opaque grains each have five bands at wavenumbers that match those of anatase. For nine clear-to-beige grains, the Raman spectra each have five bands at wavenumbers that match those of a K-feldspar (orthoclase) standard (see Fig. 43). The anatase + K-feldspar grains are typically blocky and subangular, and they may represent K-feldspar grains that are mantled by secondary white anatase. The Raman spectra for two anatase + K-feldspar grains have bands at wavenumbers 265 and 464 cm⁻¹ that are attributed to quartz (see Fig. 41). A Raman spectrum for a transparent grain that is clear with a light yellow tint shows ~20 bands that have similar wavenumbers and intensities to those in the Raman spectrum for the clinozoisite grain in the 63-125 µm size fraction (see Fig. 153).

4.2.5.2.2 Context Layer #1 (BB (#1))

Subsample 5.4035 g was used to characterize Bee Gorge context layer #1 in sample BB. For the 63-125 μ m size fraction, there are 16 dark red-to-reddish brown and 3 black opaque grains that resemble the secondary iron oxide/oxyhydroxide grains in the spherule layer. A Raman spectrum for one of the black grains has bands at wavenumbers that match those of a hematite standard (Appendix BB, Fig. 307). The heavy mineral grains are described in Appendix V, and their abundance is shown in Figure 158.



Figure 158: Heavy mineral abundance for Bee Gorge context layer #1 in sample BB.

A Raman spectrum for a white opaque subrounded grain has five bands at wavenumbers that match those of an anatase standard (Appendix BB, Fig. 308). A Raman spectrum for a translucent grain that is clear with a very light green-yellow tint has several bands at wavenumbers that show a fairly good match with a clinozoisite standard (Fig. 159). This Raman spectrum shows bands at wavenumbers 145 (very strong intensity) and 638 cm⁻¹ that are attributed to anatase (see Fig. 150).



Figure 159: Raman spectra of a clinozoisite + anatase (A) grain from Bee Gorge context layer #1 in sample BB, and a clinozoisite standard from the RRUFF Raman spectral database.

Raman spectra for one buff and two peach opaque grains have bands at wavenumbers that clearly match those of rutile ± anatase (e.g., Appendix BB, Fig. 309). For a translucent olive green grain, a Raman spectrum has bands attributed to tourmaline and anatase, and possibly quartz (Fig. 160). This grain is interpreted as a tourmaline grain with very fine-grained anatase and quartz (?) matrix material on its surface.



Figure 160: Raman spectra of a tourmaline (T) + anatase (A) grain from Bee Gorge context layer #1 in sample BB, and anatase and dravite standards from the RRUFF Raman spectral database. The bands at wavenumbers 353 and 464 cm⁻¹ may indicate quartz (Q), and a Raman spectrum for a quartz standard is shown in Figure 41. No baseline correction was made for the sample spectrum. The Raman spectra for the anatase and dravite standards were acquired using a 514-nm laser.

A Raman spectrum for a prismatic grain that is similar in appearance to the zircon grains in the Bee Gorge spherule layer in sample BB has \sim 12 bands at wavenumbers that match those of a zircon standard (Fig. 161). For the 125-250 µm size fraction, there are three dark red secondary iron oxide/oxyhydroxide grains, but there are no primary heavy mineral grains.



Figure 161: Raman spectra of a zircon grain from Bee Gorge context layer #1 in sample BB, and a zircon standard from the RRUFF Raman spectral database.

4.2.5.2.3 Context Layer #2 (BB (#2))

Subsample 14.89 g was used to characterize Bee Gorge context layer #2 in sample BB. For the 63-125 μ m size fraction, there are four dark red and reddish brown secondary iron oxide/oxyhydroxide grains. The heavy mineral grains are described in Appendix V, and their abundance is shown in Figure 162. Anatase (n = 4), rutile ± anatase (n = 14), tourmaline (n = 4), and zircon (n = 6) are major phases in the heavy mineral assemblage; each of the other phases is a minor component.



Figure 162: Heavy mineral abundance for Bee Gorge context layer #2 in sample BB.

Raman spectra for two light peach opaque grains each have five bands at wavenumbers that match those of an anatase standard (e.g., Appendix BB, Fig. 310). A Raman spectrum for a translucent grain that is clear with a very light yellow tint has bands at wavenumbers that match those of an anglesite standard (Fig. 163). The unindexed band at wavenumber 228 cm⁻¹ in this Raman spectrum is not present in the Raman spectra for the anglesite grains in the Carawine (see Fig. 22) and Jeerinah (see Fig. 133) spherule layer samples. Furthermore, this unindexed band is not present in the Raman spectra for anglesite, baryte, celestine, cerussite, galena, and strontianite standards (RRUFF Project, 2014). However, hematite has a band of strong intensity close to wavenumber 228 cm⁻¹ (see Fig. 140), but it also has bands of moderate-to-very strong intensities at wavenumbers ~247, ~292/294, ~410/412, and ~1316/1322 cm⁻¹ (see Fig. 140; de Faria et al., 1997). None of the latter four bands is present in the Raman spectrum for the anglesite grain (Fig. 163), and therefore, the unindexed band at wavenumber 228 cm⁻¹ is not attributed to hematite. More work is necessary to ascertain the origin of this band.



Figure 163: Raman spectra of an anglesite grain from Bee Gorge context layer #2 in sample BB, and an anglesite standard from the RRUFF Raman spectral database. There is an unindexed (U) band at wavenumber 228 cm⁻¹.

A Raman spectrum for a dark brownish black opaque grain has bands at wavenumbers that suggest that it is a chrome spinel (Fig. 164).



Figure 164: Raman spectra of a chrome spinel grain from Bee Gorge context layer #2 in sample BB, and a magnesiochromite standard from the RRUFF Raman spectral database.

For a translucent grain that is clear with a light yellow tint, the Raman spectrum (Appendix BB, Fig. 311) is almost identical to that for the clinozoisite grain in the Bee Gorge spherule layer in sample BB (see Fig. 153). For 12 varicolored grains, the Raman spectra for three of them have bands at wavenumbers that match those of a rutile standard (e.g., Fig. 165), and the Raman spectra for nine of them have bands at wavenumbers that

match those of rutile and anatase (e.g., Appendix BB, Fig. 312). Therefore, ~86% (n = 12) of the estimated total number (n = 14) of rutile ± anatase grains in the 63-125 µm size fraction of context layer #2 in sample BB were analyzed by micro-Raman spectroscopy. None of the Raman spectra for the rutile ± anatase grains show any evidence for the TiO₂ II phase.



Figure 165: Raman spectra of a rutile grain from Bee Gorge context layer #2 in sample BB, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for a light greenish golden translucent grain and an olive green transparent grain (e.g., Fig. 166) have bands at wavenumbers that show a reasonably good match with those of tourmaline.



Figure 166: Raman spectra of an olive green tourmaline grain from Bee Gorge context layer #2 in sample BB, and a dravite standard from the RRUFF Raman spectral database.

Raman spectra for an amber grain and five grains that are clear with a light yellow or green tint typically have \sim 3-17 bands at wavenumbers that match those of a zircon standard (e.g., Fig. 167). For one of these grains, the Raman spectrum has only one band of low intensity at wavenumber 353 cm⁻¹. This grain has a prismatic habit, and it is probably a zircon.



Figure 167: Raman spectra of a zircon grain from Bee Gorge context layer #2 in sample BB, and a zircon standard from the RRUFF Raman spectral database.

Most of the zircon grains have similar colors to those in the spherule layer and in context layer #1 of this sample. There are no white opaque zircon grains. In contrast to the Carawine and Jeerinah spherule layer samples, no pale pink, pink, or champagne zircon grains (see Appendix V) were recovered from Bee Gorge context layer #2 in sample BB. For the 125-250 µm size fraction, there is one dark red secondary iron oxide/oxyhydroxide grain, but there are no primary heavy mineral grains.

4.2.5.3 Sample 96714A

4.2.5.3.1 Introduction

Bee Gorge sample 96714A consists of a basal context layer and the overlying spherule layer (Appendix D). The sample was sawn into four subdivisions (see Appendix D, Fig. 283; Appendix L): a basal carbonate lutite context layer (Bcl) and three spherule layer subdivisions. In ascending stratigraphic order, the latter three subdivisions are referred to as the lowermost spherule-rich sublayer (Lspsl), the spherule-bearing lutite sublayer (Splsl), and the upper spherule/lutite sublayers (Usplsl). The 63-125 µm size fractions of the basal carbonate lutite context layer and each of the three spherule layer subdivisions were used to characterize Bee Gorge sample 96714A. The heavy mineral grains are described in Appendix V, and their abundance is shown in Figure 168. A rutile grain from the lowermost spherule-rich sublayer (Lspsl) was identified by XRD analysis, but all other phase identification was done by micro-Raman spectroscopy. The four subdivisions are described in ascending stratigraphic order, so the following discussion begins with the basal carbonate lutite context layer (Bcl).



Figure 168: Heavy mineral abundance for the 63-125 µm size fraction of Bee Gorge sample 96714A.

4.2.5.3.2 Basal Carbonate Lutite Context Layer (Bcl)

Subsamples 6.8001 g, 9.5376 g, 10.0687 g, 10.5610 g, 10.9594 g, 11.1877 g, 11.4911 g, and 11.6547 g ($\Sigma \approx 82.26$ g) were used to characterize the basal carbonate lutite context layer of Bee Gorge sample 96714A. There are ~17 dark red-to-dark reddish brown grains of secondary iron oxide/oxyhydroxide. Anatase (n = 6), anatase + K-feldspar (n = 31), and rutile ± anatase (n = 4) comprise 14.6%, 75.6%, and 9.8%, respectively, of the total grains (n = 41). A Raman spectrum (Fig. 169) for a beige opaque grain has three bands at wavenumbers that match those of anatase, and a band at wavenumber 464 cm^{-1} that is interpreted as the strongest band for quartz.



Figure 169: Unnormalized Raman spectrum of an anatase (A) + quartz (Q) grain from the basal carbonate lutite context layer (Bcl) that is stratigraphically below the spherule layer in Bee Gorge sample 96714A (cf., Figs. 39 and 40). A Raman spectrum for a quartz standard is shown in Figure 41.

For five grains that are beige or clear-to-white, the Raman spectra (e.g., Fig. 170) have 4-5 bands at wavenumbers that match those of anatase, and 1-10 bands at wavenumbers that match those of the K-feldspar (orthoclase) standard shown in Figure 43. For two of the anatase + K-feldspar grains, the Raman spectra have 3-4 additional bands at wavenumbers 202, 262/263, 354, 390, and 464 (moderate) cm⁻¹ that match those of the quartz standard shown in Figure 41. These two grains are opaque, and one of them has colorless translucent matrix material on its surface. They are interpreted as anatase grains that have K-feldspar + quartz matrix material on their surfaces. The other three grains are translucent or translucent-to-opaque, and they may represent K-feldspar grains that are partly mantled by white opaque anatase.



Figure 170: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from the basal carbonate lutite context layer (Bcl) that is stratigraphically below the spherule layer in Bee Gorge sample 96714A (cf., Figs. 42 and 53). A Raman spectrum for a K-feldspar (orthoclase) standard is shown in Figure 43. The bands at wavenumbers 962, 1225, and 1522 cm⁻¹ are unindexed (U).

Raman spectra for three beige opaque grains have bands at wavenumbers that match those for rutile, and 1-6 bands at wavenumbers that match those for quartz. One of the grains has white matrix material on its surface, and its Raman spectrum has five additional bands at wavenumbers that match those of anatase (Fig. 171). For one of the other two grains, the Raman spectrum has additional bands at wavenumbers 283 and 513 cm⁻¹ that are attributed to K-feldspar (see Fig. 43).



Figure 171: Unnormalized Raman spectrum of a rutile (R) + anatase (A) + quartz (Q) grain from the basal carbonate lutite context layer (Bcl) that is stratigraphically below the spherule layer in Bee Gorge sample 96714A (cf., Figs. 27 and 28). A Raman spectrum for a quartz standard is shown in Figure 41. The band at wavenumber 1507 cm⁻¹ is unindexed (U).

For a black opaque grain, a Raman spectrum has four bands at wavenumbers that match those of rutile, as well as two bands at wavenumbers 224 (moderate) and 286 cm⁻¹ that are attributed to hematite (see Fig. 48). This grain is interpreted as a rutile grain with hematite on its surface. Only four rutile \pm anatase grains were identified in the basal carbonate lutite context layer (Bcl) of Bee Gorge sample 96714A, and the Raman spectra for these four grains do not show any evidence for the TiO₂ II phase.

4.2.5.3.3 Lowermost Spherule-Rich Sublayer (Lspsl)

Subsamples 7.3433 g and 8.5769 g ($\Sigma \approx 15.92$ g) were used to characterize the lowermost spherule-rich sublayer of Bee Gorge sample 96714A. There are ~17 red-to-reddish brown grains of secondary iron oxide/oxyhydroxide. Rutile ± anatase (n = 515) comprises 99.2% of the total grains (n = 519; Fig. 168). A Raman spectrum for a transparent grain with a glassy luster that is clear with a light green tint shows a good match with an almandine standard (Fig. 172).


Figure 172: Raman spectra of an almandine grain from the lowermost spherule-rich sublayer (Lspsl) in Bee Gorge sample 96714A, and an almandine standard from the RRUFF Raman spectral database.

For a beige opaque grain that is similar to the anatase grains in the basal carbonate lutite context layer, a Raman spectrum has five bands at wavenumbers that match those of an anatase standard (Appendix BB, Fig. 313). The Raman spectra for two translucent grains that are clear with a very light yellow tint have bands that are similar in wavenumbers and relative intensities to those in the Raman spectrum for an anatase + Kfeldspar grain from the basal carbonate lutite context layer (see Fig. 170). The two grains are blocky, and one grain has a minor amount of white matrix material on its surface. These two grains are very similar in color, opacity, and habit to two K-feldspar grains in this sublayer that were identified by micro-Raman spectroscopy, and they may simply be K-feldspar grains that have very minor amounts of white anatase matrix on their surfaces.

Most (>99%) of the heavy mineral grains in the lowermost spherule-rich sublayer are grayish yellow or medium dark gray-to-yellow, subangular-to-angular, and opaque. These grains are distinctive: they typically have an irregular shape or an irregular margin, and they have a granular appearance. Raman spectra for nine of the grains have bands at wavenumbers that match those of a rutile standard (e.g., Fig. 173). For two of the nine grains, the Raman spectra have additional bands at wavenumbers that match those of anatase (e.g., Appendix BB, Fig. 314), and for a third grain, the Raman spectrum has a band at wavenumber 462 cm⁻¹ that is attributed to quartz (see Fig. 41). None of the Raman spectra for these nine grains show any evidence for the TiO₂ II phase, but only ~1.7% of the estimated total number (n = 515) of rutile ± anatase grains in this sublayer were analyzed by micro-Raman spectroscopy.

An XRD pattern for one of the granular grains that were described in the previous paragraph contains lines that match those of rutile and quartz (Table 49). The granular rutile grains are quite different in appearance than any of the rutile grains in the previously described samples. They abruptly appear in the lowermost spherule-rich sublayer, and more work is necessary to ascertain their mode of origin.



Figure 173: Raman spectra of a granular rutile grain from the lowermost spherule-rich sublayer (Lspsl) in Bee Gorge sample 96714A, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Table 49:XRD data for a granular rutile grain from the lowermost spherule-rich
sublayer (Lspsl) in Bee Gorge sample 96714A, and rutile and quartz
standards. Lines with intensities <1.2 in the standards that were not
observed in the pattern for the grain are not listed in the table.

| Grain ID: G 9-7-05 | | Rutile 21-1276 | | Quartz 5-0490 | |
|-----------------------|------------------|-------------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| ~4.2 | 3 | | | 4.26 | 3.5 |
| ~3.3 | 10 | 3.25 | 10 | 3.342 | 10 |
| 2.50 | 6 | 2.487 | 5 | 2.458 | 1.2 |
| 2.3 | 1 | 2.297 | 0.8 | 2.282 | 1.2 |
| 2.19 | 3 | 2.188 | 2.5 | | |
| 2.15 | 1 | | | 2.128 | 0.9 |
| 2.06 | 1 | 2.054 | 1 | | |
| 1.83 | 2 | | | 1.817 | 1.7 |
| 1.7 | 7 | 1.6874 | 6 | | |
| 1.645 | 2 | 1.6237 | 2 | | |
| 1.55 | 2 | | | 1.541 | 1.5 |
| 1.49 | 1 | 1.4797 | 1 | | |
| 1.46 | 1 | 1.4528 | 1 | 1.453 | 0.3 |
| 1.375 | 1.5 | 1.3598 | 2 | 1.375 | 1.1 |
| | | 1.3465 | 1.2 | | |
| 1.205 | 1 | 1.2006 | 0.2 | | |
| 1.189 | 1 | 1.1702 | 0.6 | 1.1838 | 0.4 |

4.2.5.3.4 Spherule-Bearing Lutite Sublayer (Splsl)

Subsample 10.3574 g was used to characterize the spherule-bearing lutite sublayer of Bee Gorge sample 96714A. There are 12 dark reddish brown and two ochre grains of secondary iron oxide/oxyhydroxide. Raman spectra for two beige opaque grains have bands that match those for anatase and K-feldspar ± quartz. A Raman spectrum (Appendix BB, Fig. 315) for a translucent blocky grain that is clear with a light yellow tint has four bands at wavenumbers that match those of anatase, and six bands at wavenumbers that match those of K-feldspar. Again, this may be a K-feldspar grain with a very minor amount of anatase matrix material on its surface.

A Raman spectrum (Fig. 174) for a translucent grain that is clear with a light yellow tint shows a good match with an anglesite standard. This Raman spectrum also has an unindexed band at wavenumber 228 cm⁻¹ (cf., Fig. 163), as well as two other unindexed bands of very low intensities. Again, the band at wavenumber 228 cm⁻¹ is not attributed to hematite (see section 4.2.5.2.3).



Figure 174: Raman spectra of an anglesite grain from the spherule-bearing lutite sublayer (Splsl) in Bee Gorge sample 96714A, and an anglesite standard from the RRUFF Raman spectral database. The bands at wavenumbers 228, 267, and 327 cm⁻¹ are unindexed (U).

4.2.5.3.5 Upper Spherule/Lutite Sublayers (Usplsl)

Subsamples 8.4057 g and 8.7879 g ($\Sigma \approx 17.19$ g) were used to characterize the upper spherule/lutite sublayers subdivision of Bee Gorge sample 96714A. There are six dark red-to-reddish brown grains of secondary iron oxide/oxyhydroxide. Rutile ± anatase (n = 66) comprises 85.7% of the total grains (n = 77), and anatase (n = 6), anatase + K-feldspar (n = 3), and anglesite (n = 2) are minor components. The grains are typically subrounded-to-subangular.

The Raman spectra for six varicolored opaque grains have bands at wavenumbers that match those of an anatase standard (e.g., Appendix BB, Fig. 316), and for five of the grains, the Raman spectra have a band at wavenumber 463/466 cm⁻¹ that is attributed to quartz (see Fig. 41). Raman spectra for three blocky grains that are clear with a very light yellow tint have bands at wavenumbers that match those of anatase and K-feldspar (e.g., Appendix BB, Fig. 317). One of the grains has a minor amount of white matrix material on its surface that may represent the anatase. For each of two grains that are clear with a very light green or yellow tint, the Raman spectrum has a single band at wavenumber ~978 cm⁻¹ (e.g., Fig. 175), and the grains are probably anglesite.



Figure 175: Raman spectra of a probable anglesite grain from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714A, and an anglesite standard from the RRUFF Raman spectral database.

The Raman spectra for 36 varicolored grains have bands at wavenumbers that match those of rutile (e.g., Appendix BB, Fig. 318), and for 20 additional varicolored grains, each of the Raman spectra have bands at wavenumbers that match those of rutile and anatase. The estimated total number of rutile \pm anatase grains in the upper spherule/lutite sublayers (UsplsI) subdivision is 66, so ~85% of the rutile \pm anatase grains in this subdivision were analyzed by micro-Raman spectroscopy. The Raman spectra for two rutile and four rutile \pm anatase grains have 1-4 additional bands at wavenumbers 209, 262, 354, 394, 403, and 461/464 cm⁻¹ that match those of quartz (see Fig. 41). A very

minor amount of clear-to-white matrix material occurs on the surfaces of ~75% of the rutile + anatase grains, and this matrix material is probably anatase. About a dozen of the rutile grains are similar in appearance to the granular rutile grains in the lowermost spherule-rich sublayer (Lspsl), but 65% (n = 43) of the rutile \pm anatase grains in the upper spherule/lutite sublayers (Usplsl) subdivision are very light buff-to-buff.

For three very light buff-to-light buff rutile \pm anatase grains (Table 50), the Raman spectra (Figs. 176, 177, and 178) have 4-9 additional bands and 1-2 shoulders at wavenumbers that match those of the TiO₂ II phase (see Fig. 90). All three Raman spectra for grain #23 (Table 50) are excellent (e.g., Fig. 178), and they have bands with wavenumbers and relative intensities that closely match those for natural TiO₂ II as shown in El Goresy et al. (2001; their Fig. 2). The TiO₂ II phase, therefore, is present in a minimum of 4.5% (n = 3) of the rutile \pm anatase grains (n = 66) in the 63-125 µm size fraction of the upper spherule/lutite sublayers (UsplsI) subdivision in Bee Gorge sample 96714A. Table 50:Description of and micro-Raman analytical data for rutile + TiO_2 II
grains from the upper spherule/lutite sublayers (Usplsl) subdivision in
Bee Gorge sample 96714A.

| Grain Identification Number//Date of Analysis | Description of Grain (Color, Diaphaneity, Shape, Size (µm), Angularity) | Number of spots analyzed/Number of spots with TiO ₂ II | Phases Present |
|---|---|---|--|
| 4//3-11-10 | Very light buff, Opaque, Blocky, 130 x 80, Subrounded | 5/3 | Rutile (TiO ₂ II) (Anatase) |
| 18//3-11-10 | Light buff, Opaque, Blocky, 170 x 120, Subangular | 3/3 | Rutile TiO ₂ II (Anatase) |
| 23//3-11-10 | Very light buff, Opaque, Blocky, 125 x 70, Subrounded | 3/3 | Rutile TiO ₂ II |

Note: Phases in parentheses were not observed at every probed spot on the grain.



Figure 176: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #4 (Table 50) from the upper spherule/lutite sublayers (Uspls1) subdivision in Bee Gorge sample 96714A (cf., Fig. 90). The bands at wavenumbers 176, 316, 340, and 357 cm⁻¹, and the shoulder at wavenumber 283 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001).



Figure 177: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #18 (Table 50) from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714A (cf., Fig. 90). The bands at wavenumbers 173, 281, 314, 339, 358, and 529 cm⁻¹, and the shoulders at wavenumbers 426 and 574 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001).



Figure 178: Unnormalized Raman spectrum of $TiO_2 II + rutile$ (R) grain #23 (Table 50) from the upper spherule/lutite sublayers (Uspls1) subdivision in Bee Gorge sample 96714A (cf., Fig. 90). The bands at wavenumbers 150, 174, 286, 315, 339, 357, 427, 532, and 572 cm⁻¹, and the shoulder at wavenumber 411 cm⁻¹ are attributed to $TiO_2 II$ (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum. This Raman spectrum is very similar to the Raman spectrum for rutile + $TiO_2 II$ from the Ries impact structure in Germany (see El Goresy et al., 2001; their Fig. 2).

4.2.5.4 Sample 96714B

4.2.5.4.1 Introduction

Bee Gorge sample 96714B consists of a basal context layer and the overlying spherule layer (Appendix D). The sample was sawn into four subdivisions (see Appendix D, Fig. 284; Appendix L): a basal carbonate lutite context layer (Bcl) and three spherule layer subdivisions. In ascending stratigraphic order, the latter three subdivisions are referred to as the lowermost spherule-rich sublayer (Lspsl), the spherule-bearing lutite sublayer (Splsl), and the upper spherule/lutite sublayers (Usplsl). The 63-125 µm size fractions of the basal carbonate lutite context layer and each of the three spherule layer subdivisions were used to characterize Bee Gorge sample 96714B. The heavy mineral grains are described in Appendix V, and their abundance is shown in Figure 179. Phase identification was done by micro-Raman spectroscopy. The four subdivisions are described in ascending stratigraphic order, so the following discussion begins with the basal carbonate lutite context layer (Bcl).



Figure 179: Heavy mineral abundance for the 63-125 µm size fraction of Bee Gorge sample 96714B.

4.2.5.4.2 Basal Carbonate Lutite Context Layer (Bcl)

Subsamples 9.5155 g, 10.3847 g, 10.7160 g, 11.0042 g, and 11.1367 g ($\Sigma \approx 52.76$ g) were used to characterize the basal carbonate lutite context layer of Bee Gorge sample 96714B. There are ~10 dark red-to-dark reddish brown grains of secondary iron oxide/oxyhydroxide. Anatase (n = 11), anatase + K-feldspar (n = 1), and sillimanite (n = 1), comprise 84.6%, 7.7%, and 7.7%, respectively, of the total grains (n = 13). The Raman spectra for six grains have 2-5 bands at wavenumbers that match those of anatase, and for five of these grains, the Raman spectra have a band at wavenumber 462/464 cm⁻¹

that is attributed to quartz (e.g., Appendix BB, Fig. 319). A Raman spectrum for a clearto-light gray grain that has a minor amount of white matrix material on its surface has bands at wavenumbers that match those of anatase and K-feldspar. This grain is translucent-to-opaque, and it probably represents a K-feldspar grain with anatase matrix material on its surface. A Raman spectrum for a transparent grain that is clear with a very light golden tint shows a good match with a sillimanite standard (Fig. 180).



Figure 180: Raman spectra of a sillimanite grain from the basal carbonate lutite context layer (Bcl) that is stratigraphically below the spherule layer in Bee Gorge sample 96714B, and a sillimanite standard from the RRUFF Raman spectral database.

4.2.5.4.3 Lowermost Spherule-Rich Sublayer (Lspsl)

Subsample 13.8178 g was used to characterize the lowermost spherule-rich sublayer of Bee Gorge sample 96714B. There are two dark red grains of secondary iron oxide/oxyhydroxide. Rutile \pm anatase (n = 434) comprises 98.9% of the total grains (n = 439), and anatase (n = 3), anatase + K-feldspar (n = 1), and monazite (n = 1) occur in trace amounts. For three light gray opaque grains, the Raman spectra for two of them have bands at wavenumbers that match those of an anatase standard (e.g., Appendix BB, Fig. 320), and the Raman spectrum for the third grain has bands at wavenumbers that match those of anatase, quartz, and K-feldspar. The latter grain is probably anatase with a minor amount of quartz + K-feldspar matrix material on its surface. A Raman spectrum for a light gray opaque grain that has an adamantine luster has ~8 bands at wavenumbers that show a good match with a monazite standard (Fig. 181). It is unclear whether the monazite is of detrital or secondary origin.



Figure 181: Raman spectra of a monazite grain from the lowermost spherule-rich sublayer (Lspsl) in Bee Gorge sample 96714B, and a monazite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

A Raman spectrum for a light gray opaque grain has bands at wavenumbers that match those of rutile, anatase, and quartz. The remainder of the grains (n = 433) in the heavy mineral assemblage are similar in appearance to the granular rutile \pm anatase grains in the corresponding sublayer in Bee Gorge sample 96714A (see section 4.2.5.3.3). A Raman spectrum for one of these granular grains has bands at wavenumbers that match those of rutile (Appendix BB, Fig. 321; cf., Fig. 173), and the Raman spectrum for another granular grain has bands at wavenumbers that match those of rutile, anatase, and

quartz. In the Raman spectrum for the latter grain, the bands at wavenumbers 202, 263, 353, and 463 (strong) cm⁻¹ match those of a quartz standard (see Fig. 41).

4.2.5.4.4 Spherule-Bearing Lutite Sublayer (Splsl)

Subsamples 6.5066 g and 12.0772 g ($\Sigma \approx 18.58$ g) were used to characterize the spherule-bearing lutite sublayer of Bee Gorge sample 96714B. There are 10 dark red-to-reddish brown grains of secondary iron oxide/oxyhydroxide. Anatase (n = 9), anatase + K-feldspar (n = 5), and rutile ± anatase (n = 10) comprise 34.6%, 19.2%, and 38.5%, respectively, of the total grains (n = 26), and actinolite (n = 2) is a minor component. Raman spectra for two light green transparent grains are similar to each other, and the Raman spectra have bands at wavenumbers that show a fairly good match with those of an actinolite standard (e.g., Fig. 182).



Figure 182: Raman spectra of an actinolite grain from the spherule-bearing lutite sublayer (Splsl) in Bee Gorge sample 96714B, and an actinolite standard from the RRUFF Raman spectral database.

Raman spectra for nine opaque grains that are typically light gray-to-white have bands at wavenumbers that match those of anatase. For seven of the anatase grains, the Raman spectra have 1-3 additional bands at wavenumbers 262/264, 403, and 461/465 cm⁻¹ that are attributed to quartz (see Fig. 41). Raman spectra for three of five transparent-to-opaque grains that are clear with a (very) light yellow tint have 4-5 bands at wavenumbers that match those of anatase, and 5-8 bands at wavenumbers 153, 177/179, 267, 282/285, 327, 367, 403, 449/453, 474/475, 512/514 (strong), ~574, and 755/758 cm⁻¹ that match those in a K-feldspar (orthoclase) standard (see Fig. 43). These five grains are blocky and subangular, and they appear to be K-feldspar grains that have minor amounts of anatase matrix material on their surfaces. A Raman spectrum for a medium dark gray grain has bands at wavenumbers that match those of rutile, whereas a Raman spectrum for a white opaque grain has bands at wavenumbers that match those of rutile, anatase, and quartz. There are eight granular grains that are similar in appearance to the granular rutile \pm anatase grains in the lowermost spherule-rich sublayer (Lspsl).

4.2.5.4.5 Upper Spherule/Lutite Sublayers (Usplsl)

Subsample 14.2225 g was used to characterize the upper spherule/lutite sublayers subdivision of Bee Gorge sample 96714B. There are two (dark red and ochre) grains of secondary iron oxide/oxyhydroxide. Anatase \pm xenotime (n = 6), rutile \pm anatase (n = 30), and xenotime (n = 14) comprise 11.3%, 56.6%, and 26.4% of the total grains (n = 53), and anatase + K-feldspar (n = 2) and monazite (n = 1) are minor phases. A Raman spectrum of a light gray opaque grain has bands at wavenumbers that match those of anatase. Raman spectra (e.g., Fig. 183) for three opaque grains that are clear with a light yellow tint each have five bands at wavenumbers that match those of anatase, and 4-7 bands at wavenumbers 371/374, 423/424, 476, 515, 576, 996, and 1053/1055 cm⁻¹. These 4-7 bands match bands of moderate-to-strong intensities in a xenotime standard that is shown in Figure 184 in which this standard is compared to a Raman spectrum of a xenotime grain (see p. 367) from this same subdivision of sample 96714B. These 4-7 bands, therefore, are interpreted to be due to xenotime; the textural relationship of the anatase and xenotime is not clear.



Figure 183: Unnormalized Raman spectrum of an anatase (A) + xenotime (X) grain from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714B. A Raman spectrum of a xenotime standard is shown in Figure 184.



Figure 184: Raman spectra of a xenotime grain from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714B, and a xenotime standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for two translucent grains that are clear with a (very) light yellow tint have bands at wavenumbers that match those of anatase and K-feldspar, and they appear to be blocky K-feldspar grains with minor amounts of anatase matrix material on their surfaces. For a light gray, opaque grain with a minor amount of colorless matrix material on its surface, a Raman spectrum has ~12 bands with wavenumbers that match those of monazite. This grain has a similar appearance to that of a few of the rutile grains (see below), so the monazite may comprise the matrix material. Raman spectra for 18 varicolored grains have bands at wavenumbers that match those of a rutile standard (e.g., Appendix BB, Fig. 322), and Raman spectra for seven varicolored grains have bands at wavenumbers that match those of rutile and anatase. Therefore, of the estimated total number (n = 30) of rutile \pm anatase grains that were recovered from the upper spherule/lutite sublayers (UsplsI) subdivision of sample 96714B, ~83% (n = 25) were analyzed by micro-Raman spectroscopy. There are no granular rutile grains (see section 4.2.5.4.3), and ~77% (n = 23) of the estimated total number of rutile \pm anatase grains in this subdivision are various shades of buff. For five of the rutile \pm anatase grains, the Raman spectra have a band at wavenumber 462/465 cm⁻¹ that is attributed to quartz (see Fig. 41).

For two light grayish buff rutile + anatase grains (Table 51), the Raman spectra (Figs. 185 and 186) have 8-9 additional bands and a shoulder at wavenumbers that match those of the TiO₂ II phase (see Fig. 90). For each of the two grains, two of the three Raman spectra show very well-developed peaks for the TiO₂ II phase. The TiO₂ II phase, therefore, is present in a minimum of 6.7% (n = 2) of the rutile \pm anatase grains (n = 30) in the 63-125 µm size fraction of the upper spherule/lutite sublayers (UsplsI) subdivision in Bee Gorge sample 96714B. For the combined upper spherule/lutite sublayers (UsplsI) subdivisions of Bee Gorge samples 96714B and 96714A, ~84.4% (n = 81) of the estimated total number (n = 96) of rutile \pm anatase grains were analyzed by micro-Raman spectroscopy. Rutile \pm anatase grains that contain the TiO₂ II phase (n = 5) comprise ~6.2% of the analyzed grains (n = 81), and they comprise a minimum of 5.2% of the estimated total number of rutile \pm anatase grains (n = 96).

Table 51:Description of and micro-Raman analytical data for rutile + TiO_2 II
grains from the upper spherule/lutite sublayers (Usplsl) subdivision in
Bee Gorge sample 96714B.

| Grain Identification Number//Date of Analysis | Description of Grain (Color, Diaphaneity, Shape, Size (µm), Angularity) | Number of spots analyzed/Number of spots with TiO ₂ II | Phases Present |
|---|---|---|--|
| 36//3-14-10 | Light grayish buff, Opaque, Subequant, 80 x 80, Subrounded | 3/3 | Rutile TiO ₂ II (Anatase) (Quartz) |
| 40//3-14-10 | Light grayish buff, Opaque, Irregular, 120 x 80, Subangular | 3/3 | Rutile TiO ₂ II (Anatase) |

Note: The phases in parentheses were not observed at every probed spot on the grain.



Figure 185: Unnormalized Raman spectrum of $TiO_2 II + rutile$ (R) grain #36 (Table 51) from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714B (cf., Fig. 90). The bands at wavenumbers 150, 173, 286, 314, 339, 355, 427, 531, and 573 cm⁻¹, and the shoulder at wavenumber 411 cm⁻¹ are attributed to $TiO_2 II$ (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.



Figure 186: Unnormalized Raman spectrum of TiO₂ II + rutile (R) + anatase (A) grain #40 (Table 51) from the upper spherule/lutite sublayers (UsplsI) subdivision in Bee Gorge sample 96714B (cf., Fig. 90). The bands at wavenumbers 173, 285, 314, 339, 355, 428, 529, and 572 cm⁻¹, and the shoulder at wavenumber 408 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). A Raman spectrum of an anatase standard is shown in Figure 21. No baseline correction was made for this spectrum.

Raman spectra for nine grains that are clear with a yellow tint have up to ~ 22 bands in the wavenumber range 140-1100 cm⁻¹ that show a very good match with a xenotime standard (e.g., see Fig. 184). The grains are blocky and subangular-to-angular. Each grain appears to consist solely of xenotime, i.e., the xenotime does not appear to be mantling another phase.

4.2.5.5 **Context Sample 92058**

Bee Gorge context sample 92058 was collected ~1 m stratigraphically above the Bee Gorge spherule layer (Table 6). Bee Gorge context sample 92058 was characterized by part of subsample 236.3 g. Monazite and xenotime, which are the predominant heavy mineral phases in Bee Gorge context sample 92058 (see below), are quite similar in appearance. For this reason, no grain count was made of the heavy mineral phases in this sample. Instead, an approximate relative abundance of the heavy mineral phases was determined only from grains that were analyzed by micro-Raman spectroscopy.

For the 63-125 μ m size fraction, there are ~1,050 secondary iron oxide/oxyhydroxide grains. About 90% of these grains appear to be cubic pseudomorphs after pyrite. These grains are brown-to-dark brown, commonly exhibit striations, and some consist of aggregates of cubes. About 10% of the secondary iron oxide/oxyhydroxide grains are dark red, reddish brown, and ochre, and they do not exhibit a cubic habit. A Raman spectrum for one of these grains has bands at wavenumbers that match those of hematite, goethite, and quartz.

In addition to the secondary iron oxide/oxyhydroxide grains, there are ~370 grains in the 63-125 μ m size fraction, and ~115 of these grains were analyzed by micro-Raman spectroscopy. For ~32 of these grains, the Raman spectra have bands at wavenumbers that match those of quartz ± K-feldspar. The Raman spectra for the remaining 83 grains are used to characterize the heavy mineral assemblage for this size fraction. The heavy mineral grains are described in Appendix V, and their relative abundance is shown in Figure 187. Monazite ± anatase (n = 24) and xenotime ± anatase (n = 50) comprise 28.9% and 60.2%, respectively, of the total grains (n = 83). Anatase ± quartz (n = 6), rutile + monazite (n = 1), and rutile ± xenotime (n = 2) are minor components.



Figure 187: Relative abundance of heavy mineral grains from Bee Gorge context sample 92058 that were analyzed by micro-Raman spectroscopy. The sample was collected ~1 m stratigraphically above the Bee Gorge spherule layer.

Raman spectra for six grains have 2-5 bands at wavenumbers that match those of anatase, and for five of the grains, the Raman spectra have 1-5 additional bands at wavenumbers that are attributed to quartz. Five of the six grains are opaque, and they may be anatase grains with quartz matrix material on their surfaces, but a translucent grain may represent a quartz grain with a minor amount of anatase matrix material on its surface. Raman spectra for 15, 6, and 3 grains have bands at wavenumbers that match those of monazite, monazite and quartz, and monazite + anatase \pm quartz, respectively. The textural relationship of the monazite and quartz is typically unclear, but for one grain that consists of dark gray, fine-grained, opaque subgrains that are enclosed by a matrix material, a Raman spectrum (Fig. 188) for the matrix material has bands at wavenumbers that match those of a monazite standard, and a Raman spectrum for the dark gray material (Fig. 189) has a band at wavenumber 464 cm⁻¹ that is interpreted as the strongest band for quartz (see Fig. 41). The quartz subgrains are interpreted as chert fragments. One of the monazite + anatase grains shows a similar textural relationship with dark gray, finegrained, opaque subgrains. Therefore, at least some of the monazite appears to be of secondary origin.



Figure 188: Raman spectra of monazite matrix material enclosing dark gray, finegrained, chert (?) subgrains from Bee Gorge context sample 92058, and a monazite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~1 m stratigraphically above the Bee Gorge spherule layer.



Figure 189: Unnormalized Raman spectrum of a dark gray, fine-grained chert (?) subgrain from Bee Gorge context sample 92058. The band at wavenumber 464 cm⁻¹ is interpreted as the band of strongest intensity for quartz (see Fig. 41 for a quartz standard). The sample was collected ~1 m stratigraphically above the Bee Gorge spherule layer.

Raman spectra for three grayish, subrounded grains have bands at wavenumbers that match those of rutile. For two of the rutile grains, Raman spectra have additional bands at wavenumbers that match those of quartz \pm xenotime. For the remaining rutile grain, a Raman spectrum has two additional distinct bands at wavenumbers 462 (strong) and 969 cm⁻¹ that suggest that the matrix material on the grain consists of quartz and monazite (Fig. 190). The Raman spectral data for the rutile grains suggest that at least some of the monazite and xenotime are of secondary origin.



Figure 190: Unnormalized Raman spectrum of a rutile (R) + monazite (MON) + quartz (Q) grain from Bee Gorge context sample 92058. This grain is interpreted as a rutile grain with monazite + quartz matrix material on its surface. The sample was collected ~1 m stratigraphically above the Bee Gorge spherule layer.

Raman spectra for 35, 12, and 3 varicolored grains have bands at wavenumbers that match those of xenotime, xenotime and quartz, and xenotime + anatase \pm quartz, respectively. The xenotime grains are typically translucent-to-opaque, subangular-toangular, and they have a blocky or irregular shape. The xenotime + quartz grains typically consist of two distinct parts: medium-to-dark gray, fine-grained, opaque subgrains that are enclosed by light olive gray, translucent matrix material. Raman spectra for the matrix material consistently have bands at wavenumbers that match those of a xenotime standard (Fig. 191), and Raman spectra for the gravish subgrains have bands at wavenumbers that match those of quartz (Fig. 192; cf., Fig. 41). The xenotime + quartz grains are interpreted as detrital chert grains enclosed by xenotime matrix material. These data again suggest that at least some of the xenotime is a secondary phase. For a light gray opaque grain that has white matrix material on its surface, a Raman spectrum for the grain has bands at wavenumbers that match those of xenotime, and a Raman spectrum of the matrix material has bands at wavenumbers that match those of anatase and quartz. Further work is necessary to determine the textural relationships and mode(s) of origin of the anatase, monazite, and xenotime.



Figure 191: Raman spectra of xenotime matrix material enclosing dark gray, finegrained chert (?) subgrains from Bee Gorge context sample 92058, and a xenotime standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~1 m stratigraphically above the Bee Gorge spherule layer.



Figure 192: Unnormalized Raman spectrum of a medium-to-dark gray, fine-grained, chert (?) subgrain from Bee Gorge context sample 92058. The subgrain is enclosed by xenotime matrix material (see Fig. 191). A Raman spectrum of a quartz standard is shown in Figure 41. The sample was collected ~1 m stratigraphically above the Bee Gorge spherule layer.

Six secondary iron oxide/oxyhydroxide grains are present in the 125-250 µm size fraction. Five of these grains consist of cubic pseudomorphs after pyrite. They are brown-to-dark brown, commonly exhibit striations, and some consist of aggregates of cubes. A Raman spectrum for the sixth grain has bands at wavenumbers that match those of goethite and quartz. In addition to these six grains, there are another 42 grains in this size fraction, and 23 of these grains were analyzed by micro-Raman spectroscopy. Raman spectra for nine of these 23 grains have bands at wavenumbers that match those of quartz.
These nine quartz grains are not included in Figure 187 since they are not heavy mineral grains. Raman spectra for the remaining 14 grains were used to characterize the heavy mineral assemblage of the 125-250 µm size fraction.

The heavy mineral grains are described in Appendix V, and their relative abundance is shown in Figure 187. Xenotime \pm anatase (n = 10) and monazite (n = 2) comprise 71.4% and 14.3%, respectively, of the total grains (n = 14), and actinolite (n = 1) and anatase + quartz (n = 1) are minor components. A Raman spectrum for a dark olive green grain has bands at wavenumbers that suggest that it is actinolite (Fig. 193). For a beige opaque grain, a Raman spectrum has bands at wavenumbers that match those of anatase and quartz. Raman spectra for two grains that are clear with a (light) yellow tint have bands that match those of monazite.

For 10 varicolored grains, the Raman spectra have bands at wavenumbers that match those of xenotime \pm anatase \pm quartz. Two of these grains consist of fine-grained, opaque subgrains that are enclosed by a light gray matrix material. Raman spectra for the subgrains have bands at wavenumbers that match those of quartz, and Raman spectra for the matrix material have bands at wavenumbers that match those of xenotime. The quartz subgrains are interpreted as detrital chert material, and the xenotime is interpreted as secondary matrix material. Most of the other grains are beige and opaque, and they may represent anatase grains that have coatings of xenotime \pm quartz. Again, more work is necessary to determine the mode(s) of origin of anatase, monazite, and xenotime.



Figure 193: Raman spectra of a possible actinolite grain from Bee Gorge context sample 92058, and an actinolite standard from the RRUFF Raman spectral database. The sample was collected ~1 m stratigraphically above the Bee Gorge spherule layer.

No chrome spinel, tourmaline, and zircon grains were recovered from Bee Gorge samples 92058 (see Fig. 187), 96714A (see Fig. 168), and 96714B (see Fig. 179) (see Fig. 4 for locations). However, for Bee Gorge sample BB (see Fig. 4 for location), chrome spinel, tourmaline, and zircon grains were recovered from both the spherule layer (BB (sl); see Fig. 148) and context layer #2 (BB (#2); see Fig. 162), whereas tourmaline and zircon grains were recovered from context layer #1 (BB (#1); see Fig. 158). For Bee Gorge samples BB, 96714A, 96714B, and 92058, granular rutile grains were only recovered from the spherule layer parts of samples 96714A and 96714B, and very light

buff-to-buff rutile grains were only recovered from the spherule layer and context layers of sample BB, and the upper spherule/lutite sublayers (UsplsI) subdivisions of samples 96714A and 96714B (see Appendix V). However, only three rutile grains were recovered from context layer #1 (BB (#1)) in sample BB, and only four rutile grains were recovered from the combined basal carbonate lutite (Bcl) context layers of samples 96714A and 96714B (see Appendix V). Finally, only three rutile grains were recovered from context sample 92058 (see Appendix V).

4.2.6 Monteville Spherule Layer Samples

4.2.6.1 Sample U63-1

Subsamples 278.0 g and 315.2 g ($\Sigma = 593.2$ g) were used to characterize Monteville spherule layer sample U63-1, and phase identification was done by micro-Raman spectroscopy. By visual estimate, there are far >10,000 grains of secondary iron and manganese oxide/oxyhydroxide phases in the 63-125 µm size fraction. Raman spectra for two of the secondary iron oxide/oxyhydroxide grains have bands at wavenumbers 220/224, 287/294, 407/414, and 1326 cm⁻¹ that match bands of moderateto-strong intensities for hematite as given in de Faria et al. (1997) and Das and Hendry (2011), and bands at wavenumbers 387, 657, and 671 cm⁻¹. The band at wavenumber 387 cm⁻¹ suggests the presence of goethite (see Fig. 103), but the phase(s) responsible for the bands at wavenumbers 657 and 671 cm⁻¹ is (are) not known. Light gray-to-beige matrix material typically occurs on the surfaces of these orange red and reddish brown grains, and Raman spectra for the matrix material on two of these grains have bands at wavenumbers that match those of anatase and quartz.

No brassy grains were observed in the heavy mineral separates. Raman spectra for six, dark steel gray, opaque, subangular grains have 1-3 bands at wavenumbers 260, 356, 530, 638/639, 643, 652, and 662 cm⁻¹. Bands with similar wavenumbers are present in Raman spectra for various manganese oxides/dioxides (e.g., Julien et al., 2004; Ciobotă et al., 2012). Two of these grains have 1-5 additional bands at wavenumbers that match those of quartz.

Grains that did not appear to be secondary iron or manganese oxide/oxyhydroxide phases were handpicked from the heavy mineral separates of the 63-125 μ m and 125-250 μ m size fractions. The heavy mineral grains are described in Appendix W, and their

abundance is shown in Figure 194. For the 63-125 μ m size fraction, anatase (n = 974) and monazite \pm anatase (n = 209) comprise 80.8% and 17.3%, respectively, of the total grains (n = 1,206). Rutile \pm anatase (n = 18) is a minor (1.5%) component, and the other phases occur in trace amounts.



Figure 194: Heavy mineral abundance for Monteville spherule layer sample U63-1.

Raman spectra for \sim 38 varicolored grains have bands at wavenumbers that match those of anatase, and for five of the grains, the Raman spectra have 1-3 additional bands at wavenumbers 206, 264/265, and 462/465 cm⁻¹ that match those for a quartz standard

(see Fig. 41). For three or four of the grains, the quartz appears to be a coating (matrix) on opaque anatase, whereas for one or two grains, the anatase appears to be a beige or white coating (matrix) on colorless translucent quartz. A Raman spectrum for a translucent grain that is clear with a light yellow-green tint has bands at wavenumbers that suggest that it is clinochlore (Fig. 195), and the grain is termed "chlorite" in Figure 194.



Figure 195: Raman spectra of a chlorite (clinochlore) grain from Monteville spherule layer sample U63-1, and a clinochlore standard from the RRUFF Raman spectral database.

Raman spectra for 30 grains that are typically clear with a (very) light yellow tint have ~8-12 bands at wavenumbers that match those of a monazite standard (e.g., Appendix CC, Fig. 323). For two of these grains, the Raman spectra have 4-5 additional bands that match those of anatase. The textural relationship of the monazite and anatase is unknown. For seven of the monazite grains, the Raman spectra have a single additional band at wavenumber 142/144, 512, or 636 cm⁻¹. These bands are attributed to anatase, but it is possible that the band at wavenumber 512 cm⁻¹ indicates K-feldspar (see Fig. 43). The monazite grains are typically irregular in shape and subangular-to-angular, and therefore, the monazite may be largely of secondary origin.

Raman spectra for seven grains have bands at wavenumbers that match those of a rutile standard (e.g., Appendix CC, Fig. 324), and Raman spectra for 11 other grains have bands at wavenumbers that match those of rutile and anatase (e.g., Appendix CC, Fig. 325). About 83% (n = 15) of these 18 rutile \pm anatase grains are very light buff-to-buff (see Appendix W). None of the Raman spectra for the rutile \pm anatase grains show any evidence for the TiO₂ II phase.

For a white opaque grain, the Raman spectrum (Appendix CC, Fig. 326) is very similar to those for the "rutile + unidentified" grains in the Carawine spherule layer samples 84-1 (see Fig. 29) and 42-1A (see Fig. 77). For two of three grains that are clear with a golden or light olive tint, the Raman spectra (Figs. 196 and 197) have bands at wavenumbers that show a fair-to-good match with those of tourmaline standards. In Figure 197, the band of strong intensity at wavenumber 142 cm⁻¹ is attributed to anatase.



Figure 196: Raman spectra of a probable tourmaline grain from Monteville spherule layer sample U63-1, and a tourmaline standard from the RRUFF Raman spectral database.



Figure 197: Raman spectra of a tourmaline + anatase (A) grain from Monteville spherule layer sample U63-1, and a tourmaline standard from the RRUFF Raman spectral database. A Raman spectrum for an anatase standard is shown in Figure 21.

For the 125-250 μ m size fraction, there are >10,000 grains of secondary iron and manganese oxide/oxyhydroxide phases by visual estimate, and the grains typically have varying amounts of light gray-to-beige matrix material on their surfaces. A Raman spectrum for an aggregate of dark brown blocky crystals has five bands at wavenumbers 168, 260, 354, 522, and 639 (strong) cm⁻¹. The latter four bands have similar wavenumbers to those that are present in Raman spectra for various manganese oxides/dioxides (e.g., see Julien et al., 2004). Anatase (n = 82) and monazite (n = 11)

comprise 79.6% and 10.7%, respectively, of the total grains (n = 103), and anatase + K-feldspar (n = 5) and rutile + anatase (n = 5) are minor components (Fig. 194).

Raman spectra for four light gray-to-beige, opaque grains each have five bands at wavenumbers that match those of anatase. Raman spectra were obtained for four of the five anatase + K-feldspar grains. The textural relationship of the two phases is uncertain for four of the grains. For the remaining grain, it appears that anatase forms a white opaque coating on a translucent K-feldspar grain. A secondary origin for at least some of the anatase in Monteville spherule layer sample U63-1 is further indicated by a Raman spectrum for a spherule that has bands at wavenumbers that match those of anatase. Raman spectra for three of 11 grains that are clear with a (very) light yellow tint have \sim 7-8 bands at wavenumbers that match those of rutile and anatase. None of the Raman spectra for the rutile + anatase grains show any evidence for the TiO₂ II phase.

4.2.6.2 Sample V111

Subsample 219.9 g was used to characterize Monteville spherule layer sample V111, and phase identification was done by micro-Raman spectroscopy. For the 63-125 µm size fraction, there are two ochre grains of secondary iron oxide/oxyhydroxide and one brassy opaque grain. A Raman spectrum for the brassy grain has bands at wavenumbers that clearly match those of pyrite and anatase (Fig. 198). The anatase is not evident, but it must be present on the surface of the pyrite grain. These data suggest that at least some of the anatase in Monteville spherule layer sample V111 (see below) is of secondary origin.



Figure 198: Raman spectra of a pyrite (P) + anatase (A) grain from Monteville spherule layer sample V111, and a pyrite standard from the RRUFF Raman spectral database. A Raman spectrum of an anatase standard is shown in Figure 21. No baseline correction was made for the sample spectrum. The heavy mineral grains are described in Appendix W, and their abundance is shown in Figure 199. For the 63-125 μ m size fraction, anatase \pm K-feldspar (n = 1,566), monazite \pm anatase (n = 785), and rutile \pm anatase \pm TiO₂ II (n = 347) comprise 56.5%, 28.3%, and 12.5%, respectively, of the total grains (n = 2,773). Zircon \pm anatase (n = 33) comprises 1.2% of the total grains, and the other phases occur in trace amounts.



Figure 199: Heavy mineral abundance for Monteville spherule layer sample V111.

Raman spectra for three light-to-dark green, elongate-to-bladed grains have \sim 10-13 bands at wavenumbers that show a good match with those for an actinolite standard (e.g., Fig. 200).



Figure 200: Raman spectra of an actinolite grain from Monteville spherule layer sample V111, and an actinolite standard from the RRUFF Raman spectral database.

Raman spectra for 34 varicolored grains that are mostly opaque have 4-5 bands at wavenumbers that match those of anatase. The Raman spectra for twelve of these grains have 1-6 additional bands at wavenumbers that match those of quartz (e.g., Appendix CC, Fig. 327), and the Raman spectra for six of these grains have 1-4 additional bands at wavenumbers that match those of K-feldspar (e.g., Appendix CC, Fig. 328). Many of the anatase grains are observed to be mantled to varying degrees by a translucent matrix that is typically clear with a light yellow tint. On the basis of the typical colors and diaphaneities that are exhibited by anatase, quartz, and K-feldspar when these phases occur singularly in the sample, it is hypothesized that these mantled grains represent opaque anatase grains with translucent coatings composed of quartz and/or K-feldspar. However, it is possible that an indeterminate number of grains included in the "anatase \pm K-feldspar" category (Fig. 199) may be quartz or K-feldspar grains that are mantled to varying degrees by anatase. Again, more work is needed to determine the mode(s) of origin of the anatase \pm K-feldspar \pm quartz grains.

For an adamantine grain that is clear with a very light yellow tint, the Raman spectrum has seven bands with wavenumbers and intensities that closely match an anglesite standard, as well as four unindexed bands (Fig. 201). The band at wavenumber 223 cm⁻¹ is of stronger intensity than the band at wavenumber 228 cm⁻¹ that occurs in the Raman spectrum of an anglesite grain from context layer #2 (BB (#2)) in Bee Gorge sample BB (see Fig. 163). More work is necessary to determine the origin of these unindexed bands in these anglesite grains.



Figure 201: Raman spectra of an anglesite grain with unindexed (U) bands at wavenumbers 182, 223, 248, and 947 cm⁻¹ from Monteville spherule layer sample V111, and an anglesite standard from the RRUFF Raman spectral database.

For two translucent grains that have a light olive or yellow-green tint, the Raman spectra have 3-8 bands at wavenumbers that match those of clinochlore. For one of the grains, the Raman spectrum has additional bands at wavenumbers 142 (strong) and 637 cm⁻¹ that are attributed to anatase (Fig. 202). These grains are termed "chlorite \pm anatase" in Figure 199.



Figure 202: Raman spectra of a clinochlore (Clch) + anatase (A) grain from Monteville spherule layer sample V111, and a clinochlore standard from the RRUFF Raman spectral database. A Raman spectrum of an anatase standard is shown in Figure 21.

There are five dark gray-to-black opaque grains that have clear-to-light green matrix material on their surfaces. For three of the grains, the Raman spectra have 1-5 bands at wavenumbers 445, 560/566, 649, 689, and 733/745 (strong) cm⁻¹ that are attributed to chrome spinel (e.g., Fig. 203). The Raman spectrum shown in Figure 203 is similar to those for chrome spinel grains from Carawine spherule layer samples X24-1 (see Fig. 54), 42-1A (see Fig. 75), and X38-2 (see Fig. 87), and Jeerinah spherule layer sample W94-1Q (see Fig. 121). The Raman spectra for two of these three chrome spinel grains from Monteville spherule layer sample V111 have 2-6 additional bands at wavenumbers 193/194, 263/266, 368, 421, 637, and 699/706 cm⁻¹ that are attributed to muscovite (Fig. 204). For the fourth grain, a Raman spectrum (Fig. 205) has bands at wavenumbers attributed to anatase (see Fig. 21), a band at wavenumber 463 cm⁻¹ that is attributed to quartz (see Fig. 41), and bands at wavenumbers attributed to muscovite (see Fig. 204). The bands at wavenumbers 197 and 638 cm⁻¹ probably have both anatase and muscovite components. For the fifth grain, a Raman spectrum of the matrix material on its surface has bands at wavenumbers attributed to clinochlore and muscovite (Fig. 206).

The Raman spectra for four of the five opaque grains mentioned above suggest that the matrix material on their surfaces is composed of one or more of the following phases: anatase, chlorite (clinochlore), muscovite, and quartz. The Raman spectra for the fourth (Fig. 205) and fifth (Fig. 206) grains do not identify the opaque grains themselves, but these two grains are hypothesized to be chrome spinels on the basis of the following indirect evidence. Raman spectra (e.g., Fig. 204) for two of these five dark gray-to-black opaque grains with green matrix material on their surfaces suggest that they are chrome spinels with muscovite matrix material. Similar-looking grains are present in Carawine spherule layer sample X38-2 (see section 4.2.2.6) and Carawine context sample 104141

(see section 4.2.3.1), and these grains were also identified as chrome spinels with muscovite matrix material on their surfaces. The presence of anatase with muscovite and quartz (Fig. 205) again suggests that at least some of the anatase in Monteville spherule layer sample V111 is of secondary origin.



Figure 203: Raman spectra of a chrome spinel grain from Monteville spherule layer sample V111, and a magnesiochromite standard from the RRUFF Raman spectral database (cf., Figs. 54, 75, 87, and 121).



Figure 204: Raman spectra of a chrome spinel (Chr) + muscovite grain from Monteville spherule layer sample V111, and magnesiochromite and muscovite standards from the RRUFF Raman spectral database (cf., Fig. 203).



Figure 205: Unnormalized Raman spectrum of anatase (A) + muscovite (M) + quartz (Q) coating on the surface of a dark gray opaque grain (probably chrome spinel, see above) from Monteville spherule layer sample V111. Raman spectra of anatase, muscovite, and quartz standards are shown in Figures 21, 204, and 41, respectively.



Figure 206: Raman spectra of clinochlore (Clch) + muscovite (M) coating on the surface of a dark gray opaque grain (probably chrome spinel, see above) from Monteville spherule layer sample V111, and a clinochlore standard from the RRUFF Raman spectral database. A Raman spectrum of a muscovite standard is shown in Figure 204.

For two transparent grains that have a light olive or yellow-green tint, the Raman spectra are similar, and they have ~12-15 bands at wavenumbers and intensities that closely match a diopside standard (Fig. 207).



Figure 207: Raman spectra of a clinopyroxene grain from Monteville spherule layer sample V111, and a diopside standard from the RRUFF Raman spectral database.

Raman spectra for 24 translucent-to-opaque grains that are typically clear with a (very) light yellow tint have up to ~11 bands at wavenumbers that match those of a monazite standard, and the band at wavenumber 969/972 cm⁻¹ is always present (e.g., Appendix CC, Fig. 329). For 18 of these grains, the Raman spectra have additional bands

at wavenumbers that match those of anatase (e.g., Appendix CC, Fig. 330). For a few of the monazite grains, the Raman spectra have additional bands at wavenumbers that match those of quartz (e.g., Appendix CC, Fig. 331) and K-feldspar. The textural relationships of these phases are uncertain, but the typically irregular shape of the monazite grains suggests a secondary origin.

Raman spectra for 187 grains that are typically various shades of buff, peach, amber, and brown have bands at wavenumbers that match those of rutile (n = 91; Fig. 208), rutile and anatase (n = 87; Appendix CC, Fig. 332) and rutile + TiO₂ II ± anatase (n = 9; see below). The Raman spectra for seven rutile grains and for seven rutile + anatase grains have 1-4 additional bands at wavenumbers 207/210, 263/264, 355/356, and 462/464 cm⁻¹ that match those of a quartz standard (see Fig. 41). For three of these grains, micro-Raman spectroscopy clearly shows that quartz (± anatase) comprises the matrix material on the surfaces of the rutile grains.

A Raman spectrum for one rutile grain that has colorless matrix material on its surface has at least 15 additional bands at wavenumbers that match those of K-feldspar (Fig. 209). In Figure 209, all the bands attributed to K-feldspar are present in the Raman spectrum for a K-feldspar (orthoclase) standard (see Fig. 43), except for the band at wavenumber 628 cm⁻¹. However, a band at wavenumber 625/629 cm⁻¹ is present in a Raman spectrum for K-feldspar as reported by Freeman et al. (2008).



Figure 208: Raman spectra of a rutile grain from Monteville spherule layer sample V111, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 209: Unnormalized Raman spectrum of a rutile (R) + K-feldspar (K) grain from Monteville spherule layer sample V111. Raman spectra of rutile and K-feldspar standards are given in Figures 208 and 43, respectively. The grain is interpreted as a rutile grain with K-feldspar matrix material on its surface. For nine rutile grains from the 63-125 μ m size fraction (Table 52), the Raman spectra (Fig. 210; Appendix CC, Figs. 333-340) have 5-10 additional bands or shoulders at wavenumbers 149/150, 173/175, 280/286, 314/319, 339/341, 356/359, 410, 428/430, 529/534, and 570/573 cm⁻¹ that match those of the TiO₂ II phase (see Fig. 90). All ten bands/shoulders have been reported for synthetic TiO₂ II (Mammone et al., 1980), and nine of the bands have been reported for both synthetic and natural TiO₂ II (El Goresy et al., 2001, their Fig. 2). The shoulder at wavenumber 410 cm⁻¹ on the band of strong intensity at wavenumber 427 cm⁻¹ (Fig. 210) was not reported by El Goresy et al. (2001).

The Raman spectra for grains (Table 52) #16 (Appendix CC, Fig. 333), #1 (Appendix CC, Fig. 334), #5 (Appendix CC, Fig. 335), and #6 (Appendix CC, Fig. 336) have 4-5 bands and a shoulder (at wavenumbers 284 or 429 cm⁻¹) that are attributed to the TiO₂ II phase. The Raman spectra for grains (Table 52) #13 (Appendix CC, Fig. 337) and #20 (Fig. 210) both show excellent bands for the TiO₂ II phase. The three Raman spectra for grain #20 (Table 52) all have the shoulder at wavenumber ~410 cm⁻¹ that occurs on the band of strong intensity at wavenumber ~427 cm⁻¹ (e.g., Fig. 210).

| Grain Identification Number//Date of Analysis | Description of Grain (Color, Diaphaneity, Shape, Size (µm), Angularity) | Number of spots analyzed/Number of spots with TiO ₂ II | Phases Present |
|---|---|---|--|
| 16//12-21-09 | Buff, Opaque, Blocky, ~80 x 120, Subrounded 3/2 | | Rutile (TiO ₂ II) |
| 1//12-22-09 | Buff, Opaque, Blocky, ~80 x 100, Subrounded 3/3 | | Rutile TiO ₂ II (Anatase) (Quartz) |
| 5//12-22-09 | Buff, Opaque, Blocky, ~80 x 90, Subrounded4/1 | | Rutile (TiO ₂ II) (Anatase) |
| 6//12-22-09 | Light buff, Opaque, Blocky, ~100 x 100, Subrounded | 2/2 | Rutile TiO ₂ II |
| 13//12-22-09 | Light buff, Opaque, Blocky, ~125 x 125, Subangular | 3/3 | Rutile TiO ₂ II |
| 14//12-22-09 | Light buff, Opaque, Blocky, ~100 x 125, Subangular | 3/3 | Rutile TiO ₂ II |
| 44//1-10-10 | Buff, Opaque, Slightly elongate, ~60 x 100, Subangular | 4/4 | Rutile TiO ₂ II |
| 20//1-11-10 | Buff, Opaque, Blocky, ~90 x 100, Subrounded | 3/3 | Rutile TiO ₂ II |
| 23//1-11-10 | Very light buff, Opaque, Blocky, ~80 x 100, Subrounded | 3/3 | Rutile TiO ₂ II (Anatase) |
| 15//1-24-10 | Very light buff, Opaque, Blocky, 3/3 ~150 x 190, Subangular | | Rutile TiO ₂ II |

Table 52:Description of and micro-Raman analytical data for rutile + TiO_2 II
grains from Monteville spherule layer sample V111.

| Note: | Phases in | parentheses | were not o | bserved | at | every p | robec | l spot | on t | he grain. |
|-------|-----------|-------------|------------|---------|----|---------|-------|--------|------|-----------|
|-------|-----------|-------------|------------|---------|----|---------|-------|--------|------|-----------|



Figure 210: Unnormalized Raman spectrum of TiO₂ II + rutile (R) grain #20 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 150, 174, 286, 315, 339, 356, 427, 531, and 570 cm⁻¹, and the shoulder at wavenumber 410 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.

Raman spectra for 17 very light-to-dark olive green grains have bands at wavenumbers that match those of tourmaline (e.g., Fig. 211). For 11 of the grains, the Raman spectra have 1-5 additional bands at wavenumbers that match those of anatase (e.g., Fig. 212), and for one of the grains, the Raman spectrum has a band of moderate intensity at wavenumber 465 cm⁻¹ that is attributed to quartz (see Fig. 41).



Figure 211: Raman spectra of a tourmaline grain from Monteville spherule layer sample V111, and a tourmaline standard from the RRUFF Raman spectral database.



Figure 212: Unnormalized Raman spectrum of a tourmaline (T) + anatase (A) grain from Monteville spherule layer sample V111. Raman spectra of anatase and tourmaline standards are shown in Figures 21 and 211, respectively.

Raman spectra for 33 grains that are typically pink, champagne, and clear with a very light yellow-to yellow tint have ~2-13 bands at wavenumbers that match those of a zircon standard (e.g., Fig. 213). Nine zircon grains are translucent-to-opaque, and one zircon grain is opaque (Appendix W). The Raman spectra for 11 of the zircon grains have only 2-3 bands that typically occur at wavenumbers 345/356, 1000/1003, and 1165/1168 cm⁻¹, and these grains are typically translucent or translucent-to-opaque. The Raman spectra for two of the zircon grains have 3-4 additional bands at wavenumbers that match those of anatase (e.g., Fig. 214). The anatase is not evident, but it probably occurs as very

fine-grained matrix material on the surfaces of the zircon grains. These Raman spectral data for the tourmaline and zircon grains further suggest that at least some of the anatase in Monteville spherule layer sample V111 is of secondary origin. None of the Raman spectra for the 33 zircon grains show any evidence of baddeleyite or reidite.



Figure 213: Raman spectra of a champagne transparent zircon grain from Monteville spherule layer sample V111, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 214: Unnormalized Raman spectrum of a zircon (Z) + anatase (A) grain from Monteville spherule layer sample V111 (cf., Figs. 32, 33, and 213).

Raman spectra for three grains remain unidentified. Two of the grains are colorless-to-clear with a light yellow-green tint, transparent, and angular, and their Raman spectra include a band of strong intensity at wavenumber 322 cm⁻¹ (e.g., Fig. 215). The third grain is colorless, transparent, and angular. The Raman spectrum for this grain (Fig. 216) includes a band of very strong intensity at wavenumber 521 cm⁻¹, and the Raman spectrum is similar to those for four of the unidentified grains in Jeerinah spherule layer sample X21-1 (e.g., see Fig. 147).

Coesite has a band of very strong intensity at wavenumber ~521 cm⁻¹, but it also has bands of moderate-to-strong intensities at wavenumbers ~178 and ~271 cm⁻¹ (Boyer et al., 1985). The latter two bands are not present in the Raman spectrum shown in Figure 216. The Raman spectrum for synthetic stishovite shows a band of strong intensity at wavenumber 753 cm⁻¹ and bands of moderate intensities at wavenumbers 231 and 589 cm⁻¹ (Liu et al., 1997). Again, the latter two bands are not present in the Raman spectrum shown in Figure 216. Furthermore, a band at wavenumber 1051 cm⁻¹ (Fig. 216) was not observed in the Raman spectra for coesite or stishovite (Liu et al., 1997). The absence of bands at wavenumbers ~178, 231, ~271, and 589 cm⁻¹ in the Raman spectrum shown in Figure 216 suggests that this grain does not contain coesite or stishovite, but more work is needed (e.g., XRD, EDX) to identify the phase(s) in this grain.



Figure 215: Unnormalized Raman spectrum of an unidentified grain from Monteville spherule layer sample V111 that has a band of strong intensity at wavenumber 322 cm⁻¹. No baseline correction was made for the sample spectrum.



Figure 216: Unnormalized Raman spectrum of an unidentified grain from Monteville spherule layer sample V111 that has a band of very strong intensity at wavenumber 521 cm⁻¹.

For the 125-250 μ m size fraction, there are three brown-to-dark red grains of secondary iron oxide/oxyhydroxide. The heavy mineral grains are described in Appendix W, and their abundance is shown in Figure 199. Anatase (n = 27), monazite ± anatase (n = 17), and rutile ± anatase ± TiO₂ II (n = 15), comprise 43.5%, 27.4%, and 24.2%, respectively, of the total grains (n = 62), and the other phases are minor components. For a dark green transparent grain, the Raman spectrum is similar to that for the actinolite grain in the 63-125 μ m size fraction (see Fig. 200). Raman spectra for five light gray-to-white, opaque grains have 2-5 bands at wavenumbers that match those of anatase, and the

Raman spectra for two of the grains have an additional band at wavenumber $464/465 \text{ cm}^{-1}$ that is attributed to quartz (see Fig. 41). A Raman spectrum for a dark steel gray opaque grain that is completely surrounded by a clear-to-light green matrix material is similar to the Raman spectrum shown in Figure 204, in that it shows four bands at wavenumbers 194, 264, ~406, and 700 cm⁻¹ that are attributed to muscovite, and two bands at wavenumbers 567 and ~736 cm⁻¹ that are attributed to chrome spinel.

Raman spectra for five grains that are light gray-to-white or clear with a light yellow tint have up to 11 bands at wavenumbers that match those of monazite. The Raman spectra for three of the grains have 2-4 additional bands at wavenumbers that match those of anatase, and a Raman spectrum for one of these grains also has four bands at wavenumbers that match those of quartz. The monazite grains are similar in shape and angularity to those in the 63-125 μ m size fraction, and again, they may be of secondary origin.

Raman spectra for eight very light buff or very light peach opaque grains have bands at wavenumbers that match those of rutile (n = 2), rutile and anatase (n = 5), and rutile + TiO₂ II (n = 1). For grain #15 (Table 52), all three Raman spectra (e.g., Appendix CC, Fig. 341) have nine well-developed bands/shoulders at wavenumbers that match those of the TiO₂ II phase (cf., Fig. 90). Therefore, ~54% (n = 195) of the estimated total number (n = 362) of rutile \pm anatase grains in the 63-250 µm size fraction of Monteville spherule layer sample V111 were analyzed by micro-Raman spectroscopy, and ~5.1% (n = 10) of the analyzed grains contain the TiO₂ II phase. The 10 grains that contain the TiO₂ II phase (Table 52) comprise a minimum of 2.8% of the estimated total number of rutile \pm anatase grains in the 63-250 µm size fraction of Monteville spherule layer sample V111.

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A Raman spectrum for one unidentified grain has a band of moderate intensity at wavenumber 520 cm⁻¹. This grain is clear with a very light yellow tint, transparent, subequant, and subangular. There are a few very small, brown opaque particles or crystals within the grain.

4.2.7 Monteville Context Samples

4.2.7.1 Sample T149-1

Sample T149-1 was collected ~1 m stratigraphically below the Monteville spherule layer (Table 7). Subsamples 105.1 g and 109.2 g ($\Sigma = 214.3$ g) were used to characterize Monteville context sample T149-1, and the phases were identified by micro-Raman spectroscopy. For the 63-125 µm size fraction, a grain count shows that there are ~108,000 ochre, brown, and dark brown grains of secondary iron oxide/oxyhydroxide. The grains typically consist of single cubes or aggregates of cubes that are commonly striated, and they appear to be pseudomorphs after pyrite crystals. By visual estimate, <10% of the grains have varying amounts of colorless-to-white, translucent-to-opaque matrix material on their surfaces. Raman spectra for two grains have ~4-5 bands at wavenumbers that match those of hematite.

Grains that did not appear to be secondary iron oxide/oxyhydroxide phases were handpicked from the heavy mineral separates. The heavy mineral grains are described in Appendix X, and their abundance is shown in Figure 217. For the 63-125 μ m size fraction, monazite (n = 117) and chlorite (n = 36) comprise 69.2% and 21.3%, respectively, of the total grains (n = 169), and anatase (n = 8) and monazite + anatase (n = 8) are minor components.



Figure 217: Heavy mineral abundance for Monteville context sample T149-1. The sample was collected ~1 m stratigraphically below the Monteville spherule layer.

For eight grains that are typically beige-to-white and opaque, the Raman spectra have 2-5 bands at wavenumbers that match those of anatase. The Raman spectra for six of these grains have 1-3 additional bands at wavenumbers 263/268, ~352, and 464/465 cm⁻¹ that match those of a quartz standard (see Fig. 41). For 30 grains that are clear with a light yellow or light yellow-green tint, the Raman spectra typically have ~3-6 bands at wavenumbers that show a fairly good match with those of a clinochlore standard (Fig. 218), and the grains are termed "chlorite" in Figure 217. The bands at wavenumbers

551/554 and 681/689 cm⁻¹ consistently show the strongest intensities. Two of the chlorite grains occur as matrix material on the surfaces of cubic grains of iron oxide/oxyhydroxide that are pseudomorphous after pyrite. These data suggest that the chlorite is of secondary origin.



Figure 218: Raman spectra of clinochlore matrix material on the surface of a cubic grain of iron oxide/oxyhydroxide that is pseudomorphous after pyrite from Monteville context sample T149-1, and a clinochlore standard from the RRUFF Raman spectral database. The sample was collected ~1 m stratigraphically below the Monteville spherule layer.

For 48 grains that are clear with a light yellow tint-to-white, the Raman spectra typically have ~5-14 bands at wavenumbers that closely match those of a monazite standard (e.g., Appendix DD, Fig. 342). The band at wavenumber 968/971 cm⁻¹ is always present, and it typically has the strongest intensity. The Raman spectra (e.g., Appendix DD, Fig. 343) for nine monazite grains have ~1-7 additional bands at wavenumbers 155, 198, 265/266, 280/287, 402, 454/456, 475/477, 512/514 (always present), and 750/755 cm⁻¹. All these bands are present in the Raman spectrum for a K-feldspar (orthoclase) standard (see Fig. 43), and they are attributed to K-feldspar. The Raman spectra for two monazite grains have 3-4 additional bands at wavenumbers 200/206, 263/264, 355, and 464/465 cm⁻¹ that match those of a quartz standard (see Fig. 41). For eight grains that are very pale peach-to-white and typically opaque, the Raman spectra have ~3-11 bands at wavenumbers that match those of monazite, as well as 3-5 bands at wavenumbers that match those of anatase (e.g., Appendix DD, Fig. 344).

For the 125-250 μ m size fraction, a grain count shows that there are ~14,100 secondary iron oxide/oxyhydroxide grains that are similar to those in the 63-125 μ m size fraction. A few grains that did not appear to be secondary iron oxide/oxyhydroxide phases were handpicked from the heavy mineral separates. Raman spectra for these grains have bands at wavenumbers that match those of K-feldspar and/or quartz. No primary heavy mineral grains were identified in the 125-250 μ m size fraction.

4.2.7.2 Sample II67-1B

Sample II67-1B was collected ~20 cm stratigraphically above the Monteville spherule layer (Table 7). Subsamples 286.9 g and 329.8 g ($\Sigma = 616.7$ g) were used to characterize Monteville context sample II67-1B, and the phases were identified by micro-Raman spectroscopy. The heavy mineral separates consist mostly of secondary iron and

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manganese oxide/oxyhydroxide grains. For the 63-125 µm size fraction, a grain count shows that there are ~11,150 grains of secondary iron oxide/oxyhydroxide, and ~1,920 grains of manganese oxide(s). The secondary iron oxide/oxyhydroxide grains are reddish brown, dark reddish brown, and dark brown, and they typically exhibit various forms (e.g., cube and octahedron) that suggest that they are pseudomorphs after pyrite. These grains typically have variable amounts of colorless-to-white, vitreous matrix material on their surfaces. Raman spectra for seven of the grains have bands at wavenumbers that match those of hematite and/or goethite (e.g., Appendix DD, Fig. 345). A Raman spectrum for the matrix material on the surface of a hematite grain shows nine bands at wavenumbers that match those of quartz. The Raman spectra for four dark steel gray, opaque, scaly grains have 3-4 bands at wavenumbers that suggest that they are manganese oxides. The manganese oxide grains typically have little or no colorless coating on their surfaces.

For the 63-125 μ m and 125-250 μ m size fractions, grains that did not appear to be secondary iron or manganese oxide/oxyhydroxide phases were handpicked from the heavy mineral separates. The heavy mineral grains are described in Appendix X, and their abundance is shown in Figure 219. For the 63-125 μ m size fraction, anatase (n = 18), chrome spinel (n = 3), and rutile (n = 1) comprise 81.8%, 13.6%, and 4.5%, respectively, of the total grains (n = 22).



Figure 219: Heavy mineral abundance for Monteville context sample II67-1B. The sample was collected ~20 cm stratigraphically above the Monteville spherule layer.

The Raman spectra for 14 grains that are typically clear with a very light yellow tint-to-very light olive green have 4-5 bands at wavenumbers that match those of anatase. For three anatase grains, the Raman spectra have 1-5 additional bands at wavenumbers that match those of quartz. For one of these grains, micro-Raman spectroscopy clearly shows that the quartz comprises matrix material on the surface of the anatase grain.

There are three medium dark gray opaque grains with light green-to-emerald green matrix material on their surfaces. These grains are similar in appearance to the chrome spinel grains in Monteville spherule layer sample V111 that have muscovite matrix material on their surfaces (e.g., see section 4.2.6.2). The Raman spectra for these three grains have 3-6 bands at wavenumbers 192/195, 261/267, 414, 701/705, 914, and 1104 cm⁻¹ that are attributed to muscovite, and 1-3 bands at wavenumbers 555, 645, and 736/754 cm⁻¹ that are attributed to chrome spinel (e.g., Fig. 220). A Raman spectrum for a light orange amber, translucent grain, has bands at wavenumbers that match those of a rutile standard (Fig. 221).



Figure 220: Raman spectra of a chrome spinel (Chr) grain with muscovite (M) matrix material on its surface from Monteville context sample II67-1B, and magnesiochromite and muscovite standards from the RRUFF Raman spectral database. There is an unindexed (U) band at wavenumber 974 cm⁻¹. The sample was collected ~20 cm stratigraphically above the Monteville spherule layer.



Figure 221: Raman spectra of a rutile grain from Monteville context sample II67-1B, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~20 cm stratigraphically above the Monteville spherule layer.

For the 125-250 μ m size fraction, there are ~790 grains of secondary iron oxide/oxyhydroxide, and ~160 grains of secondary manganese oxide(s). These grains are similar in appearance to those in the 63-125 μ m size fraction. Approximately 10 grains that did not appear to be secondary iron oxide/oxyhydroxide or manganese oxide phases were handpicked from the heavy mineral separates. For four of these grains, the Raman spectra have bands at wavenumbers that match those of quartz and/or K-feldspar. Primary heavy mineral grains appear to be absent from the 125-250 μ m size fraction.

4.2.8 Grænsesø Spherule Layer Samples

4.2.8.1 Sample GL8904-1

Subsample 349.3 g was used to characterize Grænsesø spherule layer sample GL8904-1, and the phases were identified by micro-Raman spectroscopy. There are <10 secondary iron oxide/oxyhydroxide grains. The heavy mineral grains are described in Appendix Y, and their abundance is shown in Figure 222. For the 63-125 μ m size fraction, rutile ± anatase (n = 12,551), tourmaline (n = 2,340), and zircon (n = 2,551) comprise 71.5%, 13.3%, and 14.5%, respectively, of the total grains (n = 17,549), and the other phases occur in trace amounts.



Figure 222: Heavy mineral abundance for Grænsesø spherule layer sample GL8904-1.

Raman spectra for 16 varicolored grains typically have five bands at wavenumbers that match those of an anatase standard (e.g., Appendix EE, Fig. 346). The Raman spectra for six anatase grains have 1-6 additional bands at wavenumbers that match those of quartz. For five of eight grains that are clear with a very light yellow-tolight green tint, the Raman spectra have a band of moderate intensity at wavenumber 980/983 cm⁻¹. For one of these grains, the Raman spectrum has three additional bands at wavenumbers that suggest the grain is anglesite (Fig. 223). For another one of these grains, the Raman spectrum has an additional band of very weak intensity at wavenumber 449 cm⁻¹, and this grain may be anglesite or barite (Fig. 224). For these eight grains, more

work (e.g., XRD, EDX) is needed to determine the relative proportion of anglesite and barite grains.



Figure 223: Raman spectra of an anglesite grain from Grænsesø spherule layer sample GL8904-1, and an anglesite standard from the RRUFF Raman spectral database.



Figure 224: Raman spectra of an anglesite or barite grain from Grænsesø spherule layer sample GL8904-1, and anglesite and baryte standards from the RRUFF Raman spectral database.

Raman spectra were obtained for four of the dark steel gray-to-black opaque grains that have green vitreous matrix material on their surfaces. The Raman spectrum for one of the grains has bands at wavenumbers that suggest it is a chrome spinel (Fig. 225), whereas for the other three grains, the Raman spectra have 3-4 bands of moderate-to-strong intensities at wavenumbers that are attributed to muscovite (e.g., Fig. 226). The muscovite is interpreted as a secondary phase on the surfaces of the opaque grains that are probably detrital chrome spinels. A Raman spectrum for a black opaque grain that has

no matrix material on its surface has a broad band at wavenumber 665 cm⁻¹ that suggests that it is magnetite (Fig. 227).



Figure 225: Raman spectra of a chrome spinel grain from Grænsesø spherule layer sample GL8904-1, and chromite and magnesiochromite standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 226: Raman spectra of muscovite matrix material on the surface of a dark steel gray grain (probably chrome spinel, see above) from Grænsesø spherule layer sample GL8904-1, and a muscovite standard from the RRUFF Raman spectral database.



Figure 227: Raman spectra of a black opaque magnetite grain from Grænsesø spherule layer sample GL8904-1, and a magnetite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

For 167 varicolored grains that are typically subrounded-to-well-rounded, the Raman spectra for 148 of them have bands at wavenumbers that match those of a rutile standard (e.g., Fig. 228), and the Raman spectra for 19 of them have bands at wavenumbers that match those of rutile and anatase (e.g., Appendix EE, Fig. 347). Therefore, Raman spectra were obtained for ~1.3% (n = 167) of the estimated total number (n = 12,551) of rutile \pm anatase grains in the 63-125 µm size fraction of Grænsesø spherule layer sample GL8904-1, and none of the Raman spectra show any evidence for the TiO₂ II phase. For seven rutile and three rutile + anatase grains, the

Raman spectra have 1-5 additional bands at wavenumbers that match those of a quartz standard (e.g., Appendix EE, Fig. 348). The quartz clearly occurs as secondary matrix material on the surfaces of the rutile \pm anatase grains. Likewise, two rutile grains have secondary albite on their surfaces (e.g., Fig. 229).



Figure 228: Raman spectra of a rutile grain from Grænsesø spherule layer sample GL8904-1, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 229: Raman spectra of albite matrix material on the surface of a rutile grain from Grænsesø spherule layer sample GL8904-1, and an albite standard from the RRUFF Raman spectral database.

Raman spectra for 13 varicolored grains typically have 11-20 bands at wavenumbers that match those of tourmaline. The Raman spectrum shown in Figure 230 shows a fairly good match with a dravite standard.



Figure 230: Raman spectra of a tourmaline grain from Grænsesø spherule layer sample GL8904-1, and a dravite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for 19 varicolored grains that are typically transparent or translucent have 3-15 bands at wavenumbers that match those of a zircon standard (e.g., Fig. 231). A few of these zircon grains are white and translucent-to-opaque or opaque. As compared to the transparent zircon grains, the Raman spectra for the

translucent-to-opaque (Fig. 232) and opaque (Fig. 233) zircon grains show bands that are broader and of lower intensity. The Raman spectrum for one zircon grain has three additional bands at wavenumbers that match those of quartz. The Raman spectrum for another zircon grain has additional bands at wavenumbers 210, 292, 480, and 508 (strong) cm⁻¹. These four bands match bands of moderate-to-strong intensities in the albite standard that is shown in Figure 229. The quartz and albite are interpreted as secondary phases that partly mantle the zircon grains.



Figure 231: Raman spectra of a transparent zircon grain from Grænsesø spherule layer sample GL8904-1, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 232: Raman spectra of a white translucent-to-opaque zircon grain from Grænsesø spherule layer sample GL8904-1, and a zircon standard from the RRUFF Raman spectral database.



Figure 233: Raman spectra of a very light peach-to-white, opaque zircon grain from Grænsesø spherule layer sample GL8904-1, and a zircon standard from the RRUFF Raman spectral database.

For ~25 varicolored grains that are typically translucent-to-opaque or opaque, the Raman spectra have 0-2 bands. Many of these grains have colors and/or shapes similar to zircon grains. For six of these grains, the Raman spectra have 1-2 bands at wavenumbers 226, 345/352, and 996/1000 cm⁻¹ that support their identification as zircon, whereas the Raman spectra for 19 grains have no distinct bands. For the 63-125 μ m size fraction, ~23% of the zircon grains are translucent-to-opaque or opaque, and ~1% of the zircon grains are white opaque. Three grains that have no distinct bands on their Raman spectra

are listed as "Unidentified" (Appendix Y; Fig. 222), though one or more of them may be zircon.

For the 125-250 μ m size fraction, rutile \pm anatase (n = 127) and tourmaline (n = 88) comprise 56.7% and 39.3%, respectively, of the total grains (n = 224). Anatase (n = 7) is a minor component, and zircon (n = 2) is a trace component (Fig. 222). The phases are similar in appearance to their respective phases in the 63-125 μ m size fraction, and they are typically subrounded (Appendix Y). Raman spectra for three grains have bands at wavenumbers that match those of rutile \pm anatase, and a Raman spectrum for a light golden amber grain has bands at wavenumbers that match those of tourmaline. Two pale pink-to-pink grains that are slightly elongate-to-prismatic were not analyzed, but they are very similar in appearance to several of the zircon grains in the 63-125 μ m size fraction that were identified by micro-Raman spectroscopy.

4.2.8.2 Sample GL8904-2

No grain count was done for Grænsesø spherule layer sample GL8904-2 for the following reasons. Prior to beginning micro-Raman spectroscopy of the Grænsesø samples, two grain mounts had been made using some of the heavy mineral grains from the 63-125 μ m size fraction of Grænsesø spherule layer sample GL8904-2 in order to do preliminary EDX analysis. By visual estimate, the two grain mounts combined contain >1000 grains. Due to time and cost considerations, only ~20 of these grains were analyzed by EDX, and no further work was done to identify the grains in the two grain mounts, so the EDX results are not included in this dissertation. Due to the large number (>1000) of unidentified grains in the grain mounts, it was decided not to do a grain count for Grænsesø spherule layer sample GL8904-2.

Sixty-five grains from the 63-125 μ m size fraction of subsample 421.4 g of Grænsesø spherule layer sample GL8904-2 were analyzed by XRD and/or micro-Raman spectroscopy. A Raman spectrum for a light gray-buff opaque grain has bands at wavenumbers that match those of anatase. An XRD pattern for a black opaque grain contains lines that match those of anatase and quartz (Table 53). The lines of weak intensities at d-spacings of 3.05, 2.75, 2.57, and 1.34 Å remain unindexed (Table 53).

Table 53:XRD data for an anatase + quartz grain from Grænsesø spherule layer
sample GL8904-2 and anatase and quartz standards. Lines with intensities
≤1.2 in the standards that were not observed in the pattern for the grain are
not listed in the table.

| Grain ID: D-S 2-3 6-22-06 | | Anata 21-12 | ise 72 | Quartz 5-0490 | | |
|---------------------------------|------------------|----------------|------------------|------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | |
| 4.3 | 1 | | | 4.26 | 3.5 | |
| 3.52 | 10 | 3.52 | 10 | | | |
| 3.33 | 7 | | | 3.343 | 10 | |
| 3.05 | 1 | | | | | |
| 2.75 | 1 | | | | | |
| 2.57 | 2 | | | | | |
| 2.43 | 3 | 2.431 | 1 | | | |
| 2.36 | 3.5 | 2.378 | 2 | | | |
| 2.13 | 1 | | | 2.128 | 0.9 | |
| 1.96 | 3.5 | | | 1.980 | 0.6 | |
| 1.89 | 6 | 1.892 | 3.5 | | | |
| 1.82 | 2 | | | 1.817 | 1.7 | |
| 1.7 | 4 | 1.6999 | 2 | | | |
| 1.66 | 5 | 1.6665 | 2 | | | |
| 1.55 | 1 | | | 1.541 | 1.5 | |
| 1.47 | 4.5 | | | 1.453 | 0.3 | |
| 1.36 | 2 | | | 1.375 | 1.1 | |
| 1.34 | 2 | | | | | |
| 1.27 | 2 | | | 1.256 | 0.4 | |

An XRD pattern for a well-rounded, transparent grain that is clear with a very light green tint contains lines that match those of barite, and there are unindexed lines at d-spacings of 2.6 and 2.95 Å (Table 54). The line of strong intensity at d = 2.104 Å in the standard was not observed in the pattern for the grain (Table 54), but a Raman spectrum for this grain shows an excellent match with a baryte standard (Fig. 234).

Table 54:XRD data for a barite grain from Grænsesø spherule layer sample GL8904-2
and a baryte standard. Lines with intensities ≤ 1.2 in the standard that were
not observed in the pattern for the grain are not listed in the table.

| Grain G 1- 7-14- | ID: -3 -06 | Baryte 5-448 | | |
|------------------------|------------------|-----------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | |
| | | 4.44 | 1.7 | |
| | | 4.34 | 3.6 | |
| ~3.85 | 2 | 3.90 | 5.7 | |
| 3.6 | 1 | 3.576 | 3.1 | |
| 3.45 | 10 | 3.442 | 10 | |
| 3.28 | 4 | 3.317 | 6.7 | |
| 3.12 | 5 | 3.101 | 9.7 | |
| 2.95 | 1 | | | |
| 2.82 | 3 | 2.834 | 5.3 | |
| | | 2.734 | 1.6 | |
| 2.71 | 2.71 4 | | 4.7 | |
| 2.6 | 1 | | | |

Table 54: continued

| Grain G 1- 7-14- | ID: -3 -06 | Baryte 5-448 | | |
|------------------------|------------------|-----------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | |
| 2.48 | 1 | 2.481 | 1.4 | |
| 2.32 | 1 | 2.322 | 1.5 | |
| 2.22 | 1 | 2.209 | 2.7 | |
| 2.12 | 5 | 2.120 | 8 | |
| | | 2.104 | 7.6 | |
| 2.02 | 1 | 2.056 | 2.3 | |
| 1.95 | 1 | 1.947 | < 0.01 | |
| 1.86 | 1 | 1.857 | 1.6 | |
| 1.76 | 1 | 1.760 | 0.9 | |
| 1.69 | 1 | 1.681 | 0.7 | |
| | | 1.673 | 1.4 | |
| 1.65 | 1 | 1.636 | 0.8 | |
| 1.6 | 1 | 1.593 | 0.8 | |



Figure 234: Raman spectra of barite grain G 1-3 7-14-06 (Table 54) from Grænsesø spherule layer sample GL8904-2, and a baryte standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

XRD patterns for eight grains that are orange amber or various shades of gray contain lines that match those of rutile \pm quartz, and the data for two of the grains are given in Table 55. For grain D-S 2-3 6-23-06 (Table 55), there are unindexed lines at d-spacings of 2.58 and 4.5 Å. These lines do not occur in the patterns for albite and anatase (see Berry, 1974), or in the pattern for TiO₂ II (see El Goresy et al., 2001). A Raman spectrum for this grain has bands at wavenumbers that match those of a rutile standard (Fig. 235). A Raman spectrum (Fig. 236) for grain D-S 1-2 7-6-06 (Table 55) has bands at wavenumbers that match those of rutile and quartz, and the Raman spectral

data confirm the XRD identification.

Table 55: XRD data for two rutile grains from Grænsesø spherule layer sample GL8904-2 and rutile and quartz standards. Lines with intensities ≤1.2 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain ID: D-S 2-3 6-23-06 | | Grain ID: D-S 1-2 7-6-06 | | Rutil 21-12 | le 76 | Quartz 5-0490 | |
|---------------------------------|------------------|--------------------------------|------------------|----------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 4.5 | 5 | | | | | | |
| | | | | | | 4.26 | 3.5 |
| | | 3.35 | 6 | | | 3.343 | 10 |
| 3.25 | 10 | 3.25 | 10 | 3.25 | 10 | | |
| 2.58 | 4 | | | | | | |
| 2.49 | 5 | 2.48 | 5 | 2.487 | 5 | | |
| 2.4 | 2 | | | | | 2.458 | 1.2 |
| 2.2 | 3 | 2.18 | 5 | 2.188 | 2.5 | | |
| | | 2.13 | 3 | | | 2.128 | 0.9 |
| 2.05 | 2 | | | 2.054 | 1 | | |
| 1.97 | 2 | | | | | 1.980 | 0.6 |
| | | | | | | 1.817 | 1.7 |
| 1.69 | 8 | 1.69 | 4 | 1.6874 | 6 | | |
| 1.62 | 3 | | | 1.6237 | 2 | | |

Table 55: continued

| Grain D-S 2 6-23- | ID: 2-3 -06 | Grain ID: D-S 1-2 7-6-06 | | Rutile 21-1276 | | Quartz 5-0490 | |
|-------------------------|-------------------|--------------------------------|------------------|-------------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| | | | | | | 1.541 | 1.5 |
| 1.505 | 1 | | | 1.4797 | 1 | | |
| 1.45 | 2 | | | 1.4528 | 1 | 1.453 | 0.3 |
| 1.35 | 4 | | | 1.3598 | 2 | | |
| 1.13 | 3 | | | 1.1143 | 0.2 | 1.1144 | < 0.01 |



Figure 235: Raman spectra of rutile grain D-S 2-3 6-23-06 (Table 55) from Grænsesø spherule layer sample GL8904-2, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 236: Raman spectra of rutile (R) + quartz (Q) grain D-S 1-2 7-6-06 (Table 55) from Grænsesø spherule layer sample GL8904-2, and a rutile standard from the RRUFF Raman spectral database. A Raman spectrum of a quartz standard is shown in Figure 41. No baseline correction was made for the sample spectrum.

Raman spectra for four of the other six grains that were identified as rutile by XRD analysis have bands at wavenumbers that clearly match those of rutile. The rutile grains that are various shades of gray appear to be polycrystalline. The D-S patterns for these gray grains typically show arcs and/or lines, and these XRD data support the polycrystalline interpretation of these grains.

In addition to the eight rutile \pm quartz grains mentioned above, 39 gray-buff and gray-yellow grains were analyzed by micro-Raman spectroscopy. For 27 of these 39

grains, the Raman spectra have bands at wavenumbers that match those of rutile, and for 12 of these 39 grains, the Raman spectra have bands at wavenumbers that match those of rutile and anatase. For one of the rutile + anatase grains, anatase clearly occurs as matrix material on the surface of the rutile grain. The Raman spectra for two of the rutile grains have 1-3 additional bands at wavenumbers that match those of quartz.

XRD patterns for six grains that are amber, olive green, forest green, or bluegreen contain lines that match those of dravite or ferrian dravite, and the data for two of the grains are given in Table 56. A Raman spectrum for grain G 2-1 6-24-06 (Table 56) that is olive green has bands at wavenumbers that show a fairly good match with a dravite standard (Fig. 237). Grain D-S 2-3 7-5-06 (Table 56) is light golden amber, and there is no Raman spectrum available for this grain. A Raman spectrum for the forest green grain has bands at wavenumbers that match those of tourmaline. The Raman spectral data support the XRD identification of these grains as tourmalines. Table 56: XRD data for two tourmaline grains from Grænsesø spherule layer sample GL8904-2 and dravite and ferrian dravite standards. Lines with intensities ≤1.8 in the standards that were not observed in the patterns for the grains are not listed in the table.

| Grain ID: G 2-1 6-24-06 | | Grain ID: D-S 2-3 7-5-06 | | Dravite 14-76 | | Dravite, ferrian 19-1372 | |
|-------------------------------|------------------|--------------------------------|------------------|------------------|------------------|-----------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 6.5 | 6 | | | | | 6.44 | 6 |
| | | | | 6.38 | 3 | | |
| | | | | 4.98 | 2.5 | 5.01 | 4 |
| | | | | 4.60 | 1.8 | 4.62 | 4 |
| 4.25 | 4 | 4.25 | 5 | | | 4.25 | 9 |
| | | | | 4.22 | 6.5 | | |
| | | 4.0 | 9 | | | 4.00 | 9 |
| 3.98 | 4 | | | 3.99 | 8.5 | | |
| | | 3.52 | 6 | | | 3.51 | 9 |
| 3.45 | 8 | | | 3.48 | 6 | | |
| | | | | | | 2.979 | 9 |
| 2.95 | 8 | 2.95 | 9 | 2.961 | 8.5 | | |
| | | 2.59 | 10 | | | 2.586 | 10 |
| 2.56 | 10 | | | 2.576 | 10 | | |
| | | | | 2.396 | 2 | | |
| | | | | 2.376 | 2 | | |
| 2.35 | 2 | | | | | 2.356 | 1 |
| | | | | 2.342 | 2 | | |

Table 56: continued

| Grain G 2 6-24 | ID: -1 -06 | Grain ID: D-S 2-3 7-5-06 | | Dravite 14-76 | | Dravite, ferrian 19-1372 | |
|----------------------|------------------|--------------------------------|------------------|------------------|------------------|-----------------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 2.17 | 1 | | | | | 2.172 | 1 |
| | | | | 2.054 | 2 | 2.052 | 3 |
| | | 2.04 | 2 | 2.040 | 4.5 | | |
| 2.03 | 3 | | | | | 2.027 | 1 |
| | | | | | | 1.932 | 2 |
| | | | | 1.920 | 3.5 | | |



Figure 237: Raman spectra of tourmaline grain G 2-1 6-24-06 (Table 56) from Grænsesø spherule layer sample GL8904-2, and a dravite standard from the RRUFF Raman spectral database.

XRD analysis was done on nine grains that are typically pinkish white or white, translucent-to-opaque or opaque, and subrounded or well-rounded. The patterns for four grains are unreadable or poor, but Raman spectra for these grains have 2-5 bands at wavenumbers 203, 220/224, 349/356, 439/441, and 1000/1004 cm⁻¹ that match those of zircon. The XRD patterns for five grains contain lines that match those for zircon, and the data for three of these grains are given in Table 57.

Grain D-S #2 5-3-06 (Table 57) is white opaque, and its pattern has unindexed lines of weak intensities at d-spacings of 2.02 and 3.65 Å. Grain D-S 2-3 6-15-06

(Table 57) is pinkish white and opaque, and its pattern has unindexed lines of weak intensities at d-spacings of 1.81, 2.45, 2.8, and 4.25 Å. Grain D-S 2-3 6-24-06 (Table 57) is pale pink-to-light gray and translucent-to-opaque, and its pattern has an unindexed line of weak intensity at d = 2.45 Å. It is not known if the nickel filter was engaged during these analyses. However, in several D-S patterns for zircon grains from Carawine spherule layer sample X38-2 that were obtained in the absence of the nickel filter, there are spurious lines at similar d-spacings. For these five zircon grains from Grænsesø spherule layer sample GL8904-2, all the D-S patterns show arcs-to-lines.

Table 57:XRD data for three zircon grains from Grænsesø spherule layer sample
GL8904-2 and a zircon standard. Lines with intensities <1 in the standard
that were not observed in the patterns for the grains are not listed in the
table.

| Grain D-S 5-3- | ID: #2 06 | Grain ID: D-S 2-3 6-15-06 | | Grain ID: D-S 2-3 6-24-06 | | Zircon 6-0266 | |
|----------------------|------------------|---------------------------------|------------------|---------------------------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 4.4 | 7 | 4.45 | 7 | 4.48 | 8 | 4.43 | 4.5 |
| | | 4.25 | 1.5 | | | | |
| 3.65 | 1 | | | | | | |
| 3.31 | 10 | 3.33 | 10 | 3.32 | 10 | 3.30 | 10 |
| | | 2.8 | 1 | | | | |
| 2.65 | 2.5 | 2.66 | 3 | 2.7 | 3 | 2.650 | 0.8 |
| 2.54 | 5 | | | 2.55 | 7 | 2.518 | 4.5 |
| | | 2.45 | 1 | 2.45 | 2 | | |
Table 57: continued

| Grain ID: D-S #2 5-3-06 | | Grain ID: D-S 2-3 6-15-06 | | Grain ID: D-S 2-3 6-24-06 | | Zircon 6-0266 | |
|-------------------------------|------------------|---------------------------------|------------------|---------------------------------|------------------|------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 2.36 | 3.5 | 2.34 | 5 | | | 2.336 | 1 |
| | | 2.25 | 1 | 2.22 | 3 | 2.217 | 0.8 |
| 2.09 | 4 | 2.07 | 6 | 2.07 | 5 | 2.066 | 2 |
| 2.02 | 1.5 | | | | | | |
| 1.91 | 1 | | | 1.93 | 2 | 1.908 | 1.4 |
| | | 1.81 | 1.5 | | | | |
| 1.77 | 4 | 1.76 | 4.5 | 1.76 | 2 | 1.751 | 1.2 |
| 1.73 | 4 | 1.7 | 4 | 1.72 | 6 | 1.712 | 4 |
| | | 1.65 | 5 | 1.66 | 6 | 1.651 | 1.4 |
| 1.57 | 1 | 1.55 | 5 | | | 1.547 | 0.4 |
| 1.48 | 1 | 1.48 | 3 | | | 1.477 | 0.8 |
| 1.4 | 1 | 1.38 | 3 | 1.39 | 2 | 1.381 | 1 |
| | | 1.29 | 2 | | | 1.290 | 0.6 |
| | | 1.19 | 2 | | | 1.1883 | 1.2 |
| | | 1.17 | 1.5 | | | 1.1672 | 0.2 |

For zircon grains D-S 2-3 6-15-06 and D-S 2-3 6-24-06 (Table 57), the Raman spectra (Figs. 238 and 239, respectively) have ~9 bands at wavenumbers that match those of a zircon standard. In these two Raman spectra, the bands that correspond to the bands at wavenumbers 357 and 1009 cm⁻¹ in the zircon standard have shifted to lower frequency wavenumbers, and they are broader and of lower intensity than the bands in

the zircon standard. The Raman spectra do not show any evidence for baddeleyite or reidite. The white opaque zircon grains show similar XRD and micro-Raman spectral characteristics to those of similar zircon grains in Carawine spherule layer sample X38-2 (see section 4.2.2.6) that are interpreted as exhibiting varying degrees of metamictization.



Figure 238: Raman spectra of pinkish white, opaque zircon grain D-S 2-3 6-15-06 (Table 57) from Grænsesø spherule layer sample GL8904-2, and a zircon standard from the RRUFF Raman spectral database.



Figure 239: Raman spectra of pale pink-to-light gray, translucent-to-opaque zircon grain D-S 2-3 6-24-06 (Table 57) from Grænsesø spherule layer sample GL8904-2, and a zircon standard from the RRUFF Raman spectral database.

4.2.8.3 Sample GL8904-3

Subsample 487.8 g was used to characterize Grænsesø spherule layer sample GL8904-3, and the phases were identified by micro-Raman spectroscopy. The heavy mineral grains are described in Appendix Y, and their abundance is shown in Figure 240. For the 63-125 μ m size fraction, rutile (n = 2,062), tourmaline (n = 369), and zircon (n = 486) comprise 70.0%, 12.5%, and 16.5%, respectively, of the total grains (n = 2,945), and the other phases occur in trace amounts.



Figure 240: Heavy mineral abundance for Grænsesø spherule layer sample GL8904-3.

For six white translucent-to-opaque grains, Raman spectra for three of them have bands at wavenumbers that match those of anatase, and Raman spectra for the other three grains have bands at wavenumbers that match those of anatase and K-feldspar. The Kfeldspar is indicated by 3-5 bands at wavenumbers 265/266, 280/287, 473/476, 513/515 (moderate intensity), and 754 cm⁻¹, all of which are present in the Raman spectrum for the K-feldspar (orthoclase) standard shown in Figure 43. A Raman spectrum for a subangular grain that is clear with a very light yellow-green tint has two bands of low intensities at wavenumbers that suggest it is anglesite (Fig. 241). Raman spectra for four of five grains that are similar in appearance to the anglesite grains have bands at wavenumbers that clearly match those of a baryte standard (e.g., Fig. 242).



Figure 241: Raman spectra of a possible anglesite grain from Grænsesø spherule layer sample GL8904-3, and an anglesite standard from the RRUFF Raman spectral database.



Figure 242: Raman spectra of a barite grain from Grænsesø spherule layer sample GL8904-3, and a baryte standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

The chrome spinel, rutile, and tourmaline grains in the 63-125 μ m size fraction of Grænsesø spherule layer sample GL8904-3 went through HF treatment (see Appendix Q) in order to remove the matrix material (e.g., muscovite, quartz) on their surfaces. After the HF treatment, the grains were observed to have little or no remnant matrix material. For two black opaque grains, the Raman spectra are similar, and they have bands at wavenumbers that suggest that the grains are chrome spinel (e.g., Fig. 243).



Figure 243: Raman spectra of a chrome spinel grain from Grænsesø spherule layer sample GL8904-3, and chromite and magnesiochromite standards from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

The Raman spectra for ~12 varicolored grains have bands at wavenumbers that match those of rutile, and the Raman spectrum for one of these grains has additional bands at wavenumbers that match those of quartz. The tourmaline grains were identified on the basis of their physical similarities to the tourmaline grains in Grænsesø spherule layer samples GL8904-1 (see section 4.2.8.1) and GL8904-2 (see section 4.2.8.2). A Raman spectrum for a transparent grain that is clear with a light yellow tint has ~18 bands with wavenumbers and relative intensities that show a good match with a zircon standard (Fig. 244). In contrast, a Raman spectrum for a white, translucent-to-opaque,

prismatic grain has only ~5 poorly-defined bands of very low intensities at wavenumbers that suggest that it is zircon (Fig. 245).



Figure 244: Raman spectra of a transparent zircon grain that is clear with a light yellow tint from Grænsesø spherule layer sample GL8904-3, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 245: Raman spectra of a white, translucent-to-opaque, prismatic zircon grain from Grænsesø spherule layer sample GL8904-3, and a zircon standard from the RRUFF Raman spectral database.

The heavy mineral assemblages of Grænsesø spherule layer samples GL8904-3 and GL8904-1 essentially consist of the same phases. Rutile \pm anatase, tourmaline, and zircon comprise \geq 99% of the grains in the 63-125 µm size fractions. The relative percentages of each of these phases are comparable for the two samples: 70% (GL8904-3) and 71.5% (GL8904-1) for rutile \pm anatase, 12.5% and 13.3% for tourmaline, and 16.5% and 14.5% for zircon. However, the abundance (number of grains per kilogram) of each of these phases in Grænsesø spherule layer sample GL8904-3 is lower by a factor of ~7 to 9 than its abundance in Grænsesø spherule layer sample GL8904-1. For the 125-250 μ m size fraction of Grænsesø spherule layer sample GL8904-3, rutile (n = 77) and tourmaline (n = 25) comprise 70.6% and 22.9%, respectively, of the total grains (n = 109), and the other phases occur in minor-to-trace amounts (Fig. 240). None of the grains underwent HF treatment. A barite grain, three rutile grains, and three zircon grains were identified by matching their Raman spectra with those of baryte, rutile, and zircon standards, respectively.

A Raman spectrum for a dark steel gray grain that has light emerald green matrix material on its surface has three bands at wavenumbers 197, 264, and 701 cm⁻¹ that match those of muscovite (see Fig. 226), and a band at wavenumber 662 cm⁻¹ that is attributed to chrome spinel (see Fig. 243). However, magnetite has a band of strong intensity near wavenumber 662 cm⁻¹ (see Fig. 227), so more work (e.g., XRD, EDX) is needed to fully characterize this grain. The matrix material on the surface of this grain is interpreted as muscovite. The tourmaline grains were identified on the basis of their physical similarities to the tourmaline grains in Grænsesø spherule layer samples GL8904-1 (see section 4.2.8.1) and GL8904-2 (see section 4.2.8.2).

For the 125-250 μ m size fractions of Grænsesø spherule layer samples GL8904-3 and GL8904-1, rutile \pm anatase, tourmaline, and zircon comprise 96.3% and 96.9%, respectively, of the heavy mineral grains. The relative percentages of each of these phases are different for the two samples. The abundances of rutile \pm anatase and tourmaline in Grænsesø spherule layer sample GL8904-3 are lower by factors of 2.3 and 4.9, respectively, than their abundances in Grænsesø spherule layer sample GL8904-1, whereas the zircon abundances are the same for the two samples.

4.2.8.4 Sample GL8904-4

Subsamples 187.9 g and 294.1 g ($\Sigma = 482.0$ g) were used to characterize Grænsesø spherule layer sample GL8904-4, and the phases were identified by micro-Raman spectroscopy. The heavy mineral grains are described in Appendix Y, and their abundance is shown in Figure 246. For the 63-125 µm size fraction, rutile ± anatase (n = 1,335), tourmaline (n = 266), and zircon (n = 219) comprise 70.7%, 14.1%, and 11.6%, respectively, of the total grains (n = 1,889), and the other phases occur in minor-to-trace amounts.



Figure 246: Heavy mineral abundance for Grænsesø spherule layer sample GL8904-4.

For 13 light gray-to-white, translucent-to-opaque grains, the Raman spectra for 10 of them have bands at wavenumbers that match those of anatase, and the Raman spectra for three of them have bands at wavenumbers that match those of anatase and K-feldspar (e.g., Fig. 247). Raman spectra for nine grains that are clear with a very light yellow or yellow-green tint have 1-2 distinct bands at wavenumbers 979/984 and 1051/1055 cm⁻¹ that suggest that the grains are anglesite. Raman spectra for three grains that are similar in appearance to the anglesite grains have bands at wavenumbers that clearly match those of a baryte standard (e.g., Fig. 248).



Figure 247: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from Grænsesø spherule layer sample GL8904-4. Raman spectra of anatase and K-feldspar (orthoclase) standards are shown in Figures 21 and 43, respectively.



Figure 248: Raman spectra of a barite grain from Grænsesø spherule layer sample GL8904-4, and a baryte standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

The chrome spinel, rutile \pm anatase, and tourmaline grains in the 63-125 μ m size fraction of Grænsesø spherule layer sample GL8904-4 went through HF treatment (see Appendix Q) in order to remove the matrix material (e.g., muscovite, quartz) on their surfaces. After the HF treatment, the grains were observed to have little or no remnant matrix material. Raman spectra for four black opaque grains have bands at wavenumbers that match those of chrome spinel, and for three of the grains, the Raman spectra show a fairly good match with a magnesiochromite standard (e.g., Fig. 249). No bands for muscovite or quartz are present on the Raman spectra for the chrome spinel grains.



Figure 249: Raman spectra of a chrome spinel grain from Grænsesø spherule layer sample GL8904-4, and a magnesiochromite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

The Raman spectra for ~125 varicolored grains have bands at wavenumbers that match those of rutile, and for ten of the grains, the Raman spectra have 2-5 additional bands at wavenumbers that match those of anatase. For only one rutile grain, the Raman spectrum has six additional bands at wavenumbers that match those of quartz. Therefore, for the chrome spinel and rutile \pm anatase grains from Grænsesø spherule layer samples GL8904-3 and GL8904-4 that underwent HF treatment, the Raman spectral data show that the HF treatment was efficient in removing matrix phases (e.g., muscovite, quartz)

from the surfaces of the grains. The Raman spectral data support the microscopic observation that these grains have little or no remnant matrix material on their surfaces.

For 18 olive green-to-blue green grains, Raman spectra typically have ~5-12 bands at wavenumbers that show a good match with tourmaline (e.g., Fig. 250).



Figure 250: Raman spectra of a tourmaline grain from Grænsesø spherule layer sample GL8904-4, and a dravite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Raman spectra for ~57 grains that are typically pink, champagne, or clear with a light yellow tint have bands at wavenumbers that match those of zircon. Many of the zircon grains are transparent, and their Raman spectra typically have ~6-13 bands (e.g., Fig. 251). About 10% of the zircon grains in the 63-125 μ m size fraction are light grayish yellow-to-light grayish white, and opaque ("white opaque"), and their Raman spectra typically have ≤8 bands (e.g., Fig. 252). For the white opaque zircon grains, the bands are typically broader than the bands for the transparent zircon grains (cf., Figs. 251 and 252). Furthermore, the bands at wavenumbers 350/355 and 999/1006 cm⁻¹ in the Raman spectra for the transparent zircon grains shift to lower frequency wavenumbers (347/349 and 995/998 cm⁻¹, respectively) in the Raman spectra for the white opaque zircon grains.

The broadening of the bands and the shift of some of the bands to lower frequency wavenumbers are features that have been observed in the Raman spectra for metamict zircons (Nasdala et al., 1995). For two white opaque grains that appear to be zircons on the basis of their color and prismatic habit, the Raman spectra show no distinct bands (e.g., Fig. 253). None of the Raman spectra for the ~57 zircon grains show any evidence for baddeleyite or reidite.



Figure 251: Raman spectra of a pink transparent zircon grain from Grænsesø spherule layer sample GL8904-4, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 252: Raman spectra of a light grayish white, opaque zircon grain from Grænsesø spherule layer sample GL8904-4, and a zircon standard from the RRUFF Raman spectral database.



Figure 253: Raman spectra of a light grayish yellow, opaque, prismatic zircon grain from Grænsesø spherule layer sample GL8904-4, and a zircon standard from the RRUFF Raman spectral database.

For the 125-250 μ m size fraction, anatase ± K-feldspar (n = 14), rutile ± anatase (n = 53) and tourmaline (n = 23) comprise 14.6%, 55.2%, and 23.9%, respectively, of the total grains (n = 96), and anglesite (n = 2), barite (n = 2), and zircon (n = 2) are minor components (Fig. 246). Five anatase ± K-feldspar grains, two barite grains, five rutile ± anatase grains, one tourmaline grain, and two zircon grains were identified by matching their Raman spectra with those of anatase (± K-feldspar), baryte, rutile (± anatase), tourmaline, and zircon standards, respectively. For two grains that are clear with a very light yellow-to-yellow-green tint, the Raman spectra have 1-2 bands at wavenumbers

981/984 and 1054 cm⁻¹ that suggest that the grains are anglesite. There are no white opaque zircon grains.

The locations of the four Grænsesø spherule layer samples in the outcrop are shown in Figure 16 (see section 2.4). Samples GL8904-1, GL8904-2, GL8904-3, and GL8904-4 (in ascending stratigraphic position) show that the Grænsesø spherule layer has a very similar heavy mineral assemblage from its lower part (GL8904-1) to its upper part (GL8904-4). In the four samples, each of the phases shows similar physical characteristics (e.g, colors, roundness).

Grænsesø spherule layer samples GL8904-1, GL8904-3, and GL8904-4 together contain a total of ~22,812 heavy mineral grains in the 63-250 μ m size fraction, and ~22,383 of these grains (~98.1%) are in the 63-125 μ m size fraction. Rutile \pm anatase, tourmaline, and zircon together comprise ~96-99% of these ~22,383 grains. The relative percentages of each of the three major phases are comparable for the three samples: 70-71.5% for rutile \pm anatase, 12.5-14.1% for tourmaline, and 11.6-16.5% for zircon. However, the abundance (number of grains per kilogram) of each of these three phases shows a large decrease from the lower (sample GL8904-1) to middle (sample GL8904-3) parts of the Grænsesø spherule layer, and a much smaller decrease by a factor of ~1.4-2 from the middle to the upper (sample GL8904-4) parts of the Grænsesø spherule layer. For these three Grænsesø spherule layer samples combined, ~1.9% and ~3.3% of the estimated total number of rutile \pm anatase and zircon grains, respectively, were analyzed by micro-Raman spectroscopy. None of the Raman spectra for the rutile \pm anatase grains show any evidence for the TiO₂ II phase, and none of the Raman spectra for the zircon grains show any evidence for baddeleyite or reidite.

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4.2.9 Grænsesø Context Samples

4.2.9.1 Sample SP3

Sample SP3 was collected a few meters stratigraphically below the Grænsesø spherule layer (Table 8). Subsample 155.0 g was used to characterize Grænsesø context sample SP3, and the phases were identified by micro-Raman spectroscopy. The heavy mineral grains are described in Appendix Z, and their abundance is shown in Figure 254. For the 63-125 μ m size fraction, rutile + tourmaline grains (n = 225) comprise 95.3% of the total grains (n = 236). Tourmaline (n = 5) is a minor component, and the other phases occur in trace amounts.



Figure 254: Heavy mineral abundance for Grænsesø context sample SP3. The sample was collected a few meters stratigraphically below the Grænsesø spherule layer.

Unlike the grains in the Grænsesø spherule layer samples whose Raman spectra suggest that they are anglesite (e.g., Fig. 241), a Raman spectrum for a similar-looking transparent grain that is clear with a very light green tint shows a good match with an anglesite standard (Fig. 255).



Figure 255: Raman spectra of an anglesite grain from Grænsesø context sample SP3, and an anglesite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected a few meters stratigraphically below the Grænsesø spherule layer.

A Raman spectrum for a black opaque grain that exhibits remnant facets shows a very good match with a magnetite standard (Fig. 256). Raman spectra for two grayish grains have bands at wavenumbers that clearly match those of a rutile standard (e.g., Fig. 257).



Figure 256: Raman spectra of a magnetite grain from Grænsesø context sample SP3, and a magnetite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected a few meters stratigraphically below the Grænsesø spherule layer.



Figure 257: Raman spectra of a rutile grain from Grænsesø context sample SP3, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected a few meters stratigraphically below the Grænsesø spherule layer.

The bulk of the heavy mineral assemblage consists of very light olive gray-tobeige grains that have a different appearance than the two grayish rutile grains or the five (light) olive green tourmaline grains (see below). Raman spectra were obtained for nine of these very light olive gray-to-beige grains. For two of these grains, the Raman spectra have bands at wavenumbers that match those of rutile, whereas for another two of these grains, the Raman spectra have bands at wavenumbers that match those of tourmaline. For five of these grains, the Raman spectra clearly have the two bands of strong intensities at wavenumbers that match those of a rutile standard, and ~10-12 bands at wavenumbers that match those of a tourmaline standard (e.g., Fig. 258). These grains exhibit a very fine-grained polycrystalline texture, and the two phases can not be distinguished from each other. Grains of this type were not observed in the Grænsesø spherule layer samples, or in Grænsesø context sample GL8904-6 (see below, section 4.2.9.2) that was collected <1 m stratigraphically above the Grænsesø spherule layer (see Table 8).



Figure 258: Raman spectra of a rutile (R) + tourmaline (T) grain from Grænsesø context sample SP3, and rutile and tourmaline standards from the RRUFF Raman spectral database. The sample was collected a few meters stratigraphically below the Grænsesø spherule layer.

Raman spectra for two of five light olive green-to-olive green grains are similar to each other, and they show a fairly good match with a tournaline standard. For one of these grains, the Raman spectrum (Fig. 259) has a band at wavenumber 464 cm⁻¹ that may represent the band of strongest intensity for quartz, and a band at wavenumber 964 cm⁻¹ that may correlate with the band at wavenumber 973 cm⁻¹ in the tournaline standard. Several of the tournaline grains have colorless matrix material on their surfaces, and the band at wavenumber 464 cm⁻¹ suggests that the matrix material is quartz. The tournaline grains are typically subangular, whereas the tournaline grains in the Grænsesø spherule layer samples are typically subrounded or well-rounded.



Figure 259: Raman spectra of a tourmaline grain from Grænsesø context sample SP3, and a tourmaline standard from the RRUFF Raman spectral database. The band at wavenumber 464 cm⁻¹ may represent the band of strongest intensity for quartz (Q). A Raman spectrum of a quartz standard is shown in Figure 41. No baseline correction was made for the sample spectrum. The sample was collected a few meters stratigraphically below the Grænsesø spherule layer.

A Raman spectrum for one of two pink transparent grains shows a very good match with a zircon standard (Fig. 260). The zircon grains are very similar in appearance to many of those in the Grænsesø spherule layer samples.



Figure 260: Raman spectra of a pink transparent zircon grain from Grænsesø context sample SP3, and a zircon standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected a few meters stratigraphically below the Grænsesø spherule layer.

The 125-250 μ m size fraction consists of 42 grains that are similar in appearance to the rutile + tourmaline grains (see above), and a black opaque grain that was not analyzed. The black opaque grain is reported as "Unidentified" (see Fig. 254). For Grænsesø context sample SP3, Raman spectra were obtained for nine rutile ± tourmaline grains, and none of the Raman spectra show any evidence for the TiO₂ II phase. There are no white opaque zircon grains.

4.2.9.2 Sample GL8904-6

Sample GL8904-6 was collected <1 m stratigraphically above the Grænsesø spherule layer (Table 8). Subsample 321.1 g was used to characterize Grænsesø context sample GL8904-6, and the phases were identified by XRD and/or micro-Raman spectroscopy. For the 63-125 μ m size fraction, there are ~1,265 dark reddish brown and ochre grains of secondary iron oxide/oxyhydroxide. These grains typically consist of pseudomorphs of aggregates of cubic crystals. XRD patterns for two of these grains have no discernible lines. A Raman spectrum for another one of these grains has no distinct bands. A Raman spectrum for the colorless vitreous matrix material on the surface of this grain has bands at wavenumbers 154, 280, 476, and 513 (strong) cm⁻¹. These four bands match bands of moderate-to-very strong intensities that are present in the orthoclase (K-feldspar) standard that is shown in Figure 43.

There are 18 brassy grains with a metallic luster, and they appear to consist of aggregates of pyrite crystals. An XRD pattern for a brassy grain contains lines that match those for pyrite (Table 58), and there is an unindexed line of weak intensity at d = 2.1 Å. A Raman spectrum for this grain shows a very good match with a pyrite standard (Fig. 261). Therefore, the secondary iron oxide/oxyhydroxide grains appear to largely consist of pseudomorphs after pyrite.

Table 58:XRD data for a pyrite grain from Grænsesø context sample GL8904-6 and a
pyrite standard. The sample was collected <1 m stratigraphically above the
Grænsesø spherule layer.

| Grain D-S 2 9-4- | ID: 2-3 06 | Pyrite 6-0710 | | |
|------------------------|------------------|------------------|------------------|--|
| d (Å) | I/I _o | d (Å) | I/I _o | |
| 3.3 | 7 | 3.128 | 3.5 | |
| 2.68 | 10 | 2.709 | 8.5 | |
| 2.4 | 10 | 2.423 | 6.5 | |
| 2.2 | 7 | 2.2118 | 5 | |
| 2.1 | 1 | | | |
| 1.9 | 9 | 1.9155 | 4 | |
| 1.63 | 9.5 | 1.6332 | 10 | |
| 1.56 | 5 | 1.5640 | 1.4 | |
| | | 1.5025 | 2 | |
| 1.44 | 3.5 | 1.4448 | 2.5 | |
| 1.24 | 1 | 1.2427 | 1.2 | |
| 1.21 | 1 | 1.2113 | 1.4 | |
| 1.18 | 1 | 1.1823 | 0.8 | |
| | | 1.1548 | 0.6 | |
| 1.1 | 1.5 | 1.1057 | 0.6 | |
| 1.03 | 2 | 1.0427 | 2.5 | |



Figure 261: Raman spectra of pyrite grain D-S 2-3 9-4-06 (Table 58) from Grænsesø context sample GL8904-6, and a pyrite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.

Grains that did not appear to be secondary iron oxide/oxyhydroxide phases or pyrite were handpicked from the heavy mineral separate. The heavy mineral grains are described in Appendix Z, and their abundance is shown in Figure 262. For the 63-125 μ m size fraction, rutile ± anatase (n = 40) comprises 76.9% of the total grains (n = 52), and anatase ± K-feldspar (n = 2), chrome spinel (n = 3), tourmaline (n = 5), and zircon (n = 2) are minor phases.



Figure 262: Heavy mineral abundance for Grænsesø context sample GL8904-6. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.

For two beige grains, the Raman spectrum for one of them has bands at wavenumbers that match those of anatase, and the Raman spectrum for the other grain has bands at wavenumbers that match those of anatase and K-feldspar (Fig. 263). There are three medium dark gray opaque grains that have colorless-to-light green matrix material on their surfaces. For one of these grains, the Raman spectrum has bands at wavenumbers that match those of a muscovite standard (Fig. 264). For the other two grains, Raman spectra have 2-7 bands at wavenumbers 192/195, 264/265, 417, 633, 703, 756, and 900 cm⁻¹ that match those of muscovite, and two bands at wavenumbers 550/559 and 671/686 cm⁻¹ that are attributed to chrome spinel (e.g., Fig. 265). These three grains are similar in appearance to the chrome spinel grains with muscovite matrix material on their surfaces that are present in Grænsesø spherule layer sample GL8904-1 (see section 4.2.8.1).



Figure 263: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from Grænsesø context sample GL8904-6. Raman spectra of anatase and K-feldspar (orthoclase) standards are shown in Figures 21 and 43, respectively. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.



Figure 264: Raman spectra of muscovite matrix material on the surface of a medium dark gray opaque grain (probably chrome spinel, see above) from Grænsesø context sample GL8904-6, and a muscovite standard from the RRUFF Raman spectral database. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.


Figure 265: Raman spectra of a chrome spinel (Chr) grain with muscovite (M) matrix material on its surface from Grænsesø context sample GL8904-6, and magnesiochromite and muscovite standards from the RRUFF Raman spectral database. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.

For 23 opaque grains that are various shades of gray and buff, the Raman spectra for 21 of them have bands at wavenumbers that match those of rutile, and the Raman spectra for the other two of these 23 grains have bands at wavenumbers that match those of rutile + anatase \pm quartz. Many of the rutile grains are observed to have a colorless, vitreous matrix material on their surfaces, and for five of these grains, the Raman spectra for the matrix material have bands at wavenumbers that clearly match those of albite. An XRD pattern for an olive green grain contains lines that show a good match with those for dravite (Table 59); however, a line of moderate intensity at d = 4.22 Å in the dravite standard was not observed in the pattern for the grain (Table 59). Raman spectra for three of four other olive-to-dark olive green grains have ~4-12 bands at wavenumbers that match those of tourmaline (e.g., Fig. 266).

Table 59: XRD data for a tourmaline grain from Grænsesø context sample GL8904-6, and dravite and ferrian dravite standards. Lines with intensities ≤1.6 in the standards that were not observed in the pattern for the grain are not listed in the table. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.

| Grain G 1- 9-4- | ID: -3 06 | Drav 14-7 | rite 76 | Dravite, 1 19-13 | ferrian 72 |
|-----------------------|------------------|--------------|------------------|---------------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 6.4 | 3 | 6.38 | 3 | 6.44 | 6 |
| | | 4.98 | 2.5 | 5.01 | 4 |
| | | | | 4.62 | 4 |
| 4.58 | 3 | 4.60 | 1.8 | | |
| | | 4.22 | 6.5 | 4.25 | 9 |
| 4.0 | 6 | 3.99 | 8.5 | 4.00 | 9 |
| | | | | 3.51 | 9 |
| 3.49 | 10 | 3.48 | 6 | | |
| | | | | 2.979 | 9 |
| 2.96 | 9.5 | 2.961 | 8.5 | | |
| 2.59 | 10 | 2.576 | 10 | 2.586 | 10 |
| | | 2.396 | 2 | | |

Table 59: continued

| Grain G 1- 9-4- | ID: -3 06 | Drav 14-7 | rite 76 | Dravite, 19-13 | ferrian 72 |
|-----------------------|------------------|--------------|------------------|----------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o | d (Å) | I/I _o |
| 2.38 | 2 | 2.376 | 2 | | |
| | | 2.342 | 2 | | |
| | | 2.189 | 1.8 | | |
| 2.13 | 2 | 2.127 | 1.6 | | |
| | | 2.054 | 2 | 2.052 | 3 |
| 2.04 | 2 | 2.040 | 4.5 | | |
| | | | | 1.932 | 2 |
| 1.92 | 2 | 1.920 | 3.5 | | |



Figure 266: Raman spectra of a tourmaline grain from Grænsesø context sample GL8904-6, and a dravite standard from the RRUFF Raman spectral database. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.

XRD patterns for two pink transparent grains contain lines that match those for zircon, and the data for one of the grains are given in Table 60. The D-S patterns for the two grains show dots. A Raman spectrum (Fig. 267) for grain D-S 2-3 9-3-06 (Table 60) has bands at wavenumbers that match those of a zircon standard, so the Raman spectral data confirm the XRD identification of this grain.

Table 60:XRD data for a zircon grain from Grænsesø context sample GL8904-6 and
a zircon standard. Lines with intensities ≤ 1.2 in the standard that were not
observed in the pattern for the grain are not listed in the table. The sample
was collected <1 m stratigraphically above the Grænsesø spherule layer.

| Grain D-S 2 9-3-0 | ID: 2-3 06 | Zirco 6-02 | on 66 |
|-------------------------|------------------|---------------|------------------|
| d (Å) | I/I _o | d (Å) | I/I _o |
| 4.45 | 4 | 4.43 | 4.5 |
| 3.3 | 10 | 3.30 | 10 |
| 2.55 | 6 | 2.518 | 4.5 |
| 2.36 | 3 | 2.336 | 1 |
| 2.22 | 2 | 2.217 | 0.8 |
| 2.07 | 2 | 2.066 | 2 |
| 1.91 | 1 | 1.908 | 1.4 |
| | | 1.712 | 4 |
| 1.66 | 4 | 1.651 | 1.4 |
| 1.48 | 1 | 1.477 | 0.8 |
| 1.38 | 1 | 1.381 | 1 |



Figure 267: Raman spectra of pink transparent zircon grain D-S 2-3 9-3-06 (Table 60) from Grænsesø context sample GL8904-6, and a zircon standard from the RRUFF Raman spectral database. There is an unindexed (U) band at wavenumber 163 cm⁻¹. The sample was collected <1 m stratigraphically above the Grænsesø spherule layer.

For the 125-250 μ m size fraction, there are 58 grains of secondary iron oxide/oxyhydroxide that resemble those in the 63-125 μ m size fraction, and there is one brassy, subangular grain with an irregular shape. This brassy grain appears to consist of an aggregate of very small cubic crystals, and this grain appears to be secondary pyrite. Therefore, the 125-250 μ m size fraction does not appear to contain any primary detrital heavy mineral grains. For Grænsesø context sample GL8904-6 that was collected <1 m stratigraphically above the Grænsesø spherule layer, Raman spectra were obtained for 23 (~58%) of the estimated total number (n = 40) of rutile ± anatase grains, and none of the Raman spectra show any evidence for the TiO₂ II phase. There are no white opaque zircon grains, but only two zircon grains were identified in Grænsesø context sample GL8904-6.

4.2.10 Quartz, Feldspar, and Gypsum Grains in Heavy Mineral Fractions

During the course of identifying the phases in the heavy mineral fractions by micro-Raman spectroscopy, 177 quartz \pm K-feldspar grains, 73 K-feldspar grains, 11 albite grains, and three gypsum grains were identified in 21, 13, 5, and 2 samples, respectively. The Raman spectra for the quartz grains typically have ~4-11 bands, and a good Raman spectrum for one of the quartz grains is shown in Figure 268. None of the Raman spectra for the quartz grains show any evidence for coesite or stishovite. The Raman spectra for the K-feldspar grains have ~3-17 bands. A good Raman spectrum for a K-feldspar grain is shown in Figure 269.



Figure 268: Raman spectra of a quartz grain from Monteville context sample II67-1B, and a quartz standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~20 cm stratigraphically above the Monteville spherule layer.



Figure 269: Raman spectra of a K-feldspar grain from Monteville context sample T149-1, and a microcline (K-feldspar) standard from the RRUFF Raman spectral database. The sample was collected ~1 m stratigraphically below the Monteville spherule layer.

The Raman spectra for the albite grains have ~4-16 bands (e.g., see Fig. 229). None of the Raman spectra for the feldspar grains show any evidence for the highpressure phases of NaAlSi₃O₈-hollandite or KAlSi₃O₈-hollandite (see discussion of these phases in Gillet et al., 2000; Kimura et al., 2003). For two white opaque grains in Carawine spherule layer sample W85-2, and one grain that is clear with a light yellow tint in Monteville context sample T149-1, the Raman spectra have ~4-7 bands at wavenumbers that clearly match those of a gypsum standard (e.g., Fig. 270). For these three grains, all the bands on the Raman spectra can be indexed to the gypsum standard.



Figure 270: Raman spectra of a gypsum grain from Monteville context sample T149-1, and a gypsum standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The sample was collected ~1 m stratigraphically below the Monteville spherule layer.

4.3 Light Fractions

The following petrographic description is taken primarily from Glass et al. (2007). The grain count values are updated, and the U-stage microscope results are reported herein for the first time. About 18,127 grains were counted in the 11 grain mounts that consist of grains from the 63-125 μ m-sized light fractions of Carawine spherule layer sample 43-1. Most of the grains are chert fragments, but sand-sized quartz grains (n ~875) comprise ~4.8% of the total number of grains.

About 20% of the quartz grains may be of authigenic origin, and no planar microstructures were observed in these grains. About 80% of the quartz grains are subrounded to angular, and they are typically cloudy or "dirty" in appearance. Fourteen of these quartz grains each contain 1-3 sets of planar microstructures. Therefore, planar microstructures were observed in ~1.6% of the quartz grains.

Eleven of these 14 quartz grains are subangular to angular. The planar microstructures are faint-to-very faint, and none of the sets were observed to traverse an entire grain. The planar microstructures are typically straight and parallel, although a few are slightly curved. The planar microstructures are $<1 \mu$ m in width, and they have a spacing of \sim 2-8 μ m.

Seven sets of planar microstructures in three quartz grains were measured with the U-stage microscope (Table 61). Five sets were indexed to rational crystallographic planes having orientations that are commonly observed for shock-induced planar deformation features (PDFs; see von Engelhardt and Bertsch, 1969; Stöffler and Langenhorst, 1994). Two of the three sets of planar microstructures in grain #1 (Table 61) are visible in Figure 271. For grain #1 (Table 61), there is some uncertainty in the measurement of the orientation of the c-axis. For grain #3 (Table 61), the set of planes parallel to $\{10\overline{1}1\}$ may be planar fractures (B. M. French, personal communication, 2009). The $\{10\overline{1}1\}$

crystallographic orientation is common for planar fractures (see Stöffler and Langenhorst, 1994; Ferrière et al., 2009).

Table 61:Polar angles determined by the U-stage microscope and crystallographic
orientations of seven sets of planar microstructures in three quartz grains
from Carawine spherule layer sample 43-1.

| Grain number | Subsample/ Slide number | Set number | Polar angle (°) ¹ | Crystallographic orientation ² |
|-----------------|----------------------------|---------------|------------------------------|---|
| 1 | 987.4 g Groups A-D/1 | 1 | 60 | Possibly s {1121} |
| | | 2 | 24 | ω {1013} |
| | | 3 | 11 | Unindexed |
| 2 | 1078.1 g/1 | 1 | 39 | Unindexed |
| | | 2 | 21 | ω {1013} |
| 3 | 1136.4 g | 1 | 52 | {1011} |
| | | 2 | 24 | ω {1013} |

¹Angle between the pole to a set of planar microstructures and the c-axis (optic axis) of the quartz grain; ²See Stöffler and Langenhorst (1994).



Figure 271: Photomicrograph with cross-polarized light of quartz grain #1 (Table 61) from Carawine spherule layer sample 43-1. Two sets of planar microstructures are visible, and their crystallographic orientations, as well as the orientation of the c-axis (c) of the quartz grain, are indicated on the figure. The grain is ~100 by 290 µm in size.

For a grain mount that contains grains from the 125-250 μ m-sized light fraction of subsample 1078.1 g of Carawine spherule layer sample 43-1 (Appendix I), quartz grains (n = 54) comprise ~8.1% of the estimated 663 grains, and no planar microstructures were observed in any of the quartz grains (B. P. Glass, personal communication, 2007). SEM analysis of 155 grains from the 63-125 μ m-sized light fraction of subsample 987.4 g Group D of Carawine spherule layer sample 43-1 (Appendix I) that were etched in HF (Appendix Q) revealed no evidence of planar microstructures in any of the grains. However, on the basis of the results for the 12 grain mounts (see above) from this same sample (43-1), most of the grains examined by SEM are probably chert fragments.

Chapter 5

DISCUSSION

5.1 Acid-Insoluble Weights

The acid-insoluble weight data accord well with the individual hand sample descriptions (Appendices A-H), and confirm that all the samples have a significant (~33-53 wt%)-to-high (>67 wt%) carbonate component (Table 10). Most of the context samples or layers contain <13 wt% acid-insoluble material (Table 10). The context samples or layers are fine-grained and several of them are laminated, and sand-to-gravelsized material was not observed in most of them. The context samples from the Carawine Dolomite and Monteville Formation, Bee Gorge context sample 92058, and the two context layers in Bee Gorge sample BB are fine-grained and typically laminated, and for each of these samples or layers, >85 wt% of the acid-insoluble material is in the <63 μ m size fraction (Table 10). In contrast, the context samples from the Grænsesø Formation have lower values of weight percent acid-insoluble material in the $<63 \mu m$ size fraction that probably reflect the presence of coarser-grained materials, e.g., quartz veinlets and/or mm-to-cm-sized secondary cherty masses (Appendix H). For Bee Gorge samples 96714A and 96714B, the basal carbonate lutite (Bcl) context layers have high values (\geq 59 wt%) of acid-insoluble material (Table 10) that are probably due to a high content of finegrained (<63 µm) siliciclastic material. Therefore, the acid-insoluble weight data for the context samples and layers accord well with the interpretation that these fine-grained, carbonate-rich rocks were deposited below storm wave base in low-energy, deep-shelf

and basinal marine environments (see Hassler et al., 2000, 2005; Hassler and Simonson, 2001; Chadwick et al., 2001).

As expected, the acid-insoluble weight data are in agreement with the fact that the spherule layers usually contain several components that are coarser-grained than those that generally occur in the context layers (e.g., Simonson and Glass, 2004). For example, five of the six Carawine spherule layer samples, the spherule layer (BB (sl)) in Bee Gorge sample BB, Monteville spherule layer sample U63-1, and the four Grænsesø spherule layer samples have \geq 53 wt% of acid-insoluble material in the \geq 250 µm size fractions (Table 10). The Carawine spherule layer samples well illustrate that the values of weight percent acid-insoluble material primarily reflect the amounts of melt particles (spherules and irregular melt particles), chert, shale/argillite, and ferruginous clasts, and siliciclastic sand-sized grains. Carawine spherule layer samples 84-1, W85-2, and X24-1 are from the lower part of the lowermost clast-bearing debris-flow deposit in the Ripon Hills area (see Fig. 4), and Hassler et al. (2005) reported that the largest irregular melt particles, up to 2 cm long, occur in the basal 2.5 m of this lowermost debris-flow deposit of the Carawine spherule layer. These three samples have the highest values of weight percent acid-insoluble material of the six Carawine spherule layer samples (Table 10), and the melt particles in the $>250 \,\mu\text{m}$ size fractions of Carawine spherule layer samples W85-2 and X24-1 comprise ~31 wt% and ~36 wt% (Appendix I), respectively, of the total acidinsoluble material in the samples (Table 10).

Carawine spherule layer sample 43-1 is from the finer-grained, spherule-poor, sandy upper part of the lowermost debris-flow deposit, and Carawine spherule layer samples 42-1A and X38-2 are from the upper sandy parts of the dolomixtite (Table 4; Appendix A). For Carawine spherule layer samples 43-1, 42-1A, and X38-2, melt

particles in the >250 μ m size fractions comprise ~5-10 wt% of the total acid-insoluble material in the samples (Appendix I; Table 10). Sand-sized siliciclastic grains were observed in Carawine spherule layer sample X38-2 (Appendix A), and compared to the other Carawine spherule layer samples, sample X38-2 has the highest proportion by far of acid-insoluble material in the 63-250 μ m size fraction (Table 10). Carawine spherule layer samples 43-1, 42-1A, and X38-2 have lower values of weight percent acid-insoluble material than Carawine spherule layer samples 84-1, W85-2, and X24-1 (Table 10), and these results appear to reflect the higher contents of melt particles in the samples from the lower part of the Carawine spherule layer. Overall, the acid-insoluble weight data for the six Carawine spherule layer samples accord well with the hand sample descriptions (Appendix A), and with the description of the Carawine spherule layer as given by Hassler et al. (2005).

Monteville spherule layer samples U63-1 and V111 have values of weight percent acid-insoluble material that also accord well with the hand sample descriptions (Appendix E). Sample U63-1 from the lower part of the Monteville spherule layer contains ferruginous clasts and spherules, and it has a higher value of weight percent acid-insoluble material than sample V111 (Table 10). Furthermore, for Monteville spherule layer sample U63-1, ~60 wt% of the acid-insoluble material is in the >250 μ m size fraction (Table 10), consistent with this sample containing ferruginous clasts and spherules. Sample V111 is from the upper sandy part of the Monteville spherule layer, and no clasts, spherules, irregular melt particles, or siliciclastic grains were observed in hand sample (Appendix E).

Simonson et al. (1999) noted that the amount of fine-grained material in the lower part of the Monteville spherule layer at the Monteville farm locality (Fig. 5) was difficult

to determine due to the abundance of secondary carbonate material. Monteville spherule layer sample U63-1 contains 18.2 wt% acid-insoluble material, and 35 wt% of this material is in the <63 μ m size fraction (Table 10). Therefore, these data suggest that finegrained (<63 μ m), acid-insoluble material comprises ~6 wt% of the lower part of the Monteville spherule layer at the Monteville farm locality, a value that is higher than those for the <63 μ m size fractions of the Carawine spherule layer samples (Table 10).

Hand sample descriptions (Appendix C) of Jeerinah spherule layer samples W94-1Q and X21-1 suggested that they should have higher values of weight percent acid-insoluble material than the Carawine spherule layer samples. The acid-insoluble weight data (Table 10) confirm this hypothesis, but the data show that samples W94-1Q and X21-1 contain a significant (~33-47 wt%) carbonate component that is apparently masked by the ferruginous matrix material. The carbonate component was removed by acid digestion only after most of the sample material had been crushed below 250 µm (Appendix K).

Bee Gorge samples 96714A and 96714B do not contain clasts or veinlets (Appendix D). For each of the samples, the values of weight percent acid-insoluble material for the spherule layer and the immediately underlying basal carbonate lutite (Bcl) context layer show a different relationship than that shown by the six Carawine, one of the Monteville (U63-1), and four Grænsesø spherule layer samples and their respective context samples (Table 10). For each of the samples 96714A and 96714B, the value of weight percent acid-insoluble material for the spherule-bearing lutite sublayer (Splsl; ~10-15 vol% spherules; Appendix D) is roughly comparable to that for the basal carbonate lutite (Bcl) context layer, whereas the lowermost spherule-rich sublayer (Lspsl; ~40-50 vol% spherules; Appendix D) and the upper spherule/lutite sublayers subdivision

(Usplsl; ~8 vol% spherules; Appendix D) have smaller values of weight percent acidinsoluble material than the underlying basal carbonate lutite (Bcl) context layer (Table 10). Furthermore, even though silt-to-very fine sand-sized grains (apparently siliciclastic) are visible in the upper spherule/lutite sublayers subdivision (Usplsl) in each of the two hand samples (Appendix D), this subdivision still has a lower value of weight percent acid-insoluble material than the basal carbonate lutite (Bcl) context layer (Table 10). For each of the samples 96714A and 96714B, these results can be explained if the spherulebearing lutite sublayer (Splsl) and the basal carbonate lutite (Bcl) context layer have higher contents of siliciclastic fine-grained material than do the lowermost spherule-rich sublayer (Lspsl) and the upper spherule/lutite sublayers subdivision (Usplsl). For each of the samples 96714A and 96714B, the values of weight percent acid-insoluble material for the three subdivisions (Lspsl, Splsl, and Usplsl) of the spherule layer are in accordance with the hand sample descriptions (Appendix D) that suggest that the spherule layer (~1.3-2.1 cm thick) was formed by more than one depositional event (see section 5.2.4).

In Bee Gorge sample BB, the value of acid-insoluble material for the spherule layer (BB (sl)) is higher than those for the adjoining context layers (BB (#1) and BB (#2)), and it is also higher than that for Bee Gorge context sample 92058 (Table 10). For the spherule layer (BB (sl)) in sample BB, 53 wt% and ~25 wt% of the acid-insoluble material are in the >250 μ m and <63 μ m size fractions, respectively (Table 10). The acid-insoluble weight data are consistent with the hand sample description that shows that the spherule layer (BB (sl)) in sample BB has >50 vol% spherules in a fine-grained matrix (Appendix D).

The four Grænsesø spherule layer samples have comparable values of weight percent acid-insoluble material; interestingly, the values for the lowermost (GL8904-1)

and uppermost (GL8904-4) spherule layer samples are equal (Table 10). These data accord well with the hand sample descriptions (Appendix G) and the field observations that show that the sampled interval of the Grænsesø spherule layer consists of a massive dolomixtite that is lithologically homogeneous to a first approximation. The acidinsoluble weight data are consistent with the hypothesis (see section 5.5) that the sampled interval of the Grænsesø spherule layer represents a single depositional event. The sampled interval of the Grænsesø spherule layer thus contrasts with those of the Carawine and Monteville spherule layers that consist of one or more distinctive, finingupward sequences (see Hassler et al., 2005; Simonson et al., 1999).

5.2 Heavy Mineral Assemblages

5.2.1 Heavy Mineral Summaries

For 23 of the 25 samples, summaries of the heavy mineral phases and their abundance for the 63-125 μ m size fraction are given in Tables 62 and 63. Bee Gorge context sample 92058 and Grænsesø spherule layer sample GL8904-2 are not included in Tables 62 and 63 since grain counts were not done for these samples (see sections 4.2.5.5 and 4.2.8.2). The 63-125 μ m size fraction was chosen since most of the recovered heavy mineral grains are in this size fraction. In Table 62, heavy mineral abundance is given in number of grains/kg, and in Table 63, the heavy mineral assemblage is given in number percent for the same weight of a given sample, layer, sublayer, or sublayers subdivision that is reported in Table 62.

A given weight (g) reported in Table 62 may differ from its respective weight that is reported in Table 10 and/or Table 11 for the following reasons. For a given sample, layer, sublayer, or sublayers subdivision, its total processed weight is given in Table 10, whereas in Table 11, the reported weight includes only subsamples that have positive derived weights for the heavy mineral fraction, or for which the weight of the heavy mineral fraction was directly measured. In Table 62, a weight refers to a subsample(s) that was (were) grain counted after its (their) grains were identified. The weights reported in Table 62 are the same as those reported in the column graphs (see Chapter 4), and they are reported to one, two, or four decimal places (see discussion in section 4.1).

For a given sample, layer, sublayer, or sublayers subdivision in Table 62, the value for weight percent acid-insoluble fraction refers to the subsample(s) whose weight(s) is (are) reported in the table, and this value may be the same as, less than, or greater than the respective value as reported in Table 10. The values for "Percent Spherules" in Table 62 are visual estimates (vol%) made from the hand samples (see Appendices A-H), and they include the percentages for the irregular melt particles that were observed in the six Carawine and two Jeerinah spherule layer samples. The values for "Percent Spherules" and the total number of heavy mineral grains/kg that are given in Table 62 are repeated in Table 63.

| Table 62: | Summary of heavy mineral assemblage and abundance (number of grains/kg) for spherule layer and |
|-----------|--|
| | context samples. |

| | | | | | H | Ieav | y Miner | al A | bund | ance | (Nu | mber | of g | rains | kg) it | the 63 | -125 µ | m Si | ze Fra | iction | 1 | |
|--|---|--|---------------------------|--------------------------------------|------------|-----------|----------|-----------|--------|----------|----------|---------------|---------------|--------------------|----------|---------|------------|----------|--------|--------------|-------|-------|
| Sample Number/ Layer/ Sublayer(s) | WL. (g) | Wt.% Acid- Insoluble Fraction | Percent Sphe- rules | No. of Heavy Mineral Grains | Actinolite | Almandine | Anatase | Anglesite | Banite | Brookite | Chlorite | Chrome Spinel | Clinopyroxene | Clinozo/Epidote | Monazite | Rutile* | Tourmaline | Xenotime | Zircon | Unidentified | Total | Notes |
| | | | | | Cara | wine | Spheru | le La | ayer | Samp | les | | | | | | | | | | | |
| X38-2 | 229.4 | 7.0 | <1 | 1667 | 13 | | 4660 | 17 | | 4 | | 248 | | 4 | | 1290 | 157 | | 872 | | 7265 | |
| 42-1A | 557.5 | 7.5 | <10 | 585 | | | 927 | | | | | 14 | | | | 54 | 2 | | 52 | | 1049 | |
| 43-1 | 5151.7 | 4.5 | 2-3 | 720 | 0.2 | | 126 | | | 0.2 | | 1 | | | | 3.2 | | | 9 | 0.2 | 140 | 1 |
| X24-1 | 1472.6 | 9.4 | <5 | 547 | 5 | 1 | 325 | | | | | 1 | 1 | 11 | | 10 | 5 | | 14 | | 373 | |
| W85-2 | 649.4 | 9.9 | ~5 | 160 | 17 | 3 | 211 | 8 | | | | 2 | | | | 2 | 2 | | 3 | | 248 | |
| 84-1 | W85-2 649.4 9.9 ~5 160 17 3 211 8 2 2 2 3 248 84-1 268.1 21.0 5-10 677 11 2182 4 4 119 104 15 75 7 2521 2 | | | | | | | | | | | | | | | | | | | | | |
| | | | | | C | araw | ine Co | ntext | San | ples | | | | | | | | | | | | |
| X68-1 | 604.7 | 1.1 | | 9 | | | 8 | | | | | | | | | 5 | 2 | | | | 15 | |
| 104175 | 235.4 | 0.5 | | 2 | | | | | | | | | | | | | | | | 8 | 8 | |
| 104141 | 357.2 | 1.8 | | 89 | | | 120 | | | | | 98 | | | | 6 | 8 | | 17 | | 249 | |
| | | | | | Jeer | inah | Spherul | e La | yer § | Samp | es | | | | | | | | | | | |
| X21-1 | 265.52 | 66.8 | 40-50 | 3639 | 4 | | 12519 | 8 | 30 | 4 | | 117 | 11 | | | 738 | 23 | | 226 | 23 | 13703 | 3 |
| W94-1Q | 38.73 | 51.7 | ~10 | 769 | | | 18952 | | | | | 52 | | | | 516 | 155 | | 155 | | 19830 | 4 |
| *Rutile abund | lances in l | bold indicat | e that som | e of the ru | tile grai | ins co | ntain ti | ie hij | zh-pr | essu | e po | lymo | rph 1 | liO ₂ 1 | п. | | | | | | | |
| 1) One hemir | norphite g | rain was al | so found i | n this samp | ole. | | | | | | | | | | | | | | | | | |
| 2) One orthog | pyroxene | grain was a | lso found | in this sam | ple. | | | | | | | | | | | | | | | | | |
| 3) One hema | tite grain | was also fo | und in this | sample. | | | | | | | | | | | | | | | | | | |
| 4) One ilmeni | ite grain w | as also fou | nd in this | sample. | | | | | | | | | | | | | | | | | | |

| | | | | | H | leavy | Miner | al Al | bund | ance | (Nun | nber | of gi | ains | (kg) in | the 63- | -125 J | ım Siz | ze Fra | ction | 1 | |
|--|-------------|--|---------------------------|--------------------------------------|------------|-----------|----------|-----------|--------|----------|----------|---------------|---------------|-------------------|----------|---------|------------|----------|--------|--------------|-------|-------|
| Sample Number/ Layer/ Sublayer(s) | Wt. (g) | Wt.% Acid- Insoluble Fraction | Percent Sphe- rules | No. of Heavy Mineral Grains | Actinolite | Almandine | Anatase | Anglesite | Barite | Brookite | Chlorite | Chrome Spinel | Clinopyroxene | Clinozo/Epidote | Monazite | Rutile* | Tourmaline | Xenotime | Zircon | Unidentified | Total | Notes |
| | | | | | Bee Go | rge S | pherul | e Lay | er/S | ublay | ver(s) | | | | | | | | | | | |
| 96714A U | 17.19 | 47.6 | ~8 | 77 | | | 524 | 116 | | | | | | | | 3839 | | | | | 4479 | |
| 96714A S | 10.3574 | 55.3 | 10-15 | 4 | | | 290 | 96 | | | | | | | | | | | | | 386 | |
| 96714A L | 15.92 | 50.6 | 40-50 | 519 | | 63 | 189 | | | | | | | | | 32349 | | | | | 32601 | |
| 96714B U | 14.2225 | 51.8 | ~8 | 53 | | | 563 | | | | | | | | 70 | 2109 | | 984 | | | 3726 | |
| 96714B S | 18.58 | 60.4 | 10-15 | 26 | 108 | | 753 | | | | | | | | | 538 | | | | | 1399 | |
| 96714B L | 13.8178 | 51.3 | 40-50 | 439 | | | 289 | | | | | | | | 72 | 31409 | | | | | 31770 | |
| BB (sl) | 31.24 | 32.0 | >50 | 69 | 64 | | 1184 | | | | | 32 | | 32 | 64 | 640 | 96 | | 96 | | 2208 | |
| | | | | | В | ee G | orge C | ontex | t La | yers | | | | | | | | | | | | |
| 96714A BL | 82.26 | 61.3 | | 41 | | | 450 | | | | | | | | | 49 | | | | | 499 | |
| 96714B BL | 52.76 | 64.4 | | 13 | | | 227 | | | | | | | | | | | | | | 227 | 5 |
| BB (#2) | 14.89 | 12.6 | | 31 | | | 269 | 67 | | | | 67 | | 67 | | 940 | 269 | | 403 | | 2082 | |
| BB (#1) | 5.4035 | 19.7 | | 9 | | | 185 | | | | | | | 185 | | 555 | 555 | | 185 | | 1665 | |
| | | | | | Monte | eville | Spheru | ile La | ayer | Samp | oles | | | | | | | | | | | |
| V111 | 219.9 | 10.4 | <1 | 2773 | 14 | | 7121 | 5 | | | 9 | 23 | 9 | | 3570 | 1578 | 118 | | 150 | 14 | 12611 | |
| U63-1 | 593.2 | 18.2 | ~5 | 1206 | | | 1642 | | | | 2 | | | | 352 | 32 | 5 | | | | 2033 | |
| | | | | | Μ | onter | ville Co | ntext | t San | nples | | | | | | | | | | | | |
| II67-1B | 616.7 | 3.4 | | 22 | | | 29 | | | | | 5 | | | | 2 | | | | | 36 | |
| T149-1 | 214.3 | 10.1 | | 169 | | | 37 | | | | 168 | | | | 583 | | | | | | 788 | |
| *Rutile abund | lances in b | old indicate | e that som | e of the ru | tile graii | ns co | ntain tl | ne hig | gh-pr | essur | e pol | ymor | ph T | iO ₂ I | II. | | | | | | | |
| 5) One sillima | anite grain | was also f | ound in thi | is context 1 | ayer. | | | | | | | | | | | | | | | | | |

Table 62: continued

| | | | | | Н | leavy | Miner | al Al | ound | ance | (Nur | nber | of gr | ains/ | kg) in | the 63 | -125 µ | m Si | ze Fra | ction | ı | |
|--|-------------------------|--|---------------------------|--------------------------------------|----------------------|-----------------|--------------------|-----------------|-------------|----------------|----------------|---------------|---------------|-------------------|-----------------|-------------------|------------------|------------------|-------------------|--------------|----------------|-------|
| Sample Number/ Layer/ Sublayer(s) | Wt. (g) | Wt.% Acid- Insoluble Fraction | Percent Sphe- rules | No. of Heavy Mineral Grains | Actinolite | Almandine | Anatase | Anglesite | Barite | Brookite | Chlorite | Chrome Spinel | Clinopyroxene | Clinozo/Epidote | Monazite | Rutile* | Tourmaline | Xenotime | Zircon | Unidentified | Total | Notes |
| Grænsesø Spherule Layer Samples | | | | | | | | | | | | | | | | | | | | | | |
| GL8904-4 | 482.0 | 26.2 | ~10 | 1889 | | | 79 | 50 | 6 | | | 8 | | | | 2770 | 552 | | 454 | | 3919 | |
| GL8904-3 | 487.8 | 18.1 | ~10 | 2945 | | | 27 | 16 | 10 | | | 4 | | | | 4227 | 756 | | 996 | | 6036 | |
| GL8904-1 | 349.3 | 20.2 | ~5 | 17549 | | | 135 | 23 | | | | 137 | | | | 35932 | 6699 | | 7303 | 9 | 50238 | 6 |
| | | | | | G | rænse | esø Co | ntext | San | ples | | | | | | | | | | | | |
| GL8904-6 | 321.1 | 3.3 | | 52 | | | 6 | | | | | 9 | | | | 125 | 16 | | 6 | | 162 | |
| SP3 | 155.0 | 6.6 | | 236 | | | | 6 | | | | | | | | 1465 | 32 | | 13 | | 1516 | 7 |
| *Rutile abund | ances in l | old indicate | e that som | e of the ru | tile grait | is co | ntain th | ne hig | h-pr | essur | e pol | ymor | ph T | ίO ₂ Ι | I. | | | | | | | |
| 6) One magne | etite grain | was also f | ound in thi | s sample. | | | | | | | | | | | | | | | | | | |
| 7) One magne | etite grain | was also f | ound in thi | s sample. | | | | | | | | | | | | | | | | | | |
| Notes: For sar bearing lutite | mples 967 sublayer (| (14A and 9 (Splsl); U = | 6714B: BI Upper spi | . = Basal o herule/lutit | carbonat e sublay | e luti ers (| te cont Usplsl) | ext la . For | ayer sam | (Bcl) ple B | ; L = BB: B | Low B (# | verm 1) = | ost sj Cont | pheru ext la | le-rich yer #1 | sublay in sam | yer (I Iple H | Lspsl); 3B; Bl | S = B (# | Sphert 2) = | ıle- |

Context layer #2 in sample BB; BB (sl) = Spherule layer in sample BB. Abbreviations: Clinozo = Clinozoisite; No. = Number; Wt. = Weight.

| | | | | | | | | He | avy N | /liner: | al As | sseml | olage | (No.% | 6) | | | | |
|--|--|---|------------|-----------|---------|-----------|--------|----------|----------|---------------|---------------|-----------------|----------|---------|------------|----------|--------|--------------|-------|
| Sample Number/ Layer/ Sublayer(s) | Percent Sphe- rules | No. of Heavy Mineral Grains/kg | Actinolite | Almandine | Anatase | Anglesite | Barite | Brookite | Chlorite | Chrome Spinel | Clinopyroxene | Clinozo/Epidote | Monazite | Rutile* | Tourmaline | Xenotime | Zircon | Unidentified | Total |
| | Carawine Spherule Layer Samples X38-2 <1 7265 0.2 64.1 0.2 0.1 3.4 0.1 17.8 2.2 12.0 100.0 | | | | | | | | | | | | | | | | | | |
| X38-2 | <1 | 7265 | 0.2 | | 64.1 | 0.2 | | 0.1 | | 3.4 | | 0.1 | | 17.8 | 2.2 | | 12.0 | | 100.0 |
| 42-1A | <10 | 1049 | | | 88.4 | | | | | 1.3 | | | | 5.1 | 0.2 | | 5.0 | | 100.0 |
| 43-1 | 2-3 | 140 | 0.1 | | 90.1 | | | 0.1 | | 0.7 | | | | 2.3 | | | 6.4 | 0.1 | 100.0 |
| X24-1 | <5 | 373 | 1.3 | 0.3 | 87.1 | | | | | 0.3 | 0.3 | 2.9 | | 2.7 | 1.3 | | 3.8 | | 100.0 |
| W85-2 | ~5 | 248 | 6.9 | 1.2 | 85.1 | 3.2 | | | | 0.8 | | | | 0.8 | 0.8 | | 1.2 | | 100.0 |
| 84-1 | 5-10 | 2521 | 0.4 | | 86.6 | 0.2 | | | | 0.2 | | 4.7 | | 4.1 | 0.6 | | 3.0 | 0.3 | 100.0 |
| | | | | | | Cara | wine | Cont | text S | ample | es | | | | | | | | |
| X68-1 | | 15 | | | 53.3 | | | | | | | | | 33.3 | 13.3 | | | | 100.0 |
| 104175 | | 8 | | | | | | | | | | | | | | | | 100.0 | 100.0 |
| 104141 | | 249 | | | 48.2 | | | | | 39.4 | | | | 2.4 | 3.2 | | 6.8 | | 100.0 |
| | | | | | Jee | erinah | . Sph | erule | Laye | r San | nples | 5 | | | | | | | |
| X21-1 | 40-50 | 13703 | 0.03 | | 91.4 | 0.1 | 0.2 | 0.03 | | 0.9 | 0.1 | | | 5.4 | 0.2 | | 1.6 | 0.2 | 100.0 |
| W94-1Q | ~10 | 19830 | | | 95.6 | | | | | 0.3 | | | | 2.6 | 0.8 | | 0.8 | | 100.0 |
| *Rutile abur | idances i | n bold indic | ate th | at so | me of | the n | utile | grains | s cont | tain th | ne hig | gh-pr | essur | e poly | morpl | n TiO | 2 II. | | |

 Table 63:
 Summary of heavy mineral assemblage (number percent) for spherule layer and context samples.

Table 63: continued

| | | | | | | | | He | avy N | Miner | al As | sseml | olage | (No.% | 6) | | | | |
|--|---------------------------|---|------------|-----------|---------|-----------|--------|----------|----------|---------------|---------------|-----------------|----------|---------|------------|----------|--------|--------------|-------|
| Sample Number/ Layer/ Sublayer(s) | Percent Sphe- rules | No. of Heavy Mineral Grains/kg | Actinolite | Almandine | Anatase | Anglesite | Barite | Brookite | Chlorite | Chrome Spinel | Clinopyroxene | Clinozo/Epidote | Monazite | Rutile* | Tourmaline | Xenotime | Zircon | Unidentified | Total |
| | | | | | Bee (| Gorge | Sph | erule | Laye | r/Sub | laye | r(s) | | | | | | | |
| 96714A U | ~8 | 4479 | | | 11.7 | 2.6 | | | | | | | | 85.7 | | | | | 100.0 |
| 96714A S | 10-15 | 386 | | | 75.1 | 24.9 | | | | | | | | | | | | | 100.0 |
| 96714A L | 40-50 | 32601 | | 0.2 | 0.6 | | | | | | | | | 99.2 | | | | | 100.0 |
| 96714B U | ~8 | 3726 | | | 15.1 | | | | | | | | 1.9 | 56.6 | | 26.4 | | | 100.0 |
| 96714B S | 10-15 | 1399 | 7.7 | | 53.8 | | | | | | | | | 38.5 | | | | | 100.0 |
| 96714B L | 40-50 | 31770 | | | 0.9 | | | | | | | | 0.2 | 98.9 | | | | | 100.0 |
| BB (sl) | >50 | 2208 | 2.9 | | 53.6 | | | | | 1.4 | | 1.4 | 2.9 | 29.0 | 4.3 | | 4.3 | | 100.0 |
| | | | | | | Bee | Gorg | ge Co | ntext | Laye | rs | | | | | | | | |
| 96714A BL | | 499 | | | 90.2 | | | | | | | | | 9.8 | | | | | 100.0 |
| 96714B BL | | 227 | | | 100.0 | | | | | | | | | | | | | | 100.0 |
| BB (#2) | | 2082 | | | 12.9 | 3.2 | | | | 3.2 | | 3.2 | | 45.1 | 12.9 | | 19.4 | | 100.0 |
| BB (#1) | | 1665 | | | 11.1 | | | | | | | 11.1 | | 33.3 | 33.3 | | 11.1 | | 100.0 |
| | | | | | Mot | ntevill | e Sp | herul | e Lay | er Sa | mple | es | | | | | | | |
| V111 | <1 | 12611 | 0.1 | | 56.5 | 0.04 | | | 0.1 | 0.2 | 0.1 | | 28.3 | 12.5 | 0.9 | | 1.2 | 0.1 | 100.0 |
| U63-1 | ~5 | 2033 | | | 80.8 | | | | 0.1 | | | | 17.3 | 1.6 | 0.2 | | | | 100.0 |
| | | | | | | Mont | eville | e Con | text § | Sampl | es | | | | | | | | |
| II67-1B | | 36 | | | 80.6 | | | | | 13.9 | | | | 5.6 | | | | | 100.0 |
| T149-1 | | 788 | | | 4.7 | | | | 21.3 | | | | 74.0 | | | | | | 100.0 |
| *Rutile abur | idances i | n bold indic | ate th | at so | me of | the n | utile | grain | s con | tain tl | ne hi | gh-pr | essur | e poly | morpi | h TiO | 2 II. | | |

Table 63: continued

| | | | | | | | | He | avy l | Miner | al As | sseml | blage | (No.% | 6) | | | | |
|---|--|--|---------------------------------|---------------------------------|--------------------------------------|-----------------------------------|-------------------------------|----------------------------|--------------------------|---------------------------|-----------------------|--------------------------|---------------------------|-----------------------------|-------------------------|-------------------------|--------------------------|-----------------------------|---------------------|
| Sample Number/ Layer/ Sublayer(s) | Percent Sphe- rules | No. of Heavy Mineral Grains/kg | Actinolite | Almandine | Anatase | Anglesite | Barite | Brookite | Chlorite | Chrome Spinel | Clinopyroxene | Clinozo/Epidote | Monazite | Rutile* | Tourmaline | Xenotime | Zircon | Unidentified | Total |
| Grænsesø Spherule Layer Samples | | | | | | | | | | | | | | | | | | | |
| GL8904-4 | ~10 | 3919 | | | 2.0 | 1.3 | 0.2 | | | 0.2 | | | | 70.7 | 14.1 | | 11.6 | | 100.0 |
| GL8904-3 | ~10 | 6036 | | | 0.4 | 0.3 | 0.2 | | | 0.1 | | | | 70.0 | 12.5 | | 16.5 | | 100.0 |
| GL8904-1 | ~5 | 50238 | | | 0.3 | 0.05 | | | | 0.3 | | | | 71.5 | 13.3 | | 14.5 | 0.02 | 100.0 |
| | | | | | | Græn | isesø | o Con | text S | Sampl | es | | | | | | | | |
| GL8904-6 | | 162 | | | 3.7 | | | | | 5.6 | | | | 77.2 | 9.9 | | 3.7 | | 100.0 |
| SP3 | | 1516 | | | | 0.4 | | | | | | | | 96.6 | 2.1 | | 0.9 | | 100.0 |
| *Rutile abur | ndances i | n bold indica | ate th | at so | ome of | f the r | utile | grain | s con | tain tl | ne hi | gh-pr | essur | e poly | morpl | ı TiO | 0 ₂ II. | | |
| Notes: For s sublayer (Ls BB (#1) = 0 BB. Abbrev | samples 9 spsl); S = Context la viations: C | 6714A and Spherule-b yer #1 in sa Jinozo = Ch | 9671 earin ample inozo | 4B: g luti e BB isite; | BL = 1 ite sub ; BB (No. = | Basal layer (#2) = • Num | carb (Spls Cor iber. | onate sl); U itext l | e lutit = Up layer | e cont oper s #2 in | text l pher sam | layer ule/lu ple B | (Bcl) tite si B; Bl | ; L = l ublaye B (sl) | Lower rs (U = Sph | rmos splsl) erule | t sphe . For layer | rule-ri sample in sar | ch 9 BB: nple |

5.2.2 Carawine Spherule Layer and Context Samples

The heavy mineral assemblages for the six Carawine spherule layer samples (Appendix S) are basically similar in terms of phases present, but several phases have a wide range in abundance (number of grains/kg; Table 62). The similarity in terms of phases present suggests a similar provenance for the sediments in the Ripon Hills area (spherule layer samples 84-1, W85-2, X24-1, 43-1, and 42-1A) and the TTT locality (spherule layer sample X38-2). The following discussion first focuses on spherule layer samples 84-1, W85-2, X24-1, 43-1 from the Ripon Hills area, and then on spherule layer sample X38-2 from the TTT locality (see Fig. 4 for locations).

For the five spherule layer samples from the Ripon Hills area, anatase comprises ~85-90% of the 63-125 μ m size fractions (Table 63), and for four of the five samples, anatase comprises ~63-86% of the 125-250 μ m size fractions; for sample 43-1, no anatase was found in the 125-250 μ m size fraction. Many of the anatase grains are subrounded-to-subangular, and they appear to be detrital grains. However, using micro-Raman spectroscopy, anatase was identified on a few zircon grains from Carawine spherule layer samples 84-1 and 42-1A, suggesting that at least some of the anatase may be of secondary origin. More work is needed to determine the mode(s) of origin of the anatase. All the other phases occur in trace-to-minor amounts (Table 63).

The rutile \pm anatase and zircon grains in samples 84-1, W85-2, X24-1, and 43-1 from the lower part of the Carawine spherule layer in the Ripon Hills area (Table 4) show some differences in their physical properties from those in sample 42-1A from the uppermost 0.75 m of the Carawine spherule layer. All the recovered rutile \pm anatase grains in samples 84-1, W85-2, X24-1, and 43-1 from the lowermost debris-flow deposit of the Carawine spherule layer (see Hassler et al., 2005) are in the 63-125 µm size fraction, and the grains are typically peach, amber, or reddish amber; only a few of them are buff. In Carawine spherule layer sample 42-1A, no amber or reddish amber rutile \pm anatase grains were recovered, and 80% (n = 16) of the rutile \pm anatase grains (n = 20) in the 63-125 µm size fraction are light buff-to-buff. Furthermore, all nine rutile \pm anatase grains in the 125-250 µm size fraction of Carawine spherule layer sample 42-1A are very light buff-to-buff, and these grains are typically subangular-to-angular, and irregular or blocky in shape. Carawine spherule layer samples 84-1, W85-2, X24-1, and 43-1 combined contain 90 zircon grains in the 63-250 µm size fraction, and only about six (~7%) of these zircon grains are white and translucent-to-opaque or opaque. Sample 42-1A from the uppermost 0.75 m of the Carawine spherule layer contains 36 zircon grains in the 63-250 µm size fraction, and 11 (~31%) of these zircon grains are translucent-to-opaque or opaque, including two grains that are light gray-to-white. These results suggest some variation in the provenance for the rutile \pm anatase and zircon grains between the lower and upper parts of the Carawine spherule layer in the Ripon Hills area.

The TTT locality of the Carawine spherule layer is located ~73 km southeast (Hassler et al., 2005) of the Carawine spherule layer sections in the Ripon Hills (Fig. 4). Sample X38-2 is a dolomixtite from the upper part of the uppermost debris-flow deposit of the Carawine spherule layer at the TTT locality (Table 4), and silt-to-fine sand-sized grains were observed in the hand sample using a hand lens (Appendix A). For Carawine spherule layer sample X38-2, ~31 wt% of the acid-insoluble material is in the >250 μ m size fraction, and ~42 wt% of the acid-insoluble material is in the 63-250 μ m size fraction (Table 10). In contrast, for the five Carawine spherule layer samples from the Ripon Hills area, ~62-86 wt% of the acid-insoluble material is in the >250 μ m size fraction, and ~4-9 wt% of the acid-insoluble material is in the >250 μ m size fraction.

spherule layer sample X38-2, therefore, contains a much higher proportion of acidinsoluble material in the 63-250 μ m size fraction and a much lower proportion of acidinsoluble material in the >250 μ m size fraction than do the five Carawine spherule layer samples from the Ripon Hills area. These acid-insoluble weight results are consistent with the fact that sample X38-2 is from the upper sandy part of the Carawine spherule layer dolomixtite (Appendix A), and the fact that sample X38-2 has by far the highest abundance of heavy mineral grains (63-125 μ m size fraction) of the six Carawine spherule layer samples (Table 62).

Anatase, chrome spinel, rutile, tourmaline, and zircon grains have much higher abundances in Carawine spherule layer sample X38-2 as compared with their respective abundances in the five Carawine spherule layer samples from the Ripon Hills area (Table 62). Sample X38-2 has the smallest mass of the six Carawine spherule layer samples (Table 62), so the higher abundance of heavy mineral grains in sample X38-2, as compared with the five Carawine spherule layer samples from the Ripon Hills area, is not due to sample size. The higher abundance of heavy mineral grains in Carawine spherule layer sample X38-2 as compared with the five Carawine spherule layer samples from the Ripon Hills area may reflect a higher proportion of 63-250 μ m-sized grains of epiclastic and/or impact ejecta origin in sample X38-2. The rutile + TiO₂ II grains in Carawine spherule layer sample X38-2 (Tables 40 and 62) support the hypothesis that at least some of the 63-250 μ m-sized grains in this sample represent impact ejecta.

Almandine, clinopyroxene, hemimorphite, orthopyroxene, rutile + unidentified, and spessartine, the latter in the 125-250 μ m size fraction, occur in one or more of the Carawine spherule layer samples from the Ripon Hills area, but none of these phases were identified in Carawine spherule layer sample X38-2 from the TTT locality. However, these phases occur only as single grains or in trace amounts. Actinolite, anglesite, brookite, chrome spinel, clinozoisite/epidote, and tourmaline occur in trace-tominor amounts in Carawine spherule layer sample X38-2 and in one or more of the Carawine spherule layer samples from the Ripon Hills area (Table 63). Therefore, those heavy mineral phases in the Carawine spherule layer at the TTT locality that occur in trace-to-minor amounts are typically the same as those heavy mineral phases that occur in trace-to-minor amounts in the Carawine spherule layer in the Ripon Hills area (Table 63).

The physical properties of each heavy mineral phase in Carawine spherule layer sample X38-2 from the TTT locality are generally similar to those of its respective phase in the Carawine spherule layer samples from the Ripon Hills area. For example, buff is a common color for the rutile \pm anatase grains in Carawine spherule layer sample X38-2, although no percentage values for the various colors were recorded (see Appendix S). Likewise, ~86% (n = 25) of the rutile \pm anatase grains (63-250 µm size fraction; n = 29) in sample 42-1A from the uppermost 0.75 m of the Carawine spherule layer in the Ripon Hills area are buff in color. In Carawine spherule layer sample X38-2, \sim 42% (n = 85) of the zircon grains (63-250 μ m size fraction; n = 202) are translucent-to-opaque or opaque, including 32 zircon grains that are white. In Carawine spherule layer sample 42-1A, \sim 31% (n = 11) of the zircon grains (63-250 µm size fraction; n = 36) are translucent-toopaque or opaque, including two zircon grains that are light gray-to-white. Therefore, the rutile \pm anatase and zircon grains in the upper parts of the uppermost debris-flow deposits of the Carawine spherule layer in the Ripon Hills area (sample 42-1A) and at the TTT locality (sample X38-2) show similar physical properties. The similarities of the heavy mineral assemblages, in terms of phases present, for sample X38-2 from the TTT locality and the five spherule layer samples from the Ripon Hills area, and the similar physical

properties of the rutile \pm anatase and zircon grains in samples X38-2 and 42-1A, are consistent with the hypothesis of Hassler et al. (2005) that the Carawine spherule layer sections in the Ripon Hills area and at the TTT locality were deposited by the same series of sediment gravity flows that moved southward (present geographic coordinates) down the paleoslope toward the deeper portion of the Hamersley Basin.

There is an important difference, however, between the heavy mineral assemblage for Carawine spherule layer sample X38-2 from the TTT locality and those for the five Carawine spherule layer samples from the Ripon Hills area: in sample X38-2, a minimum of ~3.3% (n = 10) of the estimated total number of rutile \pm anatase grains (n = 300) in the 63-250 µm size fraction contain the TiO₂ II phase, whereas no rutile + TiO₂ II grains were identified in this same size fraction in the samples from the Ripon Hills area (Table 62). In sample X38-2, the ten rutile grains that contain the TiO₂ II phase are basically buff-colored, and 90% of them are blocky (Table 40).

For samples 84-1, W85-2, X24-1, and 43-1 from the lowermost debris-flow deposit of the Carawine spherule layer in the Ripon Hills area (Appendix A; Fig. 4) there are a total of 55 rutile \pm anatase grains, all in the 63-125 µm size fraction (Appendix S), and ~62% (n = 34) of these grains were analyzed by micro-Raman spectroscopy. If this population of 55 rutile \pm anatase grains has the same concentration of rutile + TiO₂ II grains as that (~3.3%) of Carawine spherule layer sample X38-2 from the TTT locality, then it should contain ~2 (1.8) rutile + TiO₂ II grains. However, none of the 34 analyzed grains contain the TiO₂ II phase. The apparent absence of rutile + TiO₂ II grains in these four spherule layer samples from the Ripon Hills area may reflect the fact that not all of the rutile \pm anatase grains in these samples were analyzed, and/or the possibility that these samples have a lower concentration of rutile + TiO₂ II grains than that observed for sample X38-2. Only a few of the 55 rutile \pm anatase grains are buff in color, and given the fact that all the rutile + TiO₂ II grains that were identified in this study are shades of buff, the apparent absence of rutile + TiO₂ II grains in Carawine spherule layer samples 84-1, W85-1, X24-1, and 43-1 is not surprising.

For Carawine spherule layer sample 42-1A that is from the uppermost 0.75 m of the Carawine spherule layer in the Ripon Hills area (Appendix A), there are 29 rutile \pm anatase grains in the 63-250 µm size fraction. About 86% of these 29 grains are buff, and 62% (n = 18) of these 29 grains were analyzed by micro-Raman spectroscopy. Again, using the proportion (~3.3%) of rutile \pm anatase grains in Carawine spherule layer sample X38-2 that contain the TiO₂ II phase as a first approximation to estimate the number of expected rutile + TiO₂ II grains in sample 42-1A, it can be seen that ~1 of the 29 rutile \pm anatase grains should contain the TiO₂ II phase. None of the 18 analyzed grains contain the TiO₂ II phase. Again, the apparent absence of rutile + TiO₂ II grains in sample 42-1A may reflect the fact that not all of the rutile \pm anatase grains in this sample were analyzed, and/or the possibility that this sample has a lower concentration of rutile + TiO₂ II grains in this sample 42-1A are buff, the apparent absence of rutile + TiO₂ II grains in this sample 42-1A are buff, the apparent absence of rutile + TiO₂ II grains in this sample form this sample may simply reflect sample size, i.e., a larger (multi-kg-sized) sample from this same stratigraphic interval may yield rutile + TiO₂ II grains.

For Carawine context sample 104175, the very low abundance (≤ 8 grains/kg) of primary heavy mineral grains (Table 62; see section 4.2.3.2) probably reflects the fact that this sample contains only 0.5 wt% acid-insoluble material (Table 10), the lowest value for any sample in this study, and the fact that 99.3 wt% of this material is in the <63 µm size fraction. For Carawine context samples 104141 and X68-1, the heavy mineral assemblages have 3-5 of the commonly observed phases in the Carawine spherule layer samples, but several of the phases that occur in trace-to-minor amounts in the spherule layer samples are not present in these context samples (Table 63). Furthermore, in the Carawine context samples, anatase grains show fewer colors than those in the Carawine spherule layer samples, none of the rutile \pm anatase grains are amber, reddish amber, or buff in color, rutile + TiO₂ II grains are absent, and there are no pink, white, or opaque zircon grains. These differences may reflect the low total number (n = 62) of anatase, rutile \pm anatase, and zircon grains in the Carawine context samples.

The higher number of heavy mineral phases and generally higher abundance of heavy minerals in the Carawine spherule layer samples as compared with those for the Carawine context samples (Table 62) probably reflect a higher proportion of sand-sized extrabasinal material in the spherule layer samples as compared with the context samples. The acid-insoluble weight data (Table 10) support this hypothesis: for the six Carawine spherule layer samples, ~70-90 wt% of the acid-insoluble material is in the >63 μ m size fraction, whereas for the three Carawine context samples, only ~1-8 wt% of the acid-insoluble material is in the >63 μ m size fraction. Furthermore, small amounts of quartzo-feldspathic sand, generally interpreted as epiclastic detritus from the Pilbara craton that was brought into the Hamersley Basin by impact-related waves and currents, have been documented in Carawine spherule layer samples from both the Ripon Hills area (e.g., Simonson et al., 1998; Jones-Zimberlin et al., 2006, and references therein) and the TTT locality (Hassler et al., 2005). The rutile + TiO₂ II grains in sample X38-2 (Table 62) suggest that some of the sand-sized extrabasinal material in the Carawine spherule layer represents impact ejecta.

5.2.3 Jeerinah Spherule Layer Samples

On the basis of their lithologic descriptions (Appendix C), float samples W94-1Q and X21-1 were derived (B. M. Simonson, personal communication, 2013) from the thinbedded zone that comprises the basal 50 cm of the 157 cm-thick Jeerinah spherule layer at the Hesta locality (see Hassler et al., 2005). The heavy mineral assemblages of the two Jeerinah spherule layer samples are basically similar to each other, as well as to those of the Carawine spherule layer samples (Table 63) from both the Ripon Hills area and TTT locality (see Fig. 4 for locations). For Jeerinah spherule layer samples W94-1Q and X21-1, anatase \pm K-feldspar comprises ~91-96% of the heavy mineral grains in the $63-125 \,\mu\text{m}$ size fraction (Table 63), and for this size fraction, the two samples have by far the highest abundances (number of grains/kg) of anatase of all the samples in this study (Table 62). Micro-Raman spectroscopy shows that, in addition to individual grains of anatase, anatase is present as white matrix material on the surfaces of chrome spinel, K-feldspar, tourmaline, and zircon grains. These results suggest that at least some of the anatase is of secondary origin. The other heavy mineral phases occur in trace-to-minor amounts (Table 63). The physical properties of these phases are basically similar for the two samples, and they are also similar to those for the respective phases in the Carawine spherule layer samples. The following discussion focuses on the rutile \pm anatase and zircon grains.

The Jeerinah spherule layer samples, W94-1Q and X21-1, together contain buff, peach, amber, and reddish amber rutile \pm anatase grains that are similar to those in the Carawine spherule layer samples. Light buff-to-buff rutile \pm anatase grains are common in Jeerinah spherule layer samples W94-1Q and X21-1. For two light buff grains from Jeerinah spherule layer sample X21-1, the Raman spectra have bands at wavenumbers that match those of rutile \pm TiO₂ II \pm anatase (Table 47). These two grains comprise 1%

of the rutile \pm anatase grains (n = 196) that were recovered in the 63-125 µm size fraction of sample X21-1, and they comprise ~3.6% of the 56 rutile \pm anatase grains that were analyzed by micro-Raman spectroscopy. The two percentage values are lower than, but roughly comparable to, those for the rutile + TiO₂ II \pm anatase grains in the same size fraction of Carawine spherule layer sample X38-2.

For the 63-250 μ m size fraction of Jeerinah spherule layer sample W94-1Q, ~61% (n = 14) of the estimated total number (n = 23) of rutile ± anatase grains were analyzed by micro-Raman spectroscopy, but no rutile + TiO₂ II grains were identified. Jeerinah spherule layer sample W94-1Q has a much smaller mass than Jeerinah spherule layer sample X21-1 (Table 62). Using the proportion (~1-3.6%; see section 4.2.4.2) of rutile ± anatase grains in sample X21-1 that contain the TiO₂ II phase as a first approximation to estimate the number of expected rutile + TiO₂ II grains in Jeerinah spherule layer sample W94-1Q, it can be seen that the expected value is <1 grain. Therefore, the apparent absence of rutile + TiO₂ II grains in Jeerinah spherule layer sample W94-1Q is not surprising.

The zircon grains in Jeerinah spherule layer samples W94-1Q and X21-1 exhibit colors that are similar to those in the Carawine spherule layer samples, i.e., pale pink, champagne, and clear with a (very) light yellow tint (Appendices S and U). However, these colors are commonly observed for zircons (e.g., Garver and Kamp, 2002, and references therein) as is evidenced by the zircon grains in the Grænsesø spherule layer samples (see Appendix Y). In the 63-125 μ m size fraction of Jeerinah spherule layer samples W94-1Q and X21-1 combined, ~12.1% (n = 8) of the zircon grains are translucent-to-opaque, and none of the zircon grains are opaque. For the same size fraction of Carawine spherule layer samples 84-1, W85-2, X24-1, and 43-1 combined,

~10.4% (n = 9) of the zircon grains are translucent-to-opaque or opaque, including only one white opaque grain. In contrast, translucent-to-opaque or opaque zircon grains from Carawine spherule layer samples 42-1A and X38-2 comprise ~31% (n = 11) and ~42% (n = 84), respectively, of the zircon populations. In terms of diaphaneity, therefore, the zircon population for Jeerinah spherule layer samples W94-1Q and X21-1 combined is more similar to that for the lower part of the Carawine spherule layer in the Ripon Hills area (samples 84-1, W85-2, X24-1, and 43-1 combined) than those for samples 42-1A and X38-2 that are from the upper parts of the Carawine spherule layer in the Ripon Hills area and TTT locality, respectively.

In common with the Carawine spherule layer, Jeerinah spherule layer sample X21-1 from the Hesta locality (see Fig. 4) contains trace amounts of actinolite, anglesite, brookite, clinopyroxene, and tourmaline (Table 63). Furthermore, petrographic analysis of samples from the basal thin-bedded zone of the Jeerinah spherule layer at the Hesta locality shows this unit to contain ~1-2 vol% of quartzo-feldspathic sand-sized detritus (Hassler et al., 2005; Jones-Zimberlin et al., 2006). The quartz appears to be epiclastic detritus that was largely derived from plutonic igneous and/or regionally-metamorphosed continental basement rocks, possibly situated on the Pilbara craton (Hassler et al., 2005; Jones-Zimberlin et al., 2006, and references therein). In contrast, the feldspathic detritus appears to have been largely derived from volcanic tuff beds that were probably situated closer to the Hesta locality than the source terrain(s) for the quartz detritus (Hassler et al., 2005; Jones-Zimberlin et al., 2006). Jeerinah spherule layer samples W94-1Q and X21-1 were both crushed below 250 µm prior to acid digestion, so the primary distribution of weight percent acid-insoluble material by size fraction is not known (Table 10). At the Hesta locality, weathered argillite beds host the Jeerinah spherule layer (Hassler et al.,
2005). Heavy mineral data are not available for these argillite beds. However, the results discussed above suggest that, like the Carawine spherule layer, the heavy mineral assemblage for the Jeerinah spherule layer at the Hesta locality may contain a significant extrabasinal component. The rutile + TiO_2 II grains in sample X21-1 (Table 62) suggest that some of the sand-sized extrabasinal material in the Jeerinah spherule layer represents impact ejecta.

The basic similarities of the heavy mineral assemblages and physical properties (e.g., color, diaphaneity) of the phases for the spherule layer samples from the Ripon Hills area, TTT, and Hesta localities (see Fig. 4 for locations), are consistent with the proposed correlation (e.g., Rasmussen and Koeberl, 2004; Rasmussen et al., 2005; Hassler et al., 2005; Simonson et al., 2009a, 2009b) of the Carawine and Jeerinah spherule layers (see section 5.4). Hassler et al. (2005) considered the Carawine and Jeerinah spherule layers to be roughly synchronous, and they favored the hypothesis that the Jeerinah spherule layer at the Hesta locality was deposited by sediment gravity flows that were moving southward (present geographic coordinates) but independently of those that deposited the Carawine spherule layer in the Ripon Hills area and at the TTT locality. This hypothesis implies that the bulk of the materials in the Carawine and Jeerinah spherule layers may have been derived from different areas. If the hypothesis favored by Hassler et al. (2005) is correct, then the source areas, both of which are probably situated on the Pilbara craton (Hassler et al., 2005; Jones-Zimberlin et al., 2006) and roughly 200 km apart (see Fig. 4), for the sand-sized epiclastic detritus in the two spherule layers, contain not only similar quartzo-feldspathic grains, but also similar suites of heavy minerals. However, the heavy mineral data could be used to support the alternative hypothesis that was discussed by Hassler et al. (2005), but considered by them

to be less likely, that the Carawine and Jeerinah spherule layers were deposited by the same series of sediment gravity flows. More heavy mineral data are needed from samples from all the main units within the spherule layer sections in the Ripon Hills area and at the TTT and Hesta localities, as well as from additional context samples from both below and above the spherule layers at these three localities, in order to fully evaluate the usefulness of using heavy minerals to test the hypotheses for the deposition of the spherule layers as proposed by Hassler et al. (2005).

5.2.4 Bee Gorge (Wittenoom) Spherule Layer and Context Samples

For Bee Gorge sample BB from the Bacon Bore locality (see Fig. 4), anatase, rutile \pm anatase, tourmaline \pm anatase, and zircon are the predominant heavy mineral phases in the 63-125 µm size fractions of the spherule layer (BB (sl)) and context layers (BB (#1) and BB (#2); Table 63). Anatase + K-feldspar grains were identified in the spherule layer, but more work is needed to determine their mode(s) of origin. Using micro-Raman spectroscopy, very fine-grained anatase was identified on the surfaces of two tourmaline grains, suggesting that at least some of the anatase is of secondary origin. In terms of phases present, the heavy mineral assemblages for the spherule layer and the two context layers in Bee Gorge sample BB are basically similar to those for the Carawine and Jeerinah samples (Table 63), suggesting an overall similarity in the provenance for the heavy mineral grains in these samples. However, the chrome spinel, rutile \pm anatase, and zircon populations for Bee Gorge sample BB (see Appendix V) show key differences with those for the Carawine and Jeerinah spherule layer samples.

The two chrome spinel grains that were recovered from Bee Gorge sample BB are dark brownish black, and grains with this particular color were not observed in the Carawine or Jeerinah samples. In the Bee Gorge spherule layer (BB (sl)) within sample

BB, there are no amber or reddish amber rutile grains such as are present in the Jeerinah spherule layer samples and most of the Carawine spherule layer samples. The zircon population for Bee Gorge sample BB shows the most striking difference with those for the Carawine and Jeerinah spherule layer samples and Carawine context sample 104141: no (pale) pink, champagne, peach, white, or opaque zircon grains were observed in the spherule layer (BB (sl)) or context layers (BB (#1) and BB (#2)) in sample BB. For Bee Gorge sample BB, 90% (n = 9) of the zircon grains, all of which are in the 63-125 μ m size fraction, are clear with a (light) yellow, green, or yellow-green tint (Appendix V).

These differences in the physical properties of the chrome spinel, rutile \pm anatase, and zircon grains in the spherule layer (BB (sl)) in Bee Gorge sample BB and those of the respective phases in the Carawine and Jeerinah spherule layer samples could be due to differences in both the source rocks for these heavy mineral phases as well as the mode of deposition of the Bee Gorge spherule layer at the Bacon Bore locality as compared with those of the Carawine and Jeerinah spherule layers. The Bee Gorge (Wittenoom) spherule layer is stratigraphically higher and roughly 90 million years younger than the Jeerinah spherule layer (see Fig. 2; Simonson et al., 2009a). Furthermore, the Bacon Bore (sample BB) locality is ~170 km west of the Jeerinah spherule layer outcrop at the Hesta locality, and it is ~360-400 km west-southwest of the Carawine spherule layer sections in the Ripon Hills area and TTT locality (see Fig. 4). Therefore, it is not unreasonable that there may be differences in the source rocks for the heavy mineral grains in Bee Gorge sample BB from the Bacon Bore locality as compared to those for the heavy mineral grains in the Carawine and Jeerinah spherule layer samples.

There are major differences in the scale and mode of deposition of the Carawine and Jeerinah spherule layers as compared with those of the Bee Gorge spherule layer at

the Bacon Bore locality. The Carawine spherule layer is 12.4 to 24.6 m thick in the Ripon Hills area, and 7.4 m thick at the TTT locality, and the Jeerinah spherule layer is 1.57 m thick at the Hesta locality (Hassler et al., 2005). The Carawine and Jeerinah spherule layers at these three localities consist mainly of debris-flow deposits that contain small amounts of epiclastic, sand-sized detritus (e.g., Hassler et al., 2005; Jones-Zimberlin et al., 2006). The sand-sized detritus consists mostly of quartzo-feldspathic grains, with the quartzose component, and some of the feldspathic component, being most likely derived from the Pilbara craton (e.g., Hassler et al., 2005; Jones-Zimberlin et al., 2006). The sand-sized (63-250 μ m) heavy mineral grains in these debris-flow deposits may also have been derived from the Pilbara craton, but some of them (e.g., rutile + TiO₂ II grains) may represent impact ejecta (see sections 5.2.2 and 5.2.3).

At the Bacon Bore locality, the Bee Gorge spherule layer in sample BB is ~1 cm thick (Appendix D), a value that is two or three orders of magnitude smaller than those for the debris-flow deposits that comprise most of the Carawine and Jeerinah spherule layers (see Hassler et al., 2005). The Bee Gorge (Wittenoom) spherule layer in sample BB is rippled, and it is sandwiched between two context layers of laminated carbonate lutite (see Hassler et al., 2000, their Figure 3; Appendix D), but the stratigraphic "up" direction for sample BB is not known (Appendix D). Hassler et al. (2000) reported small ferruginous flat pebbles in the rippled Bee Gorge (Wittenoom) spherule layer, and they interpreted the pebbles as intraclasts that were eroded from the subjacent black shale and then redeposited during the ripple-forming event. Hassler et al. (2000) proposed that the rippled Bee Gorge (Wittenoom) spherule layer by impact-generated tsunami waves.

Epiclastic quartzo-feldspathic detritus that is mostly 63-200 µm in size (Hassler et al., 2005), and that was probably derived from a source terrain of regionally metamorphosed rocks (Simonson et al., 1998), occurs in small amounts in the Bee Gorge (Wittenoom) spherule layer (Simonson, 1992). However, this epiclastic detritus has not been observed in samples of the rippled spherule-rich bedforms of the Bee Gorge (Wittenoom) spherule layer (Hassler et al., 2005). For Bee Gorge sample BB, ~22 wt% of the acid-insoluble material in the spherule layer (BB (sl)) is in the 63-250 µm size fraction, whereas for the two context layers (BB (#1) and BB (#2)), only 1.2-2.5 wt% of the acid-insoluble material is in this size fraction (Table 10). More detailed work is needed to determine whether or not the acid-insoluble material in the 63-250 µm size fraction of the Bee Gorge spherule layer (BB (sl)) in sample BB has an epiclastic quartzo-feldspathic component.

In Bee Gorge sample BB, the spherule layer (BB (sl)), as compared to the two context layers (BB (#1) and BB (#2)), has a much higher abundance of anatase grains, a comparable abundance of rutile grains, and lower abundances of tourmaline and zircon grains (Table 62). Minor amounts of actinolite and monazite grains are present in the spherule layer, but these phases were not identified in the context layers (Table 63). The heavy mineral abundance data (Table 62) suggest that anatase and minor amounts of actinolite and monazite were brought to this site during the formation of the spherule layer. However, more detailed work is needed to determine the mode(s) of origin (detrital and/or secondary) of the anatase and monazite grains. Furthermore, the abundances of rutile, tourmaline, and zircon grains in the spherule layer as compared to their respective abundances in the two context layers apparently provide no evidence that these phases were brought to this site as part of an increased flux of sand-sized epiclastic detritus

during the formation of the spherule layer. This conclusion is consistent with the petrographic results of Hassler et al. (2005) that reveal an absence of epiclastic detritus in the rippled spherule-rich bedforms of the Bee Gorge (Wittenoom) spherule layer. In fact, the lower abundances for the tourmaline and zircon grains in the spherule layer as compared with their respective abundances in the two context layers (Table 62) is somewhat puzzling, and more detailed work is needed in order to explain these results. Micro-Raman spectra for ~56% (n = 38) of the total number of anatase \pm K-feldspar (n = 48) and rutile \pm anatase (n = 20) grains combined in the 63-250 μ m size fraction of the spherule layer show no evidence of the TiO₂ II phase. Nine of the 20 rutile \pm anatase grains are shades of buff (Appendix V). The analyzed mass (31.24 g) of the spherule layer sample X38-2 and Jeerinah spherule layer sample X21-1 (see Table 62), the latter two samples containing rutile + TiO₂ II grains, so the apparent absence of these grains in the Bee Gorge spherule layer in sample BB may in part be due to a small sample size.

Bee Gorge samples 96714A and 96714B from the Tom Price locality (Fig. 4) each consist of a basal carbonate lutite context layer (Bcl; ~2.0-2.4 cm thick) that is sharply overlain by a spherule layer (~1.3-2.1 cm thick; Appendix D). At the Tom Price locality, the spherules are concentrated in lenses up to several centimeters thick that occur just below a distinctive fine-grained dolomitic turbidite bed that is 20 cm thick (Simonson and Glass, 2004, their Figure 8). For each of the Bee Gorge samples 96714A and 96714B, anatase \pm K-feldspar grains comprise >90% of the heavy mineral assemblage of the basal carbonate lutite context layer (Table 63; see sections 4.2.5.3.2 and 4.2.5.4.2), and these grains occur in each of the three subdivisions of the spherule layer (Table 63; Figs. 168 and 179). Micro-Raman spectroscopy shows that anatase can occur as white matrix material on the surfaces of K-feldspar and rutile grains. More work is needed to fully determine the origin of the anatase \pm K-feldspar grains, but it appears that at least some of the anatase is of secondary origin.

The presence of monazite and xenotime grains in a portion of the spherule layer in Bee Gorge sample 96714B, and their absence in Bee Gorge sample 96714A (Table 63), suggest a secondary origin for the phases, but again, more work is needed to determine their origin. Trace amounts of actinolite, almandine, and anglesite grains in the spherule layer, and their absence in the basal carbonate lutite context layer (Table 62), suggest an extrabasinal origin for these grains. However, a single grain of anglesite was recovered from context layer BB (#2) in Bee Gorge sample BB (Table 62) from the Bacon Bore locality (Fig. 4), so it is possible that the presence of actinolite, almandine, and anglesite grains may reflect the much higher abundance (in general) of heavy mineral grains in the spherule layer as compared to that of the basal carbonate lutite context layer (Table 62).

For each of the Bee Gorge samples 96714A and 96714B, the key difference in the heavy mineral assemblages of the basal carbonate lutite context layer and the overlying spherule layer is the presence in the spherule layer of two relatively abundant types of rutile \pm anatase grains: granular ("grainy-looking") grains, and buff grains, with a few of the buff grains containing the TiO₂ II phase. Furthermore, in contrast to Bee Gorge sample BB, the Carawine and Jeerinah spherule layer samples, and Carawine context sample 104141, no chrome spinel, tourmaline, or zircon grains were recovered from Bee Gorge samples 96714A and 96714B (Table 63). Therefore, the granular and buff rutile \pm anatase grains may comprise the only abundant (Table 62) extrabasinal heavy mineral grains in the Bee Gorge spherule layer at the Tom Price locality.

Granular and buff rutile \pm anatase grains were not recovered from the basal carbonate lutite context layer (Appendix V), so these grains do not appear to have been reworked from the subjacent strata. The granular and buff rutile \pm anatase grains may represent epiclastic detritus and/or impact ejecta. Granular rutile \pm anatase grains were not recovered from Bee Gorge samples BB and 92058 from the Bacon Bore and Wittenoom Gorge localities, respectively, both sites being near the Pilbara craton (see Fig. 4 for locations), so if these grains in Bee Gorge samples 96714A and 96714B are epiclastic detritus, then they may have been derived from a source other than the Pilbara craton. None of the Raman spectra for about a dozen granular rutile \pm anatase grains show any evidence for the TiO₂ II phase. At present, other than their spatial association with the spherules, there is no evidence that the granular rutile \pm anatase grains are impact ejecta. However, more work (e.g., petrographic, micro-Raman spectroscopy, SEM/EDX) is needed to determine the origin of the granular rutile \pm anatase grains.

Buff rutile \pm anatase grains were recovered from the spherule layer and both of the context layers in Bee Gorge sample BB from the Bacon Bore locality, but not from Bee Gorge context sample 92058 from the Wittenoom Gorge locality (see Fig. 4 for locations; Appendix V). However, only three rutile grains were identified in Bee Gorge context sample 92058 (Appendix V). Given these results for Bee Gorge sample BB, it is possible that the buff rutile \pm anatase grains in the spherule layer parts of Bee Gorge samples 96714A and 96714B may be epiclastic detritus derived from the Pilbara craton. However, if these grains merely represent epiclastic detritus from the Pilbara craton, then the absence of chrome spinel, tourmaline, and zircon grains in Bee Gorge samples 96714A and 96714B (Table 62) is puzzling, especially given the fact that these three phases are present in Bee Gorge sample BB (Table 63). As discussed in more detail

below, the TiO₂ II phase was identified in five buff rutile \pm anatase grains from the upper spherule/lutite sublayers subdivisions combined of Bee Gorge samples 96714A and 96714B. If the buff rutile \pm TiO₂ II grains in Bee Gorge samples 96714A and 96714B are impact ejecta with the TiO₂ II phase being syngenetic with respect to the Bee Gorge spherule layer, then the absence of chrome spinel, tourmaline, and zircon grains in the two samples may simply reflect the fact that the sediments at the Tom Price locality (Fig. 4) were deposited farther from the Pilbara craton in deeper water (Simonson et al., 1993a), and therefore, the samples may contain little, if any, sand-sized detritus that was derived from the Pilbara craton (see Simonson, 1992; Hassler et al., 2000, 2005). No data are available, however, for the original size fraction distribution of acid-insoluble material for Bee Gorge samples 96714A and 96714B (Table 10; see Appendix L).

For each of the Bee Gorge samples 96714A and 96714B, the spherule layer was divided into three stratigraphic subdivisions that were processed and analyzed separately (see Appendices D, L, and V). The lowermost spherule-rich sublayer (Lspsl) appears to be rippled (B. M. Simonson, personal communication, 2002), and at the Tom Price locality (Fig.4; cf., Hassler et al., 2000, their Fig. 1), the rippled spherule-rich bedforms were interpreted to be a result of the reworking of a fallout impact spherule layer by impact-generated tsunami waves (Hassler et al., 2000). For Bee Gorge samples 96714A and 96714B combined, 948 granular rutile \pm anatase grains and a single light gray non-granular rutile + anatase grain were recovered from the 63-125 µm size fraction of the lowermost spherule-rich sublayer (Lspsl), and these grains comprise ~99% of the heavy mineral grains in this sublayer (Lspsl), the granular rutile \pm anatase grains have the highest abundance (>31,000 grains/kg) of any heavy mineral phase in the Carawine,

Jeerinah, Bee Gorge, and Monteville samples (Table 62). The number of granular rutile \pm anatase grains and their percentage of the total number of rutile \pm anatase grains both decrease markedly upsection in the spherule layer. For Bee Gorge samples 96714A and 96714B combined, the granular rutile \pm anatase grains comprise 99.9% of the total number of rutile \pm anatase grains in the lowermost spherule-rich sublayer (Lspsl), whereas they comprise eight of the 10 (80%) rutile \pm anatase grains in the spherule-bearing lutite sublayer (Splsl), and about a dozen of the 96 (~13%) rutile \pm anatase grains in the upper spherule/lutite sublayers subdivision.

As discussed above, the origin of the granular rutile \pm anatase grains is unknown. If these grains represent impact ejecta, then it appears that the bulk of these grains arrived concurrently with the bulk of the spherules. If the lowermost spherule-rich sublayer (Lspsl) represents a fallout impact spherule layer that was reworked by impact-generated tsunami waves (see Hassler et al., 2000), and the granular rutile \pm anatase grains represent epiclastic detritus, then it appears that the bulk of these grains were brought to this site by the waves and/or currents that reworked and rippled the spherules to form the lowermost spherule-rich sublayer.

For each of the Bee Gorge samples 96714A and 96714B, the depositional modes of the mm-scale spherule-bearing lutite sublayer (Splsl) and the upper spherule/lutite sublayers (Usplsl) subdivision (see Appendix D) are not well understood (B. M. Simonson, personal communication, 2014). The spherule-bearing lutite sublayer (Splsl), which directly overlies the lowermost spherule-rich sublayer (Lspsl), consists of ~10-15 vol% of spherules that are dispersed in a lutite matrix, and the spherules appear to be a little smaller on average than those in the lowermost spherule-rich sublayer (Appendix D). For Bee Gorge samples 96714A and 96714B combined, there are only 30 heavy mineral grains in the spherule-bearing lutite sublayer (SplsI; Table 62), and anatase \pm K-feldspar and rutile \pm anatase comprise 90% (n = 27) of these grains (see Figs. 168 and 179; Appendix V). The heavy mineral assemblage for the spherule-bearing lutite sublayer (SplsI) is basically similar to that of the basal carbonate lutite context layer (Bcl), with the addition of a few granular rutile \pm anatase grains. These heavy mineral results would be consistent with a scenario in which material that had been put in suspension by the impact-generated waves and/or currents was deposited to form the spherule-bearing lutite sublayer (SplsI) immediately after the waves and/or currents had reworked the fallout impact spherule layer to form the lowermost spherule-rich sublayer (LspsI).

For each of the Bee Gorge samples 96714A and 96714B, the upper spherule/lutite sublayers subdivision consists of four sublayers, each ≤ 2 mm thick, that are individually described in Appendix D. For each of these samples, the upper spherule/lutite sublayers subdivision was processed as a single unit (Appendices D and L), so the distribution of the heavy mineral grains within the four sublayers of this subdivision is unknown. Furthermore, there is still uncertainty as to the details of the depositional modes for the four sublayers in this subdivision (B. M. Simonson, personal communication, 2014). However, for each of the Bee Gorge samples 96714A and 96714B, the heavy mineral assemblage of the upper spherule/lutite sublayers subdivision shows an important difference with those for the subjacent subdivisions of the spherule layer and the basal carbonate lutite context layer (see sections 4.2.5.3 and 4.2.5.4).

For each of the Bee Gorge samples 96714A and 96714B, buff rutile \pm anatase grains were only recovered from the upper spherule/lutite sublayers subdivision. Therefore, the buff rutile \pm anatase grains arrived at this site after the deposition of the bulk of the granular rutile \pm anatase grains. For Bee Gorge samples 96714A and 96714B

combined, the buff rutile \pm anatase grains (n = 66) comprise ~69% of the total (n = 96) rutile \pm anatase grains in the upper spherule/lutite sublayers subdivision (Appendix V). Micro-Raman spectroscopy shows that a minimum of five rutile grains, all buff in color, of this population (n = 96) contain the TiO₂ II phase (see Tables 50 and 51). Furthermore, the high abundances (>2,100 grains/kg) of rutile \pm anatase grains in the upper spherule/lutite sublayers subdivisions of Bee Gorge samples 96714A and 96714B (Table 62) attest to a second large influx of rutile \pm anatase grains into the spherule layer that occurred after the deposition of the spherule-bearing lutite sublayer (Splsl).

Of all the spherule layer samples in this study that contain rutile + TiO_2 II grains, the heavy mineral assemblages of the spherule layer subdivisions in Bee Gorge samples 96714A and 96714B provide the clearest evidence that the TiO_2 II phase in the rutile grains is syngenetic with respect to its host spherule layer. The fact that chrome spinel, tourmaline, and zircon grains were not recovered from the 63-125 µm size fractions of Bee Gorge samples 96714A and 96714B (Table 63), suggests that the samples contain little, if any, epiclastic detritus (see Hassler et al., 2005), but more work is needed on these samples to evaluate this hypothesis. For each of the Bee Gorge samples 96714A and 96714B, the key to the interpretation that the TiO_2 II phase in the buff rutile grains is syngenetic with respect to the Bee Gorge spherule layer is the confinement of the buff rutile \pm TiO₂ II grains to the upper spherule/lutite sublayers subdivision.

In a similar manner, in the dual-layer K-Pg boundary event deposits at the Western Interior and Demerara Rise localities, shock-metamorphosed grains are concentrated in the upper or uppermost parts of the spherule layers (see section 1.2.3). These K-Pg couplets are essentially fallout deposits (Bohor and Glass, 1995, and references therein; Schulte et al., 2009). In contrast, the Bee Gorge (Wittenoom) spherule

layer at the Tom Price locality (Fig. 4) has been interpreted as a reworked fallout impact spherule layer (e.g., Hassler et al., 2000). However, the thicknesses of the K-Pg couplet deposits at the Western Interior and Demerara Rise localities (see section 1.2.3) are comparable to those for the Bee Gorge (Wittenoom) spherule layer parts of samples 96714A and 96714B (Appendix D). Furthermore, near Beloc, Haiti, in a normallygraded, K-Pg couplet deposit that is 46 cm thick and consists largely of spherule-bearing clay, the proportion of shock-metamorphosed quartz grains increases with stratigraphic height, being highest in the uppermost stratigraphic interval (Kring et al., 1994). Finally, in deep-sea cores from two sites on the continental slope off New Jersey, unmelted impact ejecta, including shock-metamorphosed grains, are concentrated in the upper parts of cm-scale, tektite-bearing impact ejecta layers; these layers are interpreted to be parts of the distal impact ejecta layer that is related to the late Eocene Chesapeake Bay impact structure (Glass et al., 1998).

Using the K-Pg couplet deposits and the upper Eocene tektite-bearing impact ejecta layer that is present on the continental slope off New Jersey (see above) as models, for each of the Bee Gorge samples 96714A and 96714B, the buff rutile + TiO₂ II grains in the upper spherule/lutite sublayers subdivision are interpreted as unmelted shockmetamorphosed rutile grains with the TiO₂ II phase being syngenetic with respect to the spherule layer. Therefore, these rutile + TiO₂ II grains provide physical evidence that confirms an impact origin for the Bee Gorge (Wittenoom) spherule layer. The buff rutile grains in the upper spherule/lutite sublayers subdivision are proposed to represent unshocked impact ejecta that accompanied the shock-metamorphosed buff rutile + TiO₂ II grains. The interpretation that the buff rutile \pm TiO₂ II grains represent impact ejecta that are related to the impact event that led to the formation of the Bee Gorge

(Wittenoom) spherule layer is consistent with the high abundances (>2,100 grains/kg) of rutile \pm anatase grains in the upper spherule/lutite sublayers subdivisions of Bee Gorge samples 96714A and 96714B (see Table 62).

Bee Gorge context sample 92058 was collected ~1 m stratigraphically above the Bee Gorge spherule layer (Table 6) at the Wittenoom Gorge/Cathedral Pool locality, and it is closer to the Pilbara craton than Bee Gorge samples 96714A and 96714B from the Tom Price locality (Fig. 4). Micro-Raman spectroscopy shows that at least some of the anatase, monazite, and xenotime crystals in Bee Gorge context sample 92058 are of secondary origin, and it is possible that monazite and xenotime are mostly, or entirely, of secondary origin. More work is needed to determine the mode(s) of origin of the monazite and xenotime, but if the phases are of secondary origin, then the primary heavy mineral assemblage of Bee Gorge context sample 92058 may consist of an actinolite grain and a few anatase and rutile grains (see Fig. 187).

If the monazite and xenotime phases, which may be mostly or entirely secondary, are ignored, then the heavy mineral assemblage of Bee Gorge context sample 92058 is similar to those for the basal carbonate lutite context layers (Bcl) in Bee Gorge samples 96714A and 96714B (Table 63). In Bee Gorge context sample 92058, there are no granular rutile grains like those observed in the spherule layer parts of Bee Gorge samples 96714A and 96714B, and none of the rutile grains are amber, reddish amber, peach, or buff in color (Appendix V). Like Bee Gorge samples 96714A and 96714B, no chrome spinel, tourmaline, or zircon grains were identified in Bee Gorge context sample 92058 (see Fig. 187). The absence of granular and buff rutile grains in Bee Gorge context sample 92058 supports the hypothesis that the granular and buff rutile grains in the Bee Gorge spherule layer (samples 96714A and 96714B) at the Tom Price locality (Fig. 4)

have an extrabasinal provenance, i.e., they may be epiclastic detritus and/or impact ejecta.

The heavy mineral assemblages for Bee Gorge context sample 92058 from the Wittenoom Gorge locality and the basal carbonate lutite context layers (Bcl) in Bee Gorge samples 96714A and 96714B from the Tom Price locality, are distinctly different than those for context layers BB (#1) and BB (#2) in Bee Gorge sample BB from the Bacon Bore (BB) locality (Table 63; see Fig. 4 for locations). The Bacon Bore and Wittenoom Gorge localities are comparable distances from the Pilbara craton (see Fig. 4), so this variability of the heavy mineral assemblages is not simply a function of proximity to the Pilbara craton. This variability may be related to differences in provenance for the heavy mineral grains and/or paleobathymetry.

5.2.5 Monteville Spherule Layer and Context Samples

Monteville context sample T149-1 is a fine-grained carbonate-rich rock (Table 10) that was collected ~1 m stratigraphically below the Monteville spherule layer (Table 7), and its three heavy mineral phases (Table 63) may be largely of secondary origin. A few of the anatase grains may be detrital, but more work is needed to determine the mode(s) of origin of the anatase. Micro-Raman spectroscopy shows that two oxidized pyrite crystals have chlorite on their surfaces, and these data, along with the subangular nature and blocky-to-irregular shapes of the chlorite grains, suggest a secondary origin for the chlorite. The mode of origin of the monazite \pm anatase grains is not clear, but again, the subangular nature and blocky-to-irregular shapes of many of the grains, suggest a secondary origin for the monazite \pm anatase grains.

Chrome spinel, rutile, tourmaline, or zircon grains were not identified in Monteville context sample T149-1, but a few chrome spinel and rutile grains were identified in Monteville context sample II67-1B (Table 62; see below) that was collected from above the spherule layer (Table 7). One or more of these four phases typically occur in one or more of the Carawine and Bee Gorge context samples or layers (Table 62; Fig. 187). These results again demonstrate the variability of the heavy mineral assemblages for the context samples or layers that may be due to differences in provenance, proximity to the craton, or paleobathymetry. The heavy mineral results suggest that Monteville context sample T149-1 contains very little, if any, sand-sized epiclastic detritus that was derived from the Kaapvaal craton. This hypothesis is supported by the acid-insoluble results that show that ~5 wt% of the acid-insoluble material in Monteville context sample T149-1 is in the >63 μ m size fraction (Table 10). Furthermore, this hypothesis is in accordance with the interpretation that the Monteville Formation represents a highstand deposit within a second-order sequence (Sumner and Beukes, 2006; Knoll and Beukes, 2009).

Sample U63-1 is from the intraclast-rich, lower part of the Monteville spherule layer (Appendix E). The heavy mineral assemblage of Monteville spherule layer sample U63-1 consists of the same phases that are present in Monteville context sample T149-1 that was collected ~1 m below the spherule layer, as well as a few grains of rutile \pm anatase, rutile + unidentified, and tourmaline \pm anatase (Table 62; Fig. 194). The difference in the heavy mineral assemblages for the two samples may reflect the fact that Monteville spherule layer sample U63-1 is larger (593.2 g) than Monteville context sample T149-1 (214.3 g) and/or the fact that the heavy mineral abundance for sample U63-1 is higher by a factor of ~2.6 than that for sample T149-1 (Table 62).

Anatase is by far the predominant heavy mineral phase in Monteville spherule layer sample U63-1 (Table 63). Micro-Raman spectroscopy shows that at least some of the anatase is of secondary origin since anatase occurs as matrix material on the surfaces of rutile, tourmaline, K-feldspar, quartz, and secondary iron oxide/oxyhydroxide grains. Furthermore, as noted in section 4.2.6.1, a Raman spectrum for a spherule from Monteville spherule layer sample U63-1 has bands at wavenumbers that match those of anatase, again suggesting that at least some of the anatase in this sample is of secondary origin. More work is needed to determine the relative proportion of detrital and secondary anatase grains in Monteville spherule layer sample U63-1. Like Monteville context sample T149-1, the subangular nature and blocky-to-irregular shapes of many of the monazite \pm anatase grains in Monteville spherule layer sample U63-1, suggest a secondary origin for these grains.

All the rutile \pm anatase grains (n = 23) that were recovered in the 63-250 µm size fraction of Monteville spherule layer sample U63-1 were analyzed by micro-Raman spectroscopy, and ~87% (n = 20) of the grains are very light buff-to-buff in color. None of the Raman spectra show evidence for the TiO₂ II phase. These results for the rutile \pm anatase grains are remarkably similar to those for Carawine spherule layer sample 42-1A (see section 4.2.2.5) from the Ripon Hills area (see Fig. 4), that has a comparable mass (557.5 g) and number of rutile \pm anatase grains (n = 29), suggesting a possible link between the Monteville and Carawine spherule layers (see section 5.4). The significance of the buff rutile \pm anatase grains and the absence of rutile + TiO₂ II grains in Monteville spherule layer sample U63-1 will be discussed below in the section concerning Monteville spherule layer sample V111. The rutile + unidentified grain in Monteville spherule layer sample U63-1 is similar to those in three of the Carawine spherule layer samples from the Ripon Hills area (see Appendices S and W), but the origin of these grains is unknown, so the significance of this commonality is not clear.

Simonson et al. (1999) interpreted the lower part of the Monteville spherule layer at the Monteville farm locality as being deposited by a high-energy event that had caused erosion of the substrate. The absence of chrome spinel and zircon grains, as well as the low abundances of rutile \pm anatase and tourmaline \pm anatase grains in sample U63-1 (Table 62; section 4.2.6.1), which is from the lower part of the Monteville spherule layer at this locality (Fig. 5), suggest that this high-energy event may have transported only a small amount of epiclastic, sand-sized detritus that was derived from the Kaapvaal craton. In Monteville spherule layer sample U63-1, ~5 wt% of the acid-insoluble material is in the 63-250 µm size fraction (Table 10), consistent with this hypothesis, but more work is needed to determine the amount of epiclastic sand-sized detritus in the lower part of the Monteville spherule layer at the Monteville farm locality (Fig. 5).

Sample V111 is from the upper part of the Monteville spherule layer (Table 7), and its heavy mineral assemblage consists of all the phases that occur in Monteville spherule layer sample U63-1, except for rutile + unidentified, as well as several additional phases that occur in trace-to-minor amounts (Table 62; Figs. 194 and 199). Sample V111 is smaller (219.9 g) than sample U63-1 (593.2 g), so this difference in their heavy mineral assemblages may reflect the fact that the heavy mineral abundance (number of grains/kg) for sample V111 is higher by a factor of ~6.2 than that for sample U63-1 (Table 62). Like sample U63-1, anatase is the most abundant heavy mineral phase in sample V111 (Table 63). Micro-Raman spectroscopy shows that, in addition to single grains of anatase, anatase is present as matrix material on the surfaces of pyrite, chrome spinel, and rutile grains, and anatase occurs in some of the Raman spectra for chlorite, monazite, tourmaline, and zircon grains. More work is needed to determine the mode(s) of origin of the anatase \pm K-feldspar grains, but the micro-Raman data, especially those for the pyrite and chlorite grains, suggest that at least some of the anatase grains are of secondary origin. Like Monteville context sample T149-1 and Monteville spherule layer sample U63-1, both of which are stratigraphically below sample V111, the subangular-to-angular nature and blocky-to-irregular shapes of the monazite \pm anatase grains in Monteville spherule layer sample V111 suggest a secondary origin for these grains. More work is needed to determine the mode(s) of origin of the monazite \pm anatase grains in Monteville samples T149-1, U63-1, and V111 (Table 63).

The physical properties (see Appendix W) of the chrome spinel, rutile \pm anatase, and zircon grains in sample V111 from the upper part of the Monteville spherule layer are more similar to those for grains of these phases in the Carawine and Jeerinah spherule layers, than in the Bee Gorge spherule layer. The chrome spinel grains in Monteville spherule layer sample V111 are dark gray-to-black, similar to those in the Carawine and Jeerinah spherule layers (see Appendices S and U), not dark brownish black as in Bee Gorge sample BB (see Appendix V). Some rutile \pm anatase grains in Monteville spherule layer sample V111 are various shades of amber, similar to those in the Carawine and Jeerinah spherule layers, but amber rutile \pm anatase grains were not identified in the Bee Gorge spherule layer. There are pink, champagne, translucent-to-opaque, and opaque zircon grains in Monteville spherule layer sample V111, similar to those in the Carawine and/or Jeerinah spherule layers, but no such grains were identified in any of the Bee Gorge samples (see Appendix V). Clinopyroxene occurs in trace amounts in Monteville spherule layer sample V111, as well as in the Carawine and Jeerinah spherule layers, but it was not identified in the Bee Gorge samples (Table 63). These results support the proposed correlation (see Simonson et al., 2009a, 2009b) of the Monteville spherule layer with the Carawine and Jeerinah spherule layers (see section 5.4).

For Monteville spherule layer sample V111, \sim 54% (n = 195) of the estimated total number (n = 362) of rutile \pm anatase grains in the 63-250 µm size fraction were analyzed by micro-Raman spectroscopy. Raman spectra for 10 grains that are very light buff-tobuff and blocky (Table 52) show bands at wavenumbers that match those of rutile + TiO₂ II \pm anatase. The rutile + TiO₂ II \pm anatase grains comprise a minimum of ~2.8% of the estimated total number (n = 362) of rutile \pm anatase grains in the 63-250 μ m size fraction of Monteville spherule layer sample V111, a value that is comparable to those for Carawine spherule layer sample X38-2 (~3.3%) and Jeerinah spherule layer sample X21-1 (\sim 1%), but lower than that (\sim 5.2%) for the combined upper spherule/lutite sublayers subdivisions of Bee Gorge samples 96714A and 96714B. These results are consistent with the proposed correlation (see Simonson et al., 2009a, 2009b) of the Monteville spherule layer with the Carawine and Jeerinah spherule layers, instead of with the Bee Gorge spherule layer. Furthermore, this result may explain the fact that even though all (n = 23) the rutile \pm anatase grains in the 63-250 µm size fraction of sample U63-1 from the lower part of the Monteville spherule layer were analyzed by micro-Raman spectroscopy, no evidence for the TiO_2 II phase was found in any of the grains. As a first approximation, if 2.8% of the rutile \pm anatase grains in Monteville spherule layer sample U63-1 were expected to contain the TiO₂ II phase, then <1 (~0.6) rutile ± anatase grain in sample U63-1 would contain the TiO_2 II phase, so the results for sample U63-1 are not surprising.

The heavy mineral results are in accord with the sedimentological data that suggest that the Monteville spherule layer was deposited by more than one event that probably involved different processes (see Simonson et al., 1999). The lower part of the Monteville spherule layer, from which sample U63-1 was collected, contains material that is interpreted to have been eroded from the basinal substrate by impact-related waves and/or currents (Simonson et al., 1999). For sample U63-1, 5.3 wt% of the acid-insoluble material is in the 63-250 μ m size fraction, a value that is comparable to that (4.8 wt%) for the acid-insoluble material in the same size fraction in Monteville context sample T149-1 that was collected ~1 m below the Monteville spherule layer (Table 10).

In terms of phases present, the heavy mineral assemblages of Monteville context sample T149-1 and Monteville spherule layer sample U63-1 are similar, with the exception that rutile \pm anatase and tourmaline grains were identified in spherule layer sample U63-1, but they were not identified in context sample T149-1 (Table 63). The presence of rutile \pm anatase and tourmaline grains in Monteville spherule layer sample U63-1 may reflect the fact that this sample has a higher abundance of heavy mineral grains as compared to that of Monteville context sample T149-1 (Table 62). However, this difference in abundance largely reflects the much higher abundance of anatase grains in Monteville spherule layer sample U63-1 (Table 62), and this difference in abundance can not be fully evaluated until additional work determines the relative proportion of detrital and secondary anatase grains in sample U63-1. The acid-insoluble and heavy mineral results suggest that only a small amount of the material in the 63-250 µm size fraction in the lower part of the Monteville spherule layer at the Monteville farm locality (see Fig. 5) may have an extrabasinal provenance.

At the Monteville farm locality, the upper part of the Monteville spherule layer, in contrast to its lower part, consists mainly of carbonate sand and a much smaller amount of sand-sized spherules (Simonson et al., 1999). The symmetrical bedforms and the nature of the cross-lamination that are present in the upper part of the Monteville spherule layer indicate that it was deposited during oscillatory or wave movement of the water

column, and it is possible that unidirectional currents were also involved in the deposition of the upper part of the spherule layer (Simonson et al., 1999). For subsample 219.9 g that was used to characterize the heavy mineral assemblage of sample V111 (Table 62) that is from the upper part of the Monteville spherule layer, ~30.4 wt% of the acidinsoluble material is in the 63-250 μ m size fraction, as calculated from data given in Appendix M. This value is much higher than those for the acid-insoluble material in the same size fraction for Monteville context sample T149-1 (4.8 wt%) and sample U63-1 (5.3 wt%) that is from the lower part of the Monteville spherule layer (Table 10).

The heavy mineral abundance for Monteville spherule layer sample V111 is much higher than those for samples T149-1 and U63-1 (Table 62). Like sample U63-1 from the lower part of the Monteville spherule layer, sample V111 contains anatase, monazite, rutile, and tourmaline, but each of these phases has a much higher abundance in sample V111 than in sample U63-1 (Table 62). Actinolite, anglesite, chrome spinel, clinopyroxene, and zircon grains are present in trace-to-minor amounts in sample V111, but these phases were not identified in Monteville context sample T149-1 or Monteville spherule layer sample U63-1 (Table 63), both of which are subjacent to sample V111. The presence of these phases in Monteville spherule layer sample V111 may reflect the much higher abundance of heavy mineral grains in this sample (Table 62), and/or the possibility that these phases have an extrabasinal provenance.

No detailed description of any quartzo-feldspathic detritus from the Monteville spherule layer at the Monteville farm locality (see Fig. 5) was given in Simonson et al. (1999), so the amount of epiclastic sand-sized detritus in the spherule layer at this locality is unknown. However, for sample V111 from the upper part of the Monteville spherule layer, the acid-insoluble results for the 63-250 µm size fraction, the high abundance of

heavy mineral grains, and the presence of phases that were not identified in the underlying samples T149-1 and U63-1, would be consistent with the presence of epiclastic sand-sized detritus of extrabasinal origin in this sample. More work is needed to determine the amount of epiclastic sand-sized detritus of extrabasinal origin in both the upper and lower parts of the Monteville spherule layer at the Monteville farm locality (see Fig. 5).

In addition to a possible epiclastic origin, it is possible that at least some of the acid-insoluble grains in the 63-250 μ m size fractions of Monteville spherule layer samples U63-1 and V111 are impact ejecta, and given the much higher abundance of heavy mineral grains in sample V111 as compared to that for sample U63-1 (Table 62), it is possible that sample V111 contains more impact ejecta in the 63-250 μ m size fraction than sample U63-1. The differences in the heavy mineral assemblages and the rutile populations between Monteville spherule layer samples V111 and U63-1 suggest that the rutile + TiO₂ II grains in sample V111 may be impact ejecta related to the impact event that led to the formation of the Monteville spherule layer. All the rutile + TiO₂ II grains that have been identified in the Carawine, Jeerinah, Bee Gorge, and Monteville spherule layers are shades of buff, and it has been argued (see section 5.2.4) that the buff rutile \pm anatase grains in the upper spherule/lutite sublayers subdivisions of Bee Gorge samples 96714A and 96714B may be unshocked impact ejecta.

In sample U63-1 from the lower part of the Monteville spherule layer, the buff rutile grains are mostly blocky or irregular in shape. If these buff rutile grains likewise represent unshocked impact ejecta that are related to the impact event that led to the formation of the Monteville spherule layer, then the absence of chrome spinel and zircon grains in sample U63-1 (Table 63) is not as puzzling as it would be if the buff rutile grains are epiclastic in origin. Furthermore, the presence of rutile + TiO₂ II grains in sample V111 from the upper part of the Monteville spherule layer is similar to their stratigraphic occurrence in the upper spherule/lutite sublayers subdivisions in Bee Gorge samples 96714A and 96714B (Table 62). Again, the stratigraphic distribution of the rutile + TiO₂ II grains in the Monteville spherule layer at the Monteville farm locality (see Fig. 5) may be analogous to the distribution of shock-metamorphosed grains in both the K-Pg couplet deposits and the upper Eocene tektite-bearing impact ejecta layer that is present on the continental slope off New Jersey (see discussion for samples 96714A and 96714B in section 5.2.4). As discussed above, the heavy mineral data are consistent with the proposed correlation (see Simonson et al., 2009a, 2009b) of the Monteville spherule layer with the Carawine and Jeerinah spherule layers, instead of with the Bee Gorge (Wittenoom) spherule layer. However, for both the Monteville (samples U63-1 and V111) and Bee Gorge (samples 96714A and 96714B) spherule layers, that differ significantly in thickness, modes of deposition, and probably age, the heavy mineral assemblages and the physical properties of the rutile \pm anatase grains suggest that the TiO₂ II phase is syngenetic with respect to its host spherule layer.

Context sample II67-1B (616.7 g) was collected ~20 cm above the Monteville spherule layer (Table 7). The heavy mineral assemblage for this context sample consists of only 22 grains that are all in the 63-125 μ m size fraction (Fig. 219), in sharp contrast to the heavy mineral assemblage and abundance for subsample 219.9 g of Monteville spherule layer sample V111 (Table 62). For Monteville context sample II67-1B, 6.9 wt% of the acid-insoluble material (3.4 wt%) is in the >63 μ m size fraction (Table 10), whereas for subsample 219.9 g of Monteville spherule layer sample V111, ~30.8 wt% of the acid-insoluble material (10.4 wt%) is in the >63 μ m size fraction (Appendix M; Table 62). The acid-insoluble weight data show that Monteville spherule layer sample V111 has a higher proportion of sand-sized (>63 μ m) material than Monteville context sample II67-1B, and these data are consistent with the difference in the heavy mineral abundances for the two samples (Table 62).

The heavy mineral assemblage for Monteville context sample II67-1B consists of only three phases, anatase (n = 18), chrome spinel (n = 3), and rutile (n = 1), whereas that for Monteville spherule layer sample V111 contains at least 10 phases (Table 62). These results are consistent with spherule layer sample V111 having a higher weight percent value of sand-sized (>63 μ m) material and a much higher abundance of heavy mineral grains than context sample II67-1B. Raman spectra show no evidence for anatase on the surfaces of the three chrome spinel grains and single rutile grain from Monteville context sample II67-1B. These results suggest that the anatase grains in this context sample may be largely of detrital origin. The single rutile grain is light orange amber in color, and a Raman spectrum for this grain shows no evidence for the TiO₂ II phase.

For the 63-250 μ m size fractions of Monteville context samples II67-1B and T149-1 combined, there is a single rutile grain, and tourmaline and zircon grains were not recovered (see sections 4.2.7.1 and 4.2.7.2). These results suggest that the rutile, tourmaline, and zircon grains that are present in Monteville spherule layer samples U63-1 and/or V111 largely have an extrabasinal origin. At the Monteville farm locality (see Fig. 5), buff rutile ± anatase grains are confined to the Monteville spherule layer samples, and rutile + TiO₂ II ± anatase grains were identified only in the upper sandy part of the Monteville spherule layer. The differences in the heavy mineral assemblages and abundances between the Monteville context and spherule layer samples (Table 62) are consistent with the interpretation that the host strata for the Monteville spherule layer

were deposited below storm wave base in a low-energy, deep-shelf or upper slope paleoenvironment, whereas the spherule layer was deposited by high-energy events that, at least locally, transported extrabasinal epiclastic sand-sized detritus that was likely derived from the Kaapvaal craton (see Simonson et al., 1999). Furthermore, the rutile + TiO₂ II grains in the upper part of the Monteville spherule layer suggest that at least some of the heavy mineral grains in this spherule layer represent impact ejecta that are related to the impact event that led to the formation of the Monteville spherule layer.

5.2.6 Grænsesø Spherule Layer and Context Samples

The heavy mineral assemblages of Grænsesø spherule layer samples GL8904-1, GL8904-3, and GL8904-4 are quite similar to each other in terms of phases present and the physical properties of the phases. For each of the samples, rutile \pm anatase, tourmaline, and zircon grains combined comprise ~96.4-99.3% of the 63-125 µm size fraction (Table 63) and ~95.6-99.4% of the 63-250 µm size fraction, and the absolute number of these grains combined is far higher than for any other sample in this study (Table 62). Rutile, tourmaline, and zircon have very high chemical and mechanical stabilities (see Hubert, 1962; Pettijohn, 1975; Morton and Hallsworth, 2007, and references therein), and these grains, as well as the barite and chrome spinel grains (Table 63), are typically subrounded-to-well-rounded. These results suggest that the heavy mineral grains were primarily derived from reworked sediment.

Raman spectra for ~1.9% (n ~312) of the estimated total number of rutile \pm anatase grains (n = 16,205) in the 63-250 µm size fractions of Grænsesø spherule layer samples GL8904-1, GL8904-3, and GL8904-4, as well as for 45 rutile \pm anatase grains from Grænsesø spherule layer sample GL8904-2, show no evidence for the TiO₂ II phase.

These Raman spectra were obtained on rutile \pm anatase grains with different physical properties, including buff-colored grains.

Raman spectra for ~3.3% (n ~107) of the estimated total number of zircon grains (n = 3,263) in the 63-250 μ m size fractions of Grænsesø spherule layer samples GL8904-1, GL8904-3, and GL8904-4, as well as for 8 zircon grains from Grænsesø spherule layer sample GL8904-2, do not show bands at wavenumbers that match those of baddeleyite or three other polymorphs of ZrO₂ as given in Wittmann et al. (2006), or reidite as given in Knittle and Williams (1993), van Westrenen et al. (2004), and Wittmann et al. (2006). These Raman spectra were obtained on zircon grains with different physical properties, including white translucent-to-opaque, and white opaque grains, some of which are well-rounded. The white, translucent-to-opaque and opaque zircon grains have Raman spectral characteristics, i.e., broadening, decrease in intensity, and shift to lower frequency wavenumbers for several of the bands, similar to those for similar zircon grains in Carawine spherule layer sample X38-2 (see section 4.2.2.6). The well-rounded nature of some of these grains, absence of reidite or baddeleyite, and their Raman spectral characteristics (see Nasdala et al., 1995), suggest that they are epiclastic, metamict zircons.

The heavy mineral results for samples GL8904-1, GL8904-3, and GL8904-4 support the hypothesis (see section 5.5) that the sampled interval of the Grænsesø spherule layer was deposited by a single event. For the three samples, the proportions of rutile: tourmaline: zircon grains in the 63-125 µm size fractions are quite similar. Furthermore, for each of these three phases, the abundance (number of grains/kg) shows a sharp decrease from sample GL8904-1 from the lower part of the Grænsesø spherule layer to sample GL8904-3 from the middle part of the Grænsesø spherule layer, and a

lesser decrease from sample GL8904-3 to sample GL8904-4 from the upper part of the Grænsesø spherule layer (Table 62). As discussed below (see section 5.5), the sampled interval of the Grænsesø spherule layer is interpreted as a debris-flow deposit, and the heavy mineral results raise the possibility that the chrome spinel, rutile, tourmaline, and zircon grains may have been settling through the debris flow at some time during its movement and/or emplacement.

The heavy mineral assemblages for Grænsesø context samples SP3 and GL8904-6 contain several of the same phases with similar properties as those observed in the Grænsesø spherule layer samples, suggesting a similar provenance, but there is one noticeable difference. For Grænsesø context sample SP3 that was collected a few meters stratigraphically below the Grænsesø spherule layer, rutile + tourmaline grains comprise ~95.7% (n = 267) of the 63-250 μ m size fraction (see section 4.2.9.1), and these grains were not observed in the Grænsesø spherule layer samples or Grænsesø context sample GL8904-6 that was collected from a dolomite bed that is <1 m stratigraphically above the Grænsesø spherule layer. Furthermore, the tourmaline grains (n = 5) in Grænsesø context sample SP3 are typically subangular, whereas those in the Grænsesø spherule layer samples are typically subrounded-to-well-rounded, but this difference may simply reflect the very low number of tourmaline grains in Grænsesø context sample SP3.

More work is needed on the rutile + tourmaline and tourmaline grains in Grænsesø context sample SP3 in order to determine whether or not these grains have a different provenance than the rutile and tourmaline grains in the Grænsesø spherule layer samples. Raman spectra for ~60% (n = 25) of the rutile \pm anatase grains (n = 42) in the two Grænsesø context samples show no bands at wavenumbers that match those of the TiO₂ II phase. These results are in accordance with those for the Grænsesø spherule layer

samples that suggest that rutile $+ \text{TiO}_2$ II grains are rare, if present at all, in the source area(s) for the heavy mineral grains.

5.2.7 White Opaque Zircon Grains

Varicolored, translucent-to-opaque or opaque zircon grains that are referred to as white opaque zircon grains (see section 4.2.1) are present in the Carawine, Jeerinah, Monteville, and Grænsesø spherule layers. No zircon grains were recovered from Bee Gorge samples 96714A and 96714B (Table 63) that contain the Bee Gorge (Wittenoom) spherule layer. No white opaque zircon grains were recovered from sample BB that contains the Bee Gorge (Wittenoom) spherule layer, or any of the context samples or layers used in this study. However, these results may partly reflect the fact that only three zircon grains were recovered from the Bee Gorge spherule layer (BB (sl)) in sample BB, and only 0-7 zircon grains were recovered for a given context sample or layer (Table 62). White opaque zircon grains occur in four spherule layers that are widely separated in space and/or time, and their absence in the context samples or layers suggests that these grains have an extrabasinal origin.

The analytical results show no definitive evidence for shock metamorphism of the white opaque zircon grains, but suggest that these grains show varying degrees of metamictization. XRD patterns for ~84 of these grains from the Carawine and Grænsesø spherule layers contain lines that match those of zircon, but the patterns show no evidence for baddeleyite or reidite. As viewed with a binocular microscope, the white opaque zircon grains appear to be monocrystalline grains. However, their D-S patterns consistently exhibit varying degrees of streakiness, indicating that the grains actually have varying degrees of internal disorder (see Hörz and Quaide, 1973).

TEM analysis of a white opaque zircon grain from Carawine spherule layer sample X38-2 that shows arcs on its D-S pattern supports this interpretation, showing this grain to be strongly metamict with asterism at the micron-scale, but showing no evidence for shock metamorphism (H. Leroux, personal communication, 2010). SEM/EDX analyses of six white opaque zircon grains that show arcs on their D-S patterns support their identification as zircons, and show a polygonal network of cracks on two of the grains, but reveal no evidence for shock-induced planar microstructures or granular texture (see Krogh et al., 1984; Bohor et al., 1993; Glass and Liu, 2001; Wittmann et al., 2006). In accordance with the XRD, TEM, and SEM/EDX results, Raman spectra for several tens of white opaque zircon grains show no evidence for reidite, baddeleyite, or other polymorphs of ZrO₂, but the Raman spectra show band characteristics that are similar to those observed for metamict zircons (e.g., see Nasdala et al., 1995). The white opaque zircon grains are interpreted as metamict zircons that are a component of the epiclastic detritus in the spherule layers.

5.2.8 Rutile + TiO₂ II Grains

Using micro-Raman spectroscopy, minor amounts of rutile + TiO_2 II grains were identified in samples X38-2, X21-1, and V111 from the Carawine, Jeerinah, and Monteville spherule layers, respectively, as well as in the Bee Gorge spherule layer within samples 96714A and 96714B that are from the same rock (Table 62). Micro-Raman spectroscopy shows that many of the rutile + TiO_2 II grains also contain anatase and/or quartz. None of the Raman spectra for the rutile + TiO_2 II grains that contain quartz show evidence for coesite or stishovite, suggesting that formation of the quartz was subsequent to that of the TiO_2 II phase. Micro-Raman spectroscopy clearly shows the presence of anatase and/or quartz on the surfaces of grains of several phases, including rutile, from several spherule layer and context samples. A total of ~390 grains of anatase recovered from the spherule layer samples were analyzed by micro-Raman spectroscopy, but none of the Raman spectra for these grains show any evidence for the TiO_2 II phase. These data suggest that for the rutile + TiO_2 II grains, rutile is the precursor phase for the TiO_2 II phase, and the associated anatase and quartz are of secondary origin.

In the terrestrial crust, the TiO₂ II phase has at present been found in two very different geological environments: ultrahigh-pressure (UHP) metamorphic domains (Liou and Tsujimori, 2013, and references therein) and rocks associated with confirmed impact structures (e.g., El Goresy et al., 2001) or their distal impact ejecta (Glass and Fries, 2008). In the UHP metamorphic environment, nanometer-sized TiO₂ II has been found within submicrometer-sized inclusions of twinned rutile crystals that occur either in garnet within diamondiferous gneiss (Hwang et al., 2000) or in omphacite in coesite-bearing eclogite (Wu et al., 2005). Recently, nano-inclusions of TiO₂ II have been identified in a micro-inclusion of porous coesite that occurs within a diamond from a placer deposit in Brazil (Wirth et al., 2009).

In shock-metamorphosed gneiss clasts from the suevitic breccia at the Ries impact structure in Germany, the α -PbO₂-structured polymorph of TiO₂ (TiO₂ II) occurs as crystals (<100 µm in size) that are concentrated along the margins of rutile crystals, and the rutile crystals form an aggregate within kink-banded shock-compacted biotite crystals (El Goresy et al., 2001). This first known occurrence of shock-induced TiO₂ II was followed by its discovery in suevitic crystalline-clast breccia and brecciated cataclastic gneiss in drill cores from the central uplift of the Cheasapeake Bay impact structure in Virginia (Jackson et al., 2006). In this occurrence, TiO₂ II \pm anatase occurs as inclusions in chlorite grains, and TiO₂ II \pm rutile crystals occur in chlorite veins or in the matrix, and

these inclusions or crystals are up to several tens of microns in size (Jackson et al., 2006, their Fig. 2). Silt-sized grains of shock-induced TiO_2 II were identified using micro-Raman spectroscopy in several coesite-bearing shock-metamorphosed rock fragments from the Australasian microtektite layer (Glass and Fries, 2008). In Figure 8C of Glass and Fries (2008), the bands at wavenumbers ~441, ~613, and ~822 cm⁻¹ in the Raman spectrum for TiO₂ II suggest that rutile is the precursor phase of the TiO₂ II.

In the present study, the micro-Raman probe spot was $\sim 2 \,\mu m$ in diameter, much larger than the nanometer-sized crystals of TiO₂ II that have at present been found in the UHP metamorphic environment (see Hwang et al., 2000; Wu et al., 2005; Wirth et al., 2009). Furthermore, the TiO₂ II crystals from the UHP metamorphic environment occur in submicron-to-micron-sized inclusions within robust host grains, e.g., garnet (Hwang et al., 2000) or diamond (Wirth et al., 2009). In contrast, crystals or grains of natural, shockinduced TiO₂ II are up to \sim 50 µm in size and they do not occur in robust host grains (see El Goresy et al., 2001, their Fig. 3; Jackson et al., 2006, their Fig. 2; Glass and Fries, 2008, their Figs. 8B and 10). Furthermore, garnet, kyanite, and omphacite commonly occur in UHP metamorphic domains (Gilotti, 2013), yet in the heavy mineral assemblages for the samples in the present study, kyanite and omphacite are absent, and there are only five grains of garnet. These results suggest that the heavy minerals in the samples used for this study are not being derived from UHP metamorphic domains. Therefore, the rutile + TiO₂ II grains in the Carawine, Jeerinah, Bee Gorge, and Monteville spherule layers are interpreted as shock-metamorphosed grains on the basis of their size; their occurrence, i.e., they are not hosted by other phases; and their lack of association with common UHP metamorphic phases.

The TiO₂ II phase can form over a wide range of pressures. Static high-pressure experiments have shown that this phase can form at pressures as low as ~4-5 GPa (Bendeliani et al., 1966; Withers et al., 2003, and references therein). Shock-recovery experiments (e.g., Linde and DeCarli, 1969; Kusaba et al., 1988, and references therein) have shown that the transformation of rutile to the TiO₂ II phase can begin in the pressure range of ~15-20 GPa, and that the yields of the TiO₂ II phase are strongly dependent on the shock propagation direction. Linde and DeCarli (1969) inferred from their results that for certain orientations, the transformation of rutile to the TiO₂ II phase appeared to be complete below a pressure of 45 GPa. However, the experimental pressures for the shock-recovery experiments of Kusaba et al. (1988) ranged up to 72 GPa, and the maximum yield (~70%) of the TiO₂ II phase occurred at peak pressures of ~36 GPa. Therefore, the rutile + TiO₂ II grains from the spherule layers were probably formed at pressures above ~15 GPa, but more detailed work is needed in order to estimate formation pressures for these grains.

For a given spherule layer, the TiO_2 II phase in the rutile grains may be syngenetic with respect to the spherule layer, thereby providing physical evidence for the impact origin of the spherule layer (see French, 1998), and/or the rutile + TiO_2 II grains may be epiclastic detritus, thereby providing physical evidence for terrestrial hypervelocity impact events that are older than, and unrelated to, the spherule layer. In the following discussion, I argue that the TiO_2 II phase in the rutile grains is syngenetic with respect to its host spherule layer, but the data do not provide conclusive evidence for one or the other of the two hypotheses.

The Carawine, Monteville, and Bee Gorge context samples and layers admittedly have low absolute abundances (0-14 grains/sample) of rutile ± anatase grains (Table 62),

but the absence of rutile + TiO_2 II grains in these context samples and layers supports the hypothesis that the TiO_2 II phase is syngenetic with respect to its host spherule layer. Using a binocular microscope, the rutile + TiO_2 II grains are observed to have blocky or irregular shapes, and they appear to be subrounded-to-subangular. However, the larger rutile + TiO_2 II grains (~120-200 µm in size) are typically subangular-to-angular. The low-resolution shape and angularity data suggest that many of the rutile + TiO_2 II grains experienced minimal amounts of reworking, in accordance with the hypothesis that the TiO_2 II phase is syngenetic with respect to its host spherule layer.

For each of the Bee Gorge samples 96714A and 96714B, the confinement of the rutile + TiO₂ II grains to the upper spherule/lutite sublayers subdivision of the spherule layer is readily explained by analogy with the distribution of shock-metamorphosed grains in both the K-Pg couplet deposits (see section 1.2.3) and the upper Eocene tektite-bearing impact ejecta layer that is present on the continental slope off New Jersey (see section 5.2.4, and Glass et al., 1998). Furthermore, the absence of chrome spinel, tourmaline, and zircon grains in these two samples (Table 63) is somewhat puzzling if the rutile + TiO₂ II grains in these two samples represent epiclastic detritus. However, if the TiO₂ II phase in the rutile grains in Bee Gorge spherule layer, then the absence of chrome spinel, tourmaline, and zircon grains in these two samples may simply indicate that there is little, if any, sand-sized epiclastic detritus in the two samples. Similar arguments pertain to the distribution of rutile + TiO₂ II grains in the Set of the samples in the two samples may simply indicate that there is little, if any, sand-sized epiclastic detritus in the two samples.

For the Monteville spherule layer at the Monteville farm locality (see Fig. 5), the presence of rutile + TiO_2 II grains in sample V111 from the upper part of the layer, and

their apparent absence in sample U63-1 from the lower part of the layer (Table 62), can again be readily explained by analogy with the distribution of shock-metamorphosed grains in, e.g., the K-Pg couplet deposits (see section 1.2.3). Alternatively, the presence of chrome spinel, tourmaline, and zircon grains in sample V111 (Table 63) could be used to support the hypothesis of an epiclastic origin for the rutile + TiO₂ II grains. However, buff rutile grains are not present in Monteville context samples T149-1 and II67-1B (see Appendix X), and if the buff rutile \pm TiO₂ II grains in both samples V111 and U63-1 represent epiclastic detritus, then again, the absence of chrome spinel and zircon grains in sample U63-1 is puzzling. However, if the buff rutile grains in Monteville spherule layer sample U63-1 are not epiclastic detritus, but instead represent unshocked impact ejecta that are related to the impact event that led to the formation of the Monteville spherule layer, then the absence of chrome spinel and zircon grains in sample U63-1 may simply indicate that there is little, if any, sand-sized epiclastic detritus in this sample. More work, however, is needed to determine the amount of epiclastic sand-sized detritus in sample U63-1.

If the TiO₂ II phase in the buff rutile grains in the Monteville spherule layer is syngenetic with respect to the spherule layer, and if the Monteville spherule layer correlates with the Jeerinah and Carawine spherule layers (Simonson et al., 2009a, 2009b, and references therein), then similar buff rutile + TiO₂ II grains would be expected in the latter two layers, and the heavy mineral results show this to be the case. However, for both the Jeerinah spherule layer at the Hesta locality (samples W94-1Q and X21-1), and the Carawine spherule layer at the TTT locality (sample X38-2), more heavy mineral data are needed from samples at different levels within the spherule layers before the origin of the rutile + TiO₂ II grains in the spherule layers at these two localities can be fully

evaluated. For example, for a given locality, if the rutile + TiO_2 II grains were found to have a similar abundance at different stratigraphic levels across the spherule layer, then this result may favor an epiclastic origin for these grains. However, if the rutile + TiO_2 II grains were found to be confined or concentrated near or at the top of a given spherule layer, then this result would support the hypothesis that the TiO_2 II phase is syngenetic with respect to its host spherule layer (see discussion of the K-Pg couplet deposits in section 1.2.3, and Glass et al., 1998).

In light of recent work that has documented reworked shock-metamorphosed grains related to the large Vredefort impact structure in South Africa (see Cavosie et al., 2010; Erickson et al., 2013), an epiclastic origin for the rutile + TiO₂ II grains in the spherule layers is possible, but this hypothesis may have difficulty in explaining the spatio-temporal distribution of the rutile + TiO₂ II grains. Detrital grains of shock-metamorphosed quartz, zircon, and monazite, that are from the Vredefort impact structure, have been documented from modern sands of the Vaal River system, both from within the Vredfort impact structure (Cavosie et al., 2010), as well as up to 759 km downriver of the Vredefort impact structure (Erickson et al., 2013). At distances of 388-759 km downriver of the Vredefort impact structure, shock-metamorphosed quartz grains comprise 1-3% of the quartz grains investigated, and shock-metamorphosed zircon grains comprise 1-8% of the zircon grains investigated (Erickson et al., 2013).

In the Carawine, Jeerinah, and Monteville spherule layer samples that contain rutile + TiO_2 II grains, these grains comprise a minimum of ~1-3.3% of the rutile grains. For Bee Gorge samples 96714A and 96714B combined, rutile + TiO_2 II grains comprise ~5.2% of the rutile grains in the upper spherule/lutite sublayers subdivision. Therefore, the present estimates for the concentration of rutile + TiO_2 II grains in these spherule
layers are comparable to those for detrital shock-metamorphosed zircon grains that occur in modern sands of a large fluvial system at distances of several hundred kilometers downriver of the large impact structure that is the source of the shock-metamorphosed grains. However, invoking the results of Cavosie et al. (2010) and Erickson et al. (2013) to support an epiclastic origin for the rutile + TiO_2 II grains in the spherule layers should be done with some caution.

The samples used by Cavosie et al. (2010) and Erickson et al. (2013), being modern sands from within, and immediately adjacent to, active channels within a single fluvial system, are somewhat restricted in time and space. Once the shockmetamorphosed quartz, zircon, and monazite grains in the Vaal River system are transported to the Atlantic coastal environment, their dispersal by currents and waves should decrease their concentrations in coastal and offshore sands. In contrast, if the rutile + TiO₂ II grains in the spherule layers are a component of the epiclastic detritus that was derived from the Pilbara and Kaapvaal cratons (see Figs. 4 and 5), then their source materials appear to have both a wide spatial distribution, e.g., hundreds of kilometers along the margin of the Pilbara craton (see Fig. 4), and a large temporal extent, cf., the ages of the Jeerinah and Bee Gorge spherule layers (see Fig. 2).

The Pilbara and Kaapvaal cratons are situated on two separate continents (see Figs. 4 and 5). However, it has been proposed (e.g., Cheney, 1996) that the Kaapvaal and Pilbara cratons were part of a single continental block, the continent of Vaalbara, during the Neoarchean and early Paleoproterozoic, and recent work provides several lines of evidence to support this hypothesis (e.g., Beukes and Gutzmer, 2008; Knoll and Beukes, 2009; de Kock et al., 2009, 2012). The paleogeographic reconstruction favored by de Kock et al. (2009, their Fig. 8) and de Kock et al. (2012, their Fig. 6) places the Pilbara

craton to the northwest of the Kaapvaal craton in present geographic coordinates, and shows that the Carawine, Jeerinah, Bee Gorge, and Monteville spherule layers would have been deposited along a single margin of the Vaalbara continent.

In this paleogeographic reconstruction (see Knoll and Beukes, 2009, their Fig. 10; de Kock et al., 2012, their Fig. 6) the paleodistance between the main part of the Hamersley Basin (see Fig. 4) and the southern part (present geographic coordinates) of the Griqualand West Basin (see Fig. 5) is roughly 1000 km. If the Carawine, Jeerinah, and Monteville spherule layers are parts of a single spherule layer (Simonson et al., 2009a, 2009b, and references therein) that was deposited along a margin of the Vaalbara continent, and the rutile + TiO₂ II grains in each of these three parts of the spherule layer are epiclastic detritus, it seems somewhat unlikely that the abundance of these grains in the source materials along a strike distance of ~1000 km would be sufficient to yield the observed concentrations of these grains in these three parts of the spherule layer, even if the source crater was situated along this margin of the Vaalbara continent. The hypothesis that the TiO_2 II phase is syngenetic with respect to the impact event that led to the formation of the "Carawine-Jeerinah-Monteville" spherule layer appears to provide a simpler explanation for the presence of the rutile + TiO₂ II grains in this proposed (e.g., see Simonson et al., 2009a, 2009b) spherule layer. The presence of buff rutile + TiO_2 II grains in both the Jeerinah spherule layer (sample X21-1) and the younger (see Fig. 2) Bee Gorge spherule layer (samples 96714A and 96714B) suggests that similar protoliths were present in the target rocks for the two separate impact events.

5.2.9 Quartz and Feldspar Grains in the Heavy Mineral Fractions

During the course of identifying the phases in the heavy mineral fractions using micro-Raman spectroscopy, ~260 single grains of quartz \pm K-feldspar, K-feldspar, and

albite were identified, but none of the Raman spectra for these grains show evidence for high-pressure phases. The absence of high-pressure phases in the ~260 grains is not surprising for several reasons. First, some of these grains are from the context samples. Secondly, for several spherule layer samples and context samples and layers, micro-Raman spectroscopy shows that quartz \pm K-feldspar, K-feldspar, and albite occur on the surfaces of several of the heavy mineral phases and are probably of secondary origin. Thirdly, some of the quartz \pm K-feldspar and K-feldspar grains are probably epiclastic detritus (see e.g., Simonson, 1992; Simonson et al., 1999; Hassler et al., 2005; Chadwick et al., 2001). Finally, some of the quartz grains and many of the feldspar grains in the Jeerinah spherule layer at the Hesta locality have features that suggest that they are of volcanic origin (Glass and Simonson, 2013; Jones-Zimberlin et al., 2006).

5.3 Light Fractions

A systematic search for shock-metamorphosed quartz grains in the spherule layers was limited to the examination of 12 grain mounts from Carawine spherule layer sample 43-1 from the Ripon Hills area (see Fig. 4 for location). Fourteen (~1.6%) of ~875 quartz grains from the 63-125 μ m size fraction contain 1-3 sets of planar microstructures. The appearance, width, and spacing of the planar microstructures, as well as the fact that some of the grains contain 2-3 sets of planar microstructures, support the interpretation that they are shock-induced planar microstructures (see Stöffler and Langenhorst, 1994). The orientations of a total of seven sets of planar microstructures in three quartz grains were measured with the U-stage microscope, and five of the sets were indexed to rational low index planes with crystallographic orientations that are commonly observed for shock-induced planar microstructures (see Stöffler and Langenhorst, 1994). The {1011} and {1013} orientations suggest that these quartz grains were subjected to shock pressures in the range of ~10-20 GPa (see Stöffler and Langenhorst, 1994). The number of sets of planar microstructures and the number of quartz grains measured with the U-stage microscope are admittedly limited, but the results suggest that shockmetamorphosed quartz grains are present in the Carawine spherule layer.

As with the TiO₂ II phase in the rutile grains, the shock-induced planar microstructures in the quartz grains may be syngenetic with respect to the Carawine spherule layer, thereby providing physical evidence for its impact origin (see French, 1998), or these quartz grains with the planar microstructures may be a component of the epiclastic detritus that has been documented in the Carawine spherule layer (e.g., Simonson, 1992; Simonson et al., 1998). Eleven (~78%) of the 14 quartz grains that contain planar microstructures are subangular-to-angular. These results for the angularity of the grains would be consistent with the hypothesis that these grains are impact ejecta, in which the shock-induced planar microstructures are syngenetic with respect to the Carawine spherule layer. Rutile + TiO₂ II grains were not identified in Carawine spherule layer sample 43-1 (Table 62), but this sample contains only 14 rutile \pm anatase grains, and most of these grains are not buff (see Appendix S). More data are needed on the distribution and concentration of shock-metamorphosed quartz grains in the other Carawine Dolomite samples in order to evaluate the origin of the quartz grains with planar microstructures that were found in Carawine spherule layer sample 43-1.

5.4 Correlation of the Spherule Layers

Several lines of evidence suggest that the Carawine, Jeerinah, and Monteville spherule layers are parts of a single spherule layer that was formed as a result of an impact event at ~2.63 Ga (Rasmussen and Koeberl, 2004; Rasmussen et al., 2005; Hassler et al., 2005; Simonson et al., 2009a, 2009b, and references therein). The

secondary focus of the present study was to evaluate the idea that heavy mineral assemblages may provide a potential tool for the correlation of the three spherule layers. The results show that the heavy mineral assemblages for the Carawine, Jeerinah, and Monteville spherule layers are indeed similar (Table 63), and therefore, they support the correlation of these three spherule layers. However, in terms of phases present, the heavy mineral assemblage for the Bee Gorge (Wittenoom) spherule layer (BB (sl)) at the Bacon Bore locality (see Fig. 4) is also similar to those for the Carawine, Jeerinah, and Monteville spherule layers (Table 63).

It appears that the physical properties of the chrome spinel, rutile, and zircon grains provide the key for the correlation of the spherule layers. The chrome spinel grains in the Carawine, Jeerinah, and Monteville spherule layers, as well as in Carawine context sample 104141 and Monteville context sample II67-1B, are typically dark (steel) gray-toblack, whereas the rare chrome spinel grains in the Bee Gorge spherule layer (BB (sl)) and adjacent context layer (BB (#2)) in sample BB (Table 62) from the Bacon Bore locality are dark brownish black. The rutile \pm anatase grains in the Carawine, Jeerinah, and Monteville spherule layers show a similar range of colors, including various shades of amber. There are no amber or reddish amber rutile \pm anatase grains in the spherule layer parts of the Bee Gorge samples. For the rutile \pm anatase grains (n = 29) in the 63-250 µm size fraction of Carawine spherule layer sample 42-1A from the Ripon Hills area (see Fig. 4), 86% (n = 25) are buff and 76% (n = 22) have an irregular or blocky shape. For the rutile \pm anatase grains (n = 23) in the 63-250 µm size fraction of Monteville spherule layer sample U63-1 from the Monteville farm locality (see Fig. 5), 87% (n = 20) are buff and 78% (n = 18) have an irregular or blocky shape. These similarities for the rutile \pm anatase grains in these two samples lend support to the

proposed correlation (see Simonson et al., 2009a, 2009b, and references therein) of the Carawine and Monteville spherule layers.

The zircon populations of the Carawine, Jeerinah, and Monteville spherule layers are similar in terms of the range of colors and diaphaneities exhibited by the grains. For example, these three spherule layers contain (pale) pink, champagne, and translucent-toopaque zircon grains. White opaque zircon grains are present in the Carawine spherule layer, and there are a few translucent-to-opaque zircon grains that are typically clear with a light yellow tint in Jeerinah spherule layer sample X21-1 and Monteville spherule layer sample V111. These varieties of zircon grains were not observed in the zircon population for Bee Gorge sample BB, and no zircon grains were recovered from Bee Gorge samples 96714A, 96714B, and 92058. These results for the chrome spinel, rutile \pm anatase, and zircon grains would not provide support for the correlation of the Carawine spherule layer and the Bee Gorge (Wittenoom) spherule layer as originally proposed by Simonson (1992). These results for the chrome spinel, rutile \pm anatase, and zircon grains provide support for the proposed correlation of both the Carawine and Monteville spherule layers with the Jeerinah spherule layer (e.g., Simonson et al., 2009a, 2009b, and references therein) that is stratigraphically lower, and therefore older, than the Bee Gorge (Wittenoom) spherule layer (see Fig. 2). Furthermore, trace amounts of clinopyroxene are present in the Carawine, Jeerinah, and Monteville spherule layers, but this phase was not identified in the Bee Gorge samples (Table 63).

The heavy mineral assemblages of the spherule layers may also provide a correlation tool for subunits within the spherule layers. For example, the rutile \pm anatase and zircon grains in the upper parts of the uppermost debris-flow deposits of the Carawine spherule layer in the Ripon Hills area (sample 42-1A) and TTT (sample X38-2)

locality (see Fig. 4) show similar physical properties. The combined heavy mineral assemblage for the two float samples (W94-1Q and X21-1) that are originally from the lower thin-bedded zone (B. M. Simonson, personal communication, 2013) of the Jeerinah spherule layer at the Hesta locality is similar to that for the lowermost debris-flow deposit of the Carawine spherule layer in the Ripon Hills area. The heavy mineral assemblages for the Carawine and Jeerinah spherule layers are more similar to that for the upper part of the Monteville spherule layer (sample V111) than that for the lower part of the Monteville spherule layer (sample U63-1; Table 62). The results of the present study suggest that heavy minerals may indeed provide a fertile field for future work concerning the correlation of the spherule layers, as well as the nature of the depositional processes involved in their formation.

Buff rutile + TiO₂ II grains are present in the Carawine, Jeerinah, and Monteville spherule layers, thereby supporting the proposed correlation of these three spherule layers (e.g., Simonson et al., 2009a, 2009b, and references therein), but buff rutile + TiO₂ II grains are also present in the Bee Gorge (Wittenoom) spherule layer, so at present, these grains do not provide a unique correlation tool. The shock-metamorphosed quartz grain reported by Rasmussen and Koeberl (2004) from the Jeerinah spherule layer is similar in size, angularity, and number of sets of PDFs to several of the putative shockmetamorphosed quartz grains from Carawine spherule layer sample 43-1. These quartz grains do not provide a unique correlation tool, but they do provide physical evidence that is consistent with the proposed correlation of the Carawine and Jeerinah spherule layers (e.g., Simonson et al., 2009a, 2009b, and references therein).

5.5 Grænsesø Spherule Layer

Field work for the present study was successful in relocating the spherule-bearing dolomite bed in the upper part of the Grænsesø Formation in the Midternæs area (see Fig. 6, and Higgins, 1970). On the basis of thin section petrographic analysis, Chadwick et al. (2001) had reported that the spherule-bearing dolomite bed contains intraclasts of cherty fragments up to ~4 mm long and flat pebbles of carbonate up to ~8 mm long. The present study documents that the spherule-bearing dolomite bed, now termed the Grænsesø spherule layer (Glass and Simonson, 2013), in the Midternæs area is a fairly homogeneous, massive dolomixtite that contains cm-to-dm-sized, subrounded-to-angular clasts of chert and dolomite. The large clasts clearly show that the Grænsesø spherule layer was deposited by a high-energy event.

A cursory examination of the strata in the upper part of the Grænsesø Formation at this locality reveals that the dolomixtite layer is the only layer that contains spherules and cm-to-dm-sized clasts. It is now clear that the Grænsesø spherule layer has many features, e.g., large lateral extent, singular nature, high-energy mode of deposition, and chert and carbonate clasts, that are characteristic of several Precambrian spherule layers (Glass and Simonson, 2013, and references therein). More detailed field work is needed to fully characterize the Grænsesø spherule layer and its mode(s) of deposition, as well as to search for additional exposures. In the following discussion, I will use the available data to posit a debris-flow origin for the sampled interval of the Grænsesø spherule layer.

The Grænsesø spherule layer at the Midternæs locality is a massive, poorly-sorted dolomixtite that contains large chert and carbonate clasts, mm-sized cherty and carbonate fragments (Chadwick et al., 2001), spherules, and siliciclastic sand-sized grains that are supported by a dolomitic matrix. Size-grading of the cm-sized clasts is not obvious, but reverse grading may be present, since the larger dolomite clasts appear to be restricted to

the upper part of the Grænsesø spherule layer. The cm-sized chert clasts exhibit different shapes. The larger chert clasts are typically angular and tabular or elongate, and their long axes are typically aligned roughly parallel to the contacts of the Grænsesø spherule layer. These sedimentological characteristics of the Grænsesø spherule layer are similar to those described for debris-flow deposits (see Nardin et al., 1979, and references therein).

Hand sample descriptions (Appendix G) and petrographic observation (see Chadwick et al., 2001, their Fig. 2c) show that the mm-sized cherty fragments can also be angular, and tabular or elongate, and they are interpreted as intraclasts (Chadwick et al., 2001). Field observation shows that locally, the dolomitic matrix invades the chert and dolomite clasts, and the matrix material can completely traverse the clasts along fractures. Some of the dolomite clasts appear to have been fragmented and rounded during transport. Therefore, it appears that some of the clasts were not fully lithified at the time of their transport and deposition. The clasts are lithologically similar to beds of chert and dolomite that were observed in the host strata for the Grænsesø spherule layer. The meter-sized clast near the top of the Grænsesø spherule layer outcrop clearly consists of two adjoining dolomite beds. These observations suggest that the chert and dolomite clasts are intraclasts, in agreement with the interpretation of Chadwick et al. (2001) for the mm-sized clasts, and they are in accordance with the debris-flow interpretation for the Grænsesø spherule layer (see Nardin et al., 1979, and references therein).

Field observation and hand sample descriptions (Appendix G) show that the spherules (D ~0.5-1 mm) are mostly spherical, and by visual estimate, they comprise roughly 10-20 vol% of the Grænsesø spherule layer, results that accord well with the petrographic data of Chadwick et al. (2001). The spherules appear to be evenly dispersed in the dolomitic matrix, and no obvious size grading was observed in the field. These

results further support the debris-flow interpretation for the Grænsesø spherule layer (see Nardin et al., 1979, and references therein). By visual estimate, epiclastic siliciclastic sand comprises ~1-2 vol% of the Grænsesø spherule layer, close to the value (3 vol%) obtained by point counting of one large thin section (Chadwick et al., 2001).

The large decrease in heavy mineral abundance (see section 4.2.8 and Table 62) and the decrease in the maximum size of the mm-sized chert grains (see section 2.4) upward in the Grænsesø spherule layer could suggest that these components were settling through the sediment gravity flow during its movement and/or emplacement. However, the settling of these components appears unlikely if the Grænsesø spherule layer was deposited by a debris flow. Furthermore, the spherules, whose diameters (~0.5-1 mm) are intermediate between those of the heavy mineral grains (63-250 μ m) and the maximum size of the mm-sized chert grains (~2-8 mm), apparently do not show a decrease in abundance or size upward in the Grænsesø spherule layer. More work is needed on additional samples from this and other outcrops of the Grænsesø spherule layer in order to evaluate whether or not the large decrease in heavy mineral abundance and the decrease in the maximum size of the mm-sized chert grains upward in the Grænsesø spherule layer are real trends or are apparent trends that are simply due to limited sampling.

The contacts of the Grænsesø spherule layer are obscured by rubble at the Midternæs locality, so it is likely that its true thickness will be up to a few decimeters more than the measured thickness of ~145 cm. Future detailed field analysis of the entire Grænsesø spherule layer may reveal that it consists of more than one depositional unit, but it is likely that the massive dolomixtite will constitute the thickest depositional unit. At present, the singular nature of the Grænsesø spherule layer contrasts markedly with

the other spherule layers in this study, each of which was clearly deposited by more than one depositional event (Simonson, 1992; Simonson et al., 1999; Hassler et al., 2000, 2005). The minimum thickness (~145 cm) of the Grænsesø spherule layer is comparable to, or exceeds, the thicknesses for the Jeerinah spherule layer (~157 cm) at the Hesta locality (Hassler et al., 2005), the Bee Gorge (Wittenoom) spherule layer (12-130 cm) in the Hamersley Basin (Simonson, 1992), and the Monteville spherule layer (29-80 cm) at the Monteville farm locality (Simonson et al., 1999). Therefore, the present characterization of the Grænsesø spherule layer that is made on the basis of field observation, hand sample descriptions, acid-insoluble weight data, and analysis of the heavy mineral assemblage enlarges the range of stratigraphic variability that is exhibited by spherule layers that are a few decimeters to ~1-2 m in thickness.

Chapter 6

CONCLUSIONS AND FUTURE WORK

6.1 Acid-Insoluble Weights

The acid-insoluble weight data accord well with the individual hand sample descriptions, and confirm that all the samples have a significant (~33-53 wt%)-to-high (>67 wt%) carbonate component (Table 10). Therefore, in future work to recover heavy minerals from these five spherule layers, samples should undergo acid dissolution, regardless of the degree of their effervescence in dilute HCl. For samples from the Jeerinah spherule layer at the Hesta locality that show no effervescence in dilute HCl like samples W94-1Q and X21-1, the samples should be partly crushed prior to acid dissolution. As expected, the acid-insoluble material in the context samples is mostly in the <63 μ m size fraction, whereas that for the spherule layer samples is mostly in the spherule layers were deposited by high-energy events below storm wave base in low-energy, deep-shelf or slope marine environments (Simonson and Glass, 2004). The acid-insoluble weight data also support the interpretation that the sampled interval of the Grænsesø spherule layer that consists of a massive dolomixtite was deposited by a single event.

6.2 Heavy Mineral Fractions

6.2.1 Heavy Mineral Assemblages

The heavy mineral assemblages of the spherule and context layers typically consist primarily of anatase, chrome spinel, rutile, tourmaline, and zircon grains (Table 63), i.e., very stable phases (e.g., Morton and Hallsworth, 2007). Micro-Raman spectroscopic results suggest that at least some of the anatase is of secondary origin. Anatase is a common diagenetic heavy mineral phase (Morton and Hallsworth, 2007; Triebold et al., 2011), so more work (e.g., SEM/EDX) is needed to determine the relative proportion of detrital and secondary anatase grains in these samples. The rutile (see Force, 1980) and zircon grains suggest that the heavy mineral grains were largely derived from adjacent cratons, and for the spherule layers, most of the heavy mineral grains probably accompanied the epiclastic, sand-sized, quartzo-feldspathic detritus that was primarily derived from granitoid and regionally-metamorphosed basement rocks (e.g., Simonson et al., 1998; Jones-Zimberlin et al., 2006; Glass and Simonson, 2013).

The similarities in both the heavy mineral assemblages (Table 63) and the physical properties of the chrome spinel, rutile, and zircon grains support the proposed correlation of the Carawine, Jeerinah, and Monteville spherule layers (e.g., Simonson et al., 2009a, 2009b, and references therein). Heavy mineral data may also provide a tool for even finer-scale correlation of subunits within the spherule layers, but heavy mineral data from additional samples are needed to evaluate this hypothesis. The heavy mineral data support the hypothesis of Hassler et al. (2005) that the spherule layers in the Carawine Dolomite in the Ripon Hills area and at the TTT locality (see Fig. 4) were deposited by the same series of sediment gravity flows. For the Monteville spherule layer, the number of heavy mineral phases and the abundance of heavy mineral grains are significantly

higher in its upper part (sample V111) as compared to its lower part (sample U63-1), and these results support the interpretation of Simonson et al. (1999) that the Monteville spherule layer at the Monteville farm locality (see Fig. 5) was deposited by separate, but related, depositional events.

6.2.2 White Opaque Zircon Grains

No definitive evidence for shock metamorphism was identified in the white opaque zircon grains. The data obtained by XRD, TEM, SEM/EDX, and micro-Raman spectroscopy suggest that the white opaque zircon grains have varying degrees of metamictization. The distribution of these grains in the spherule layers, and their absence in the context samples, suggest that the white opaque zircon grains are epiclastic detritus derived from cratonal areas (see Simonson et al., 1999; Chadwick et al., 2001; Hassler et al., 2005).

6.2.3 Shock-Metamorphosed Rutile + TiO₂ II Grains

Micro-Raman spectroscopy shows the presence of rutile + $TiO_2 II$ (± anatase, ± quartz) grains in the Carawine (sample X38-2), Jeerinah (sample X21-1), Bee Gorge (Wittenoom) (samples 96714A and 96714B), and Monteville (sample V111) spherule layers. Micro-Raman spectroscopy suggests that rutile is the precursor phase for the $TiO_2 II$ phase, and that the associated anatase and quartz are of secondary origin. The apparent absence of rutile + $TiO_2 II$ grains in Carawine spherule layer samples 84-1, W85-2, X24-1, 43-1, and 42-1A from the Ripon Hills area (see Fig. 4) and in Monteville spherule layer sample U63-1 from the Monteville farm locality (see Fig. 5) may reflect the fact that these six samples have much lower abundances of rutile grains than those samples that contain the rutile + $TiO_2 II$ grains (see Table 62). It is possible that these six samples have lower concentrations of rutile + TiO₂ II grains as compared to those in Carawine spherule layer sample X38-2 and Monteville spherule layer sample V111. Furthermore, if the TiO₂ II phase is syngenetic with respect to its host spherule layer (see below), then it is possible that Carawine spherule layer samples 84-1, W85-2, X24-1, 43-1, and 42-1A, and Monteville spherule layer sample U63-1 are from strata that were deposited before the arrival of the rutile + TiO₂ II grains that represent impact ejecta. The apparent absence of rutile + TiO₂ II grains in Jeerinah spherule layer sample W94-1Q may be due to the small mass (38.73 g) of this sample as compared to that (265.52 g) for Jeerinah spherule layer sample X21-1 that contains rutile + TiO₂ II grains (Table 62). The apparent absence of rutile + TiO₂ II grains in the Bee Gorge spherule layer (BB (sl)) in sample BB may also be due to a small sample size (31.24 g) and/or a much lower abundance of rutile grains as compared to those for the upper spherule/lutite sublayers subdivisions (UsplsI) in Bee Gorge samples 96714A and 96714B that contain rutile + TiO₂ II grains (Table 62).

The TiO₂ II phase was produced by shock metamorphism, not by ultra-high pressure metamorphism. At present, the pressures at which the TiO₂ II phase in these grains formed are not known, but shock-recovery experiments (e.g., Linde and DeCarli, 1969; Kusaba et al., 1988, and references therein) have shown that the transformation of rutile to the TiO₂ II phase can begin in the pressure range of ~15-20 GPa. The present study documents that the TiO₂ II phase can be stable for ~2.63 billion years in terrestrial supracrustal successions that have undergone low-strain and low-grade metamorphism (see Smith et al., 1982; Sumner and Beukes, 2006, and references therein). This conclusion is in accord with isothermal annealing experiments for rutile + TiO₂ II crystals that showed that the TiO₂ II phase is rather stable at 340 °C, transforms slowly (weeks) to

rutile at 440 °C, and transforms rapidly (hours) to rutile at 550 °C (Linde and DeCarli, 1969).

Several lines of evidence suggest that the TiO₂ II phase is syngenetic with respect to its host spherule layer, and if this hypothesis is correct, then the rutile + TiO₂ II grains provide definitive physical evidence for an impact origin of the spherule layers (see French, 1998). Rutile + TiO₂ II grains were not identified in the context samples or layers. The rutile + TiO₂ II grains are typically blocky or irregular in shape, and those in the 125-250 μ m size fraction are typically subangular-to-angular. These physical attributes of the TiO₂ II grains suggest minimal reworking that is in accord with the hypothesis that the TiO₂ II phase is syngenetic with respect to its host spherule layer.

The confinement or concentration of the rutile + TiO_2 II grains in the upper parts of the Bee Gorge (Wittenoom) and Monteville spherule layers appears to be somewhat analogous to the distribution of shock-metamorphosed grains in both the K-Pg couplet deposits (see Kring et al., 1994; Bohor and Glass, 1995, and references therein; Schulte et al., 2009) and the upper Eocene tektite-bearing impact ejecta layer that is present on the continental slope off New Jersey (see Glass et al., 1998), thereby supporting the hypothesis that the TiO₂ II phase is syngenetic with respect to its host spherule layer. If the paleogeographic reconstruction of the Kaapvaal and Pilbara cratons for the Neoarchean (see de Kock et al., 2009, 2012) is correct, then an epiclastic origin for the rutile + TiO₂ II grains seems unlikely, given the large (~1000 km or more) paleodistance between the Hamersley Basin and southern (present geographic coordinates) part of the Griqualand West Basin, and the minimum concentrations of these grains in the rutile populations of the four spherule layers. The presence of buff rutile + TiO₂ II grains in both the Jeerinah spherule layer and the younger (see Fig. 2) Bee Gorge (Wittenoom)

spherule layer suggests that similar protoliths were present in the target rocks for the two impact events.

6.3 Shock-Metamorphosed Quartz Grains and Their Implications

A small number of quartz grains containing planar microstructures were identified in the 63-125 μ m size fraction of Carawine spherule layer sample 43-1 from the Ripon Hills area (see Fig. 4). The appearance, width, and spacing of the planar microstructures are typical for shock-induced PDFs (see Stöffler and Langenhorst, 1994). The presence of two or three sets of planar microstructures in a few of these grains, and the {1011} and {1013} crystallographic orientations of four sets of planar microstructures in three of the quartz grains suggest that the planar microstructures are shock-induced PDFs that formed in the pressure range of ~10-20 GPa (see Stöffler and Langenhorst, 1994).

If these planar microstructures are shock-induced PDFs that are syngenetic with respect to the Carawine spherule layer, then they provide additional definitive physical evidence for an impact origin of the Carawine spherule layer (see French, 1998). In light of the single shock-metamorphosed quartz grain from the Jeerinah spherule layer (Rasmussen and Koeberl, 2004), shock-metamorphosed quartz grains in the Carawine spherule layer would be consistent with the proposed correlation of the Carawine and Jeerinah spherule layers (e.g., Simonson et al., 2009a, 2009b, and references therein). As noted by Rasmussen and Koeberl (2004), shock-metamorphosed quartz grains would favor an impact event on continental crust, rather than on oceanic crust (e.g., see Simonson et al., 1998).

6.4 Grænsesø Spherule Layer

At the Midternæs locality (see Fig. 6), the sampled interval of the Grænsesø spherule layer consists of a massive dolomixtite that contains spherules and sand-togravel-sized intraclasts of chert and carbonate that are supported by a dolomitic matrix, and a minor amount of epiclastic, sand-sized, quartzo-feldspathic detritus (Chadwick et al., 2001). The spherules, intraclasts, and sand-sized detritus are reworked components that were transported and deposited by a high-energy event that formed a singular layer in the upper Grænsesø Formation. Field observation suggests a debris-flow origin for the sampled interval of the Grænsesø spherule layer. Therefore, the Grænsesø spherule layer exhibits several features that are commonly observed in Precambrian spherule layers (see Simonson and Glass, 2004).

The heavy mineral assemblage of the Grænsesø spherule layer predominantly consists of rutile, tourmaline, and zircon grains that were largely derived from reworked sediments. These heavy mineral grains probably have a continental provenance, in light of the interpretation by Chadwick et al. (2001) that the epiclastic, quartzo-feldspathic detritus that occurs mostly in the 63-250 µm size fraction was derived from a continental source area. The abundance (number of grains/kg) of the chrome spinel, rutile, tourmaline, and zircon grains, and the maximum size of the sand-to-pebble-sized chert fragments, both decrease upward in the Grænsesø spherule layer; however, additional samples from this and other outcrops of the Grænsesø spherule layer are needed to confirm these trends. The massive bedding and homogeneous nature of the Grænsesø spherule layer, and the similar heavy mineral assemblages in the basal, middle, and upper parts of this layer, support the interpretation that the sampled interval of the Grænsesø spherule layer represents a single depositional event. No definitively shock-metamorphosed heavy mineral grains were identified in the Grænsesø spherule layer.

6.5 Impact Origin and Correlation of the Spherule Layers

Recently, Bottke et al. (2012) and Johnson and Melosh (2012) have used the Precambrian spherule layers as terrestrial evidence to support their hypothesis that an increased cratering flux for Earth occurred subsequent to the Late Heavy Bombardment (LHB; see section 1.1), and that this increased cratering flux extended into the Paleoproterozoic. Both Bottke et al. (2012) and Johnson and Melosh (2012) implicitly assume an impact origin for the Precambrian spherule layers, yet prior to the present study, the only definitive physical evidence for an impact origin for any of the Archean and Paleoproterozoic spherule layers consisted of one shock-metamorphosed quartz grain from the Neoarchean Jeerinah spherule layer (Rasmussen and Koeberl, 2004).

The present study has documented shock-metamorphosed grains in four Neoarchean spherule layers. I have argued that the TiO_2 II phase in the rutile + TiO_2 II grains is shock-induced and that it is syngenetic with respect to its host spherule layer. Therefore, the rutile + TiO_2 II grains provide definitive physical evidence for an impact origin of these spherule layers (see French, 1998). Furthermore, the present study has provided heavy mineral data that support the proposed correlation (e.g., Simonson et al., 2009a, 2009b, and references therein) of the Carawine, Jeerinah, and Monteville spherule layers. Therefore, the present study has provided the physical evidence for two separate Neoarchean impact events, one at ~2.63 Ga that produced the "Carawine-Jeerinah-Monteville" spherule layer, and a younger one at ~2.54 Ga that produced the Bee Gorge (Wittenoom) spherule layer (see Simonson et al., 2009a, 2009b, and references therein). The implicit assumption of Bottke et al. (2012) and Johnson and Melosh (2012) that the Precambrian spherule layers are of impact origin now has a much firmer foundation, and it now appears that these spherule layers can serve as terrestrial constraints for the post-LHB cratering flux for Earth well into the Paleoproterozoic.

6.6 Searching for Shock-Metamorphosed Rutile + TiO₂ II Grains

At present, shock-metamorphosed grains have been found in four Precambrian spherule layers, but finding them in Precambrian spherule layers can be a laborious and very time-consuming process. Searching for shock-metamorphosed rutile + TiO_2 II grains in the heavy mineral fractions of these spherule layers appears to be a good strategy. For continental crustal rocks, high-grade (upper amphibolite and above) metamorphic rocks that have a widespread occurrence on the cratons are ultimately the major source of detrital rutile (Force, 1980, and references therein), and detrital rutile grains are very stable, both physically and chemically (Hubert, 1962; Pettijohn, 1975). Prior to the present study, shock-induced rutile + TiO_2 II crystals or grains had been found associated with two confirmed impact structures (El Goresy et al., 2001; Jackson et al., 2006), as well as within a distal impact ejecta layer (Glass and Fries, 2008), all of Cenozoic age. The present study documents that shock-induced rutile + TiO_2 II grains can survive in rocks of Neoarchean age, and therefore, researchers who are searching for shock-metamorphosed grains in sediments or rocks should include rutile + TiO_2 II grains or crystals in their search programs.

The present study has affirmed the conclusion of Glass and Fries (2008) that micro-Raman spectroscopy is an excellent tool for investigating fine-grained, shock-metamorphosed impact ejecta. Micro-Raman spectroscopy provides a rapid, non-destructive method for mineral identification down to the scale of a few microns. In the present study, Raman spectra of loose unpolished grains of anatase, brookite, and rutile \pm TiO₂ II were typically of good-to-excellent quality, and they were readily identifiable. A grain or crystal of rutile \pm TiO₂ II can be identified using micro-Raman spectroscopy in ~2-3 minutes, and several hundred rutile grains can be analyzed in a week.

6.7 Suggestions for Future Sample Preparation

Future research to search for shock-metamorphosed grains, especially in Precambrian spherule layers, should utilize the heavy mineral fraction in conjunction with micro-Raman spectroscopy. The downside of this approach is the time involved for the preparation of samples that are hundreds of grams or more in mass, but these masses are probably necessary to increase the chance of success. On the basis of experience gained from the present study, the following procedures should decrease the time for sample preparation involving the recovery of the heavy mineral fraction: 1) If two researchers and multiple fume hoods are available, then the researchers should work consecutive shifts using 3-4 hotplates for acid digestion, and a similar number of separatory funnels for heavy liquid separation. 2) All acid digestion should be done on a hotplate using concentrated (15.8 N) HNO₃ to ensure the dissolution of fine-grained sulfide crystals that may not be visible in hand sample. 3) At the start of the project, one should decide how much, if any, of the $<63 \mu$ m-sized material should be recovered during wet sieving of the acid-insoluble residues. If one wants to search for shockmetamorphosed grains in the silt-sized fraction (see Morgan et al., 2006), then a 38 µm sieve should be used, in addition to the 63 μ m, 125 μ m, and 250 μ m sieves. If one wants to search for Ni-rich spinels, then at least some of the <38 µm-sized material should be recovered. Wet sieving the 38-63 μ m size fraction, and recovering the <38 μ m-sized material, especially all of it, can be very time-consuming processes. 4) For a heavy liquid separation, it may be possible to reduce the settling time from overnight to that of a workshift or less (see Lewis and McConchie, 1994). Experiments should be run to evaluate the feasibility of this idea. 5) In conjunction with heavy liquid separation, a Frantz isodynamic magnetic separator could be used to help separate the heavy mineral phases (see Lewis and McConchie, 1994). For example, the magnetic separator would be

especially useful for separating hundreds to thousands of grains of secondary iron oxides/oxyhydroxides or tourmaline from several of the other common phases, e.g., anatase, rutile, and zircon (see Lewis and McConchie, 1994). The sample preparation procedures used in this study will remain somewhat laborious and time-consuming, but they yield both heavy mineral and light fractions in which to search for shockmetamorphosed grains, thereby increasing the chance of success.

6.8 Objectives for Future Research on the Spherule Layers

Future work on these and associated spherule layers, e.g., the recently discovered Paraburdoo spherule layer (see Hassler et al., 2011), should include the following objectives. It took almost 20 years after the first paper (Lowe and Byerly, 1986) that postulated an impact origin for a Precambrian spherule layer to find a shockmetamorphosed grain in any of the spherule layers, and this single quartz grain was found in a spherule layer that is 1-2 mm thick (Rasmussen and Koeberl, 2004). Searching for shock-metamorphosed grains in reworked spherule layers that are typically a few decimeters-to-meters in thickness has generally been a frustrating effort with negative results: no shock-metamorphosed grains in the heavy mineral fractions were identified in most of the spherule layer samples that were analyzed in the present study. If there is a pattern to the distribution of shock-metamorphosed grains within these spherule layers, then the identification of this pattern would greatly facilitate the discovery of these grains.

The results of the present study may provide a hint of a possible pattern: the distribution of rutile + TiO_2 II grains in the Bee Gorge (Wittenoom) and Monteville spherule layers may be analogous to the distribution of shock-metamorphosed grains in both the K-Pg couplet deposits (see section 1.2.3) and the upper Eocene tektite-bearing

impact ejecta layer that is present on the continental slope off New Jersey (see Glass et al., 1998). This tektite-bearing impact ejecta layer has been linked to the late Eocene Chesapeake Bay impact structure (Glass et al., 1998). Furthermore, Carawine spherule layer sample X38-2 from the upper part of the uppermost debris-flow deposit at the TTT locality (see Fig. 4) contains rutile + TiO₂ II grains. The hypothesis that shockmetamorphosed grains may be concentrated in the upper parts of the spherule layers should be tested beginning with detailed sampling of the entire spherule layer sections at the TTT, Hesta, Tom Price (see Fig. 4), and Monteville farm (see Fig. 5) localities. Highresolution (cm-to-dm-scale) sampling should be done of the uppermost fine-grained zones of the Carawine and Jeerinah spherule layers at the TTT and Hesta localities, respectively (see Hassler et al., 2005), the spherule-rich lenses of the Bee Gorge (Wittenoom) spherule layer and overlying dolomitic turbidite bed at the Tom Price locality (see Simonson and Glass, 2004, their Fig. 8), and both the lower and upper parts of the Monteville spherule layer at the Monteville farm locality (see Simonson et al., 1999, their Fig. 7). Centimeter-scale sampling should be done within the uppermost decimeter of all the spherule layers.

For well-stratified, sandy layers, sample masses of a few hundred grams are probably adequate, but sample masses of \geq 1-2 kg should be used for dolomixtite layers. For example, sample 42-1A (557.5 g; Table 62) is a sandy dolomixtite from the uppermost 0.75 m of the Carawine spherule layer (Table 4) in the Ripon Hills area (see Fig. 4). For this sample, 29 rutile ± anatase grains were recovered from the 63-250 µm size fraction, and 62% (n = 18) were analyzed by micro-Raman spectroscopy, but no evidence of the TiO₂ II phase was found in these grains. However, 86% (n = 25) of the rutile ± anatase grains are buff, and this uppermost interval of the Carawine spherule

layer at this locality should be searched again for rutile + TiO_2 II grains using multikilogram-sized samples. The Bee Gorge spherule layer (BB (sl)) in sample BB from the Bacon Bore locality (see Fig. 4) contains ~290 buff rutile ± anatase grains per kilogram; therefore, this spherule layer at this locality should be searched again for rutile + TiO_2 II grains using samples with masses of ~1-2 kg.

For Bee Gorge samples 96714A and 96714B from the Tom Price locality (see Fig. 4), the origin of the abundant granular rutile grains that occur primarily in the lowermost spherule-rich sublayer (Lspsl) needs to be determined, and this study should begin with optical microscopy and SEM/EDX analysis of polished grain mounts, in conjunction with micro-Raman spectroscopy. Since rutile + TiO_2 II grains are confined to the upper spherule/lutite sublayers (Usplsl) subdivision in each of these samples, a future search for shock-metamorphosed grains of other phases, e.g., quartz, in the Bee Gorge spherule layer at the Tom Price locality should first focus on this stratigraphic interval. It may be possible to focus the search to a thinner (mm-scale) stratigraphic interval by first determining the distribution of rutile + TiO_2 II grains within the four sublayers of this subdivision (see Appendix D).

For future samples, each of the four mm-scale sublayers that comprise the upper spherule/lutite subdivision should be processed separately in recovering heavy minerals in order to determine the stratigraphic distribution of the rutile + TiO_2 II grains. In hand sample, two of these four sublayers consist of lutite, one sublayer is rich in spherules, and one sublayer contains spherule fragments and sand-sized grains (Appendix D). It is hereby hypothesized that the rutile + TiO_2 II grains in this subdivision occur in one or both of the latter two sublayers. Regardless of whether or not this hypothesis is correct, if it turns out that the rutile + TiO_2 II grains are confined to only one or two of the four

sublayers in this subdivision, then the search for other shock-metamorphosed phases can focus on this (these) sublayer(s).

The spherules in the Bee Gorge (Wittenoom) spherule layer have been interpreted as microkrystites that were roughly of basaltic composition (Scally and Simonson, 2005). If the impact event that led to the formation of the Bee Gorge (Wittenoom) spherule layer occurred in the deep ocean, then there should be little, if any, shock-metamorphosed quartz in this spherule layer (Simonson et al., 1998). Furthermore, the Bee Gorge (Wittenoom) spherule layer at the Tom Price locality (see Fig. 4) should contain little, if any, epiclastic, quartzo-feldspathic detritus (see Hassler et al., 2000, 2005). Therefore, the upper spherule/lutite sublayers (UsplsI) subdivision of the Bee Gorge spherule layer at the Tom Price locality appears to be an appropriate stratigraphic interval for a future search for shock-metamorphosed quartz grains that could provide a test of the hypothesis that the formation of the Bee Gorge (Wittenoom) spherule layer was related to a deepocean impact event (Simonson et al., 1998).

The Bee Gorge (Wittenoom) spherule layer is present at a minimum of ~15-16 localities (see Hassler et al., 2000; Scally and Simonson, 2005) over a lateral distance of >350 km in the Hamersley Basin (see Fig. 4), so much more work is needed to determine the heavy mineral assemblages and distribution of rutile + TiO_2 II grains in the spherulerich lenses and/or turbiditic beds that comprise the Bee Gorge spherule layer (see Hassler et al., 2000; Scally and Simonson, 2005). Heavy mineral data for the Bee Gorge spherule layer and context layers at 15-16 localities over this lateral distance should help in evaluating whether the TiO_2 II grains represent epiclastic detritus. Again, the discovery of rutile + TiO_2 II grains in other sections of the Bee Gorge (Wittenoom) spherule layer could help focus the search for other shock-metamorphosed phases in those sections.

Prior to the recognition of the Chicxulub impact structure as the source crater for the impact ejecta in the K/T (now K/Pg) boundary sediments (Hildebrand et al., 1991; Sharpton et al., 1992; Swisher et al., 1992), measurements of the maximum sizes of shock-metamorphosed quartz grains in these sediments on a global scale suggested that the source crater may be in or near North America (e.g., Bohor and Izett, 1986; Bohor, 1990). If the proposed correlation of the Carawine, Jeerinah, and Monteville spherule layers (Simonson et al., 2009a, 2009b, and references therein) is correct, then geographic variation in the average and/or maximum size of the shock-metamorphosed grains in these layers may eventually provide a clue as to whether the Hamersley Basin or the Griqualand West Basin was closer to the source crater. However, there is still uncertainty in the relative positions of the Kaapvaal and Pilbara cratons during the Neoarchean (e.g., de Kock et al., 2009). In any case, recovery of as many shock-metamorphosed grains as possible from these spherule layers should be a high priority in future research.

The 38-63 μ m size fractions of the spherule layer samples should be searched for shock-metamorphosed grains (see Morgan et al., 2006), and the irregular melt particles in the Carawine, Jeerinah, and Monteville spherule layers (Glass and Simonson, 2013, and references therein) should also be searched for shock-metamorphosed grains. Simonson et al. (2000c, their Fig. 7) reported parallel lines of minute inclusions that are candidates for relict PDFs in a few quartz crystals that occur in a few irregular melt particles from the Carawine spherule layer. The irregular melt particles should also be searched for inclusions of rutile grains. If the irregular melt particles incorporated rutile + TiO₂ II grains, then in light of the results (see section 6.2.3) of the isothermal annealing

experiments on rutile + TiO_2 II crystals (Linde and DeCarli, 1969), it is likely that the TiO_2 II phase inverted back to rutile while the irregular melt particles were still molten. However, if inclusions of rutile grains were identified in the irregular melt particles, then it would demonstrate that rutile was present in the target materials, and this observation would be consistent with the hypothesis that the TiO_2 II phase is syngenetic with respect to its host spherule layer. The discovery of shock-metamorphosed grains in the irregular melt particles would provide a strong argument that the spherule layers are of impact origin.

The search for inclusions of shock-metamorphosed grains in the irregular melt particles (e.g., Simonson et al., 2000c) could begin with optical microscopy and SEM/EDX analysis of polished thin sections. A second approach could involve lightly grinding the irregular melt particles using a mortar and pestle in conjunction with ultrasonic agitation. The ground and disaggregated material should undergo HNO₃ digestion to remove any carbonate material that may be present (see Simonson et al., 2000c). The acid-insoluble material should be wet sieved using 63 µm and 125 µm sieves, and the two larger size fractions should go through heavy liquid separation. The heavy mineral grains, if any, could be identified by micro-Raman spectroscopy and possibly XRD. Again, polished thin sections of the light fraction grains should be searched for shock-metamorphosed quartz grains using optical microscopy and SEM/EDX analysis.

The rutile + TiO_2 II grains may help to resolve the long-standing question (e.g., see Simonson, 1992; Simonson et al., 1998; Simonson et al., 2009b) as to the nature of the target rocks for the impact events responsible for the spherule layers. Over the last decade, several studies of the trace element geochemistry of detrital rutile grains,

especially using Cr and niobium (Nb) concentrations, have shown that rutile grains derived from metapelitic rocks can be discriminated from those derived from metamafic rocks (e.g., Zack et al., 2004; Triebold et al., 2012). Trace element geochemical studies of the rutile + TiO_2 II grains may shed light on whether the impact events occurred on continental and/or oceanic crust.

The search for shock-metamorphic effects in the white opaque zircon grains should continue, using optical microscopy, SEM/EDX analysis, and micro-Raman spectroscopy on polished thin sections (see Bohor et al., 1993; Wittmann et al., 2006) and TEM analysis (see Leroux et al., 1999; Reimold et al., 2002). Zircon grains were recovered from all five spherule layers (Table 63). U-Pb geochronology of the zircon grains (e.g., see Trendall et al., 2004; Rasmussen et al., 2005) may potentially provide maximum depositional ages of the spherule layers that could test their proposed correlation (see Simonson et al., 2009a, 2009b), and together with additional trace element and isotopic analyses of the zircon grains, these data could be used for petrologic and provenance studies (see Gehrels, 2012).

In fact, results from the present study show that spherule layers may be very useful for zircon provenance studies: the abundance (number of grains/kilogram) of zircon grains in them can be orders of magnitude higher than the values for the associated context samples. For example, for the 63-125 μ m size fraction, the dolomixtite from the upper part of the Carawine spherule layer (sample X38-2) at the TTT locality (see Fig. 4) has >800 zircon grains/kg, whereas the three Carawine context samples have 0-17 zircon grains/kg (Table 62). For this same size fraction, the dolomixtite of the Grænsesø spherule layer has ~450 to 7,300 zircon grains/kg, whereas the two Grænsesø context samples each have \leq 13 zircon grains/kg (Table 62).

For a robust provenance study, a threshold value of ~100 zircon grains is probably an underestimate from a practical standpoint, and a much larger number of zircon grains would be needed to recognize all the minor age populations (Gehrels, 2012, and references therein). For example, for a recent provenance study, U-Pb ages were obtained for 1,655 individual detrital zircon grains from 18 samples of Jurassic sandstones from the Colorado Plateau, USA, with each sample having a mass of 22-24 kg (Dickinson and Gehrels, 2009).

For the dolomixtites of the Grænsesø spherule layer and the upper part of the Carawine spherule layer at the TTT locality, samples with masses of 1-5 kg should yield ≥ 2000 zircon grains (Table 62). For the basal thin-bedded zone of the Jeerinah spherule layer at the Hesta locality, the upper sandy part of the Monteville spherule layer at the Monteville farm locality, and the rippled Bee Gorge spherule layer at the Bacon Bore locality, samples with masses of 10-15 kg should yield zircon amounts (Table 62) comparable to that (n = 1,655) used in the provenance study of the Jurassic sandstones (see Dickinson and Gehrels, 2009). The Carawine spherule layer dolomixtite in the Ripon Hills area shows an order of magnitude variation in zircon abundance (Table 62), so samples of the Carawine spherule layer from this area that are used for a future zircon provenance study should have masses $\geq 20-25$ kg. Furthermore, the epiclastic zircon grains in a spherule layer are potentially being derived from a large area that may contain rocks and sediments having a wide range in age. Detrital zircon geochronology studies have greatly increased in number during the past ~20 years (Gehrels, 2012), and Precambrian spherule layers may prove to be very useful for these studies.

U-stage measurements should be completed on the quartz grains with planar microstructures that were found in Carawine spherule layer sample 43-1. In addition to

the upper spherule/lutite sublayer (UsplsI) subdivision in Bee Gorge samples 96714A and 96714B, searches for shock-metamorphosed quartz grains, using light fraction grain mounts, should begin with the other spherule layer samples that contain rutile + TiO_2 II grains: sample X38-2 (Carawine), sample X21-1 (Jeerinah), and sample V111 (Monteville) (see Table 63). Sample 42-1A from the uppermost 0.75 m of the Carawine spherule layer in the Ripon Hills area should also be carefully searched for shock-metamorphosed quartz grains are found in these samples and/or additional samples from these spherule layers, then their distribution and abundance could help in evaluating their origin as well as the nature of the target rocks (continental and/or oceanic crust) for the impact events.

Electron microprobe analysis of the chrome spinel grains (see Bevan and Rodgers, 1977) may yield data that are useful for both provenance studies and correlation of the spherule layers. The white opaque rutile + unidentified grains should be analyzed by XRD and SEM/EDX to complete their identification. For several samples, the origin (detrital and/or secondary) of the anatase, monazite, and xenotime grains needs to be determined. Micro-Raman spectroscopy shows that each of these phases can occur singularly or together, e.g., anatase + monazite, as well as in association with other phases, e.g., rutile and quartz. SEM/EDX analysis of loose grains of anatase, monazite, and xenotime should be done to examine their surfaces for evidence of transport, e.g., degree of roundness and abrasion features. SEM/EDX analysis of loose multi-phase grains should be done to determine the textural relationship of the phases that should help to determine their origin. SEM/EDX analysis and optical microscopy of polished grain mounts of multi-phase grains, in conjunction with micro-Raman spectroscopy, can yield

additional textural and mineralogical data that should help to determine the origin(s) of the anatase, monazite, and xenotime grains.

Field work is needed on the Grænsesø spherule layer to search for additional outcrops and to map its full extent. The lower and upper contacts of the Grænsesø spherule layer at the Midternæs outcrop need to be cleared of rubble, and a detailed sedimentological analysis needs to be done of the entire Grænsesø spherule layer. Highresolution (cm-scale) sampling of the Grænsesø spherule layer near its contacts, especially its upper contact, needs to be conducted to continue the search for shockmetamorphosed grains.

The Grænsesø Formation, that is the uppermost formation in the Vallen Group (Higgins, 1970), should be carefully searched for tuff layers that may yield syneruptive zircon grains suitable for U-Pb radiometric dating (see Rasmussen and Fletcher, 2010) in order to better constrain the age of deposition of the Grænsesø spherule layer (see section 2.4). In the Midternæs area, samples of intermediate-to-felsic pyroclastic rocks in the Sortis Group, that directly overlies the Vallen Group (Higgins, 1970), should be collected and searched for syneruptive zircon grains suitable for U-Pb radiometric dating that could yield a minimum age of deposition for the Grænsesø spherule layer. It is important for modeling both the cratering flux of Earth (see Bottke et al., 2012) and the formation of distal impact ejecta layers, to determine whether the Grænsesø spherule layer is part of the ejecta layer for the Vredefort or Sudbury impact events (see section 1.1), or if it is part of a distal impact ejecta layer from a third large Paleoproterozoic impact event (see Glass and Simonson, 2013).

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Appendix A

DESCRIPTIONS OF CARAWINE SPHERULE LAYER HAND SAMPLES

Sample number: X38-2

Sample notes by Dr. Bruce M. Simonson: The sample is from the sandy upper part of the

dolomixtite at the Tarra Tarra turnoff (TTT) locality.

Number of pieces: Three (sawn as received)

Original weight of pieces: 27.0 g (smallest piece); 31.9 g; 324.9 g (largest piece);

total weight = 383.8 g

Size: ~4.4 by 1.8 by 1.7 cm (smallest piece); 4 by 1.7 by (0.8 to 3) cm; ~11.3 by 5 by

3.8 cm (largest piece)

Shape: Blocky (smallest piece); irregular; blocky (largest piece)

Colors: The sample is pale red (5R 6/2) to moderate red (5R 5/4) on a sawn surface, and it is moderate orange pink (10R 7/4) on a weathered surface.

Effervescence in 10% HCl at room temperature: Generally weak; the caliche has a strong reaction.

Lithology: The sample is a dolomixtite with a fine-to-medium-grained crystalline dolomitic matrix. A light-colored zone of caliche, up to ~15 mm thick, occurs along one of the long sides of the largest piece (Fig. 272). This zone is strongly oxidized and contains solution cavities. There are medium dark gray (N4), irregularly-shaped splotches $(D \sim 1-2 \text{ mm})$ of fine-grained material. This material appears to consist of secondary manganese and iron oxide/oxyhydroxide phases.

Medium dark gray (N4), subangular chert clasts, typically ≤ 5 mm in size, are dispersed in the rock, and they comprise <5 vol% of the rock. One tabular chert clast is ~ 1 cm long. There is one subangular dolomite clast that is ~ 1.5 cm in size. Silt-to-fine sand-sized siliciclastic grains are dispersed in the rock, and they stand in relief on a weathered surface. There are two light-colored spherical spherules (D ~ 0.5 -1 mm), and one ovoid spherule that is replaced by iron oxide/oxyhydroxide. There are a few light-colored, blocky, irregular melt particles, typically < 0.5 cm in size, that stand in relief on a weathered surface.



Figure 272: A sawn surface of the largest piece of Carawine spherule layer sample X38-2 showing medium dark gray (N4) chert (ch) clasts. The rock is a dolomixtite.

Sample number: W85-2

Sample notes by Dr. Bruce M. Simonson: The sample is a dolomitic piece that is rich in large irregular (melt) particles. It is float from the slope in front of the outcrop (Ripon Hills (RH)), but it is undoubtedly from the lower part of the spherule layer.

Number of pieces: One

Original weight of piece: 715.3 g

Size: ~9 by 8 by 7 cm

Shape: Approximately equant

Colors: The sample is medium gray (N5) on a fresh surface, and pale brown (5YR 5/2) to dark yellowish brown (10YR 4/2) on a weathered surface.

Effervescence in 10% HCl at room temperature: Very weak along thin fractures and very thin calcite veinlets

Lithology: The sample is a dolomixtite with a medium-grained crystalline dolomitic matrix (Fig. 273). No layering is apparent in the rock. The weathered surface is manganiferous. There is a single black (N1), tabular clast (~3 by 55 mm), and a few spherical spherules. Grayish orange pink (5YR 7/2) irregular melt particles, up to 1.4 cm in size, comprise ~5 vol% of the rock. There are a few thin fractures, and very thin calcite veinlets. The rock does not attract a pencil magnet.



Figure 273: Carawine spherule layer float sample W85-2 showing a black (N1) tabular clast (tc) and a grayish orange pink (5YR 7/2) irregular melt particle (irr). The rock is a dolomixtite.

Sample number: 84-1

Sample notes by Dr. Bruce M. Simonson: The sample is from the basal 20 cm of the spherule layer at the west end of the exposure (Ripon Hills south (RS)). The sample is rich in large irregular (melt) particles, and it is rather manganiferous.

Number of pieces: One

Original weight of piece: 1,179.3 g

Size: ~11 by 10 by 9 cm

Shape: Approximately equant

Colors: All surfaces are very weathered to a grayish brown (5YR 3/2) to dusky yellowish brown (10YR 2/2).

Effervescence in 10% HCl at room temperature: Good

Lithology: The sample is a moderately weathered calcareous dolomixtite with secondary iron and manganese oxide/oxyhydroxide phases (Fig. 274). No layering was observed in the rock. Light brown (5YR 6/4) weathered spherules ($D \le 1$ mm) and irregular melt particles (up to 8 mm in size) are dispersed in the rock, and they comprise ~5-10 vol% of the rock. The spherules and irregular melt particles stand in relief on one side of the sample. Most of the spherules are spherical, but I observed one dumbbell. The irregular melt particles are blocky and elongate. An irregular network of white (N9), thin (≤ 0.5 mm wide) calcite veinlets comprises <3 vol% of the rock. The rock does not attract a pencil magnet.



Figure 274: Carawine spherule layer sample 84-1 that is a calcareous dolomixtite with secondary iron and manganese oxide/oxyhydroxide phases.

Sample number: X24-1

Sample notes by Dr. Bruce M. Simonson: The sample is a dolomitic piece that is rich in large irregular (melt) particles. The sample is from the lower part of the spherule layer from a new site found in 2001 that is a bit southwest of the main exposure (Ripon Hills (RH)).

Number of pieces: Two (each sawn as received)

Original weight of pieces: 995.7 g (smaller piece); 1,296.6 g (larger piece);

total weight = 2,292.3 g

Size: ~11.5 by 10 by 3.5 cm (smaller piece); ~17 by 12 by 3 cm (larger piece)

Shape: Blocky (smaller piece); blocky (larger piece)

Colors: The sample is medium light gray (N6) to medium bluish gray (5B 5/1) on a sawn surface, and dark yellowish brown (10YR 4/2) to moderate yellowish brown (10YR 5/4) on weathered surfaces that have a manganiferous coating.

Effervescence in 10% HCl at room temperature: Very weak

Lithology: The sample is a dolomixtite with subrounded-to-subangular clasts of carbonate and very fine-grained chert in a dolomitic matrix (Fig. 275). The clasts are typically 1-2 cm in size, but some are up to ~4.5 cm in size. The rock contains spherules and light-colored irregular melt particles. The irregular melt particles are ~1-6 mm long, and they are ovoid-to-blocky in shape. The irregular melt particles appear to be very finely laminated, and some of them contain very small vesicles.

Dark brown-to-black, very small ovoid specks and splotches that may represent oxidized sulfide crystals comprise ~1-2 vol% of the rock. There are a few white (N9) veinlets that are typically <1 mm wide, but portions of them may be up to 6 mm wide. A penknife appears to scratch the veinlets, but the veinlets have little or no reaction with 10% HCl, and they may be dolomitic in composition. The rock does not attract a pencil magnet.



Figure 275: A sawn surface of the larger piece of Carawine spherule layer sample X24-1 showing chert (ch) clasts and dolomitic (?) veinlets (vnlts). The rock is a dolomixtite.

Sample number: 43-1

Sample notes by Dr. Bruce M. Simonson: The sample is from the finer zone near the top of the lowermost subunit at the main exposure (Ripon Hills south (RS)). The sample is dolomite-rich, and spherules and irregular (melt) particles are somewhat sparse.

Number of pieces: One (with a sawn surface as received)

Original weight of piece: 10,650 g

Size: ~22 by 19 by 17 cm

Shape: Blocky

Colors: The sample is pale red (5R 6/2) to medium gray (N5) on the sawn surface, and it is medium dark gray (N4) on the chipped surface. The weathered surface is dark yellowish brown (10YR 4/2).

Effervescence in 10% HCl at room temperature: Very weak

Lithology: The sample is a dolomixtite with a fine-to-medium-grained crystalline dolomitic matrix that comprises ~80 vol% of the rock (Fig. 276). Dark gray (N3), subangular-to-angular, very fine-grained lithic fragments (~0.05-1.9 cm in size) are dispersed in the rock, and they comprise ~3-4 vol% of the rock. Very light gray (N8) to light gray (N7), rounded, elliptical-to-irregular-shaped clasts (~0.2-1.6 cm in size) comprise ~10 vol% of the rock, and they do not react with 10% HCl. Reddish brown angular fragments, up to ~0.3 cm in size, comprise <5 vol% of the rock. The clasts are matrix-supported, and some of the clasts show a preferred orientation.

Spherical spherules (D <1 mm) are dispersed in the rock, and they comprise \sim 2 vol% of the rock. Dark yellowish brown (10YR 4/2) irregular melt particles, up to \sim 0.9 cm in size, comprise <1 vol% of the rock. Some of the irregular melt particles appear to contain very small crystalline aggregates and possibly lithic fragments. It is

difficult to see siliciclastic grains in the sample. Irregular patches of secondary iron oxide/oxyhydroxide, up to \sim 2-4 mm in size, typically occur along or near very thin fractures.



Figure 276: A sawn surface of Carawine spherule layer sample 43-1. The rock is a dolomixtite.

Sample number: 42-1A

Note on sample labeling: This is a replicate sample of sample 42-1. Sample 42-1 was initially processed, but it may have been accidently contaminated during sample preparation, so it is not considered in this study. Dr. Bruce M. Simonson sent me this replicate sample, and I refer to it as sample "42-1A".

Sample notes by Dr. Scott W. Hassler: The sample is from the RH-1 section (Ripon Hills south (RS)) that was measured in 1993. The lower and upper contacts of the spherule layer (dolomixtite) are exposed, and the spherule layer measures 26.22 m in total thickness. The spherule layer consists of three flow intervals that are delineated on the basis of grain size trends. Sample 42-1 is from the uppermost 0.75 m of the uppermost flow interval that measures 4.3 m in total thickness. This uppermost 0.75 m-thick section is fine-grained, and it contains spherules, rare large pebbles, and chert-silicate clasts (~15%), but no tabular clasts.

Number of pieces: One (two sawn surfaces at ~80° as received)

Original weight of piece: 2,165.1 g

Size: ~17 by 11 by 7.5 cm

Shape: Blocky

Colors: The rock is pale red (10R 6/2) on a sawn surface, and it is grayish red (10R 4/2), grayish brown (5YR 3/2), and pale brown (5YR 5/2) on the weathered surface. Effervescence in 10% HCl at room temperature: Very weak to weak

Lithology: The sample is a sandy dolomixtite with a fine-grained, crystalline dolomitic matrix (Fig. 277). The weathered surface has a rough and sandy texture. There are low-relief corrugations on the weathered surface that may represent mm-scale primary stratification. Spherules (D \sim 0.5-1 mm) with light-colored rims are dispersed through the
sample, and they comprise <10 vol% of the sample. Moderate orange pink (10R 7/4) to moderate reddish orange (10R 6/6) oval particles, up to $\sim1-2$ mm in size, are dispersed through the sample, and they comprise <5 vol% of the sample. These objects may be spherules and/or irregular melt particles.

Medium gray (N5) to medium dark gray (N4), subangular-to-angular, very finegrained lithic fragments, up to ~7 mm long, are dispersed through the sample, and they comprise ~1-2 vol% of the sample. The lithic fragments are typically elongate, and their long axes are approximately parallel to the corrugations on the weathered surface that may represent stratification. The lithic fragments do not effervesce in 10% HCl. Small (<0.5 mm), red brown, box-shaped, very fine-grained particles are dispersed through the sample, and they comprise <2 vol% of the sample. These particles are probably oxidized crystals of secondary sulfide, probably pyrite. No brassy-colored pyrite was observed.

The sample contains one set of fairly prominent thin ($\leq 1 \text{ mm wide}$) veinlets that show a variable effervescence in 10% HCl.The veinlets are sub-parallel, and they have a spacing of ~0.5-2 cm. The veinlets consist of medium-to-light gray, fine-grained crystals that appear to be calcite and quartz. On a sawn surface, there are 3 or 4 similar veinlets that strike at a high-angle to the prominent set of veinlets. The veinlets comprise ~1 vol% of the sample.



Figure 277: A sawn surface of Carawine spherule layer sample 42-1A showing two lithic fragments (lf). The lithic fragments show alignment of their long axes. The rock is a sandy dolomixtite.

Appendix B

DESCRIPTIONS OF CARAWINE CONTEXT HAND SAMPLES

Sample number: X68-1

Sample notes by Dr. Bruce M. Simonson: The sample is from the Tarra Tarra turnoff

(TTT) locality, and it is from the laminated dolomite that underlies the spherule layer

(dolomixtite). The sample is $\sim 10-20$ m below the dolomixtite.

Number of pieces: One

Original weight of piece: ~710 g

Size: 9 by 6.5 by 4.5 cm

Shape: Like a shoebox

Colors: The fresh matrix is medium dark gray (N4) to dark gray (N3), and the oxidized parts (see below) are dark yellowish brown (10YR 4/2), moderate brown (5YR 4/4), and pale brown (5YR 5/2).

Effervescence in 10% HCl at room temperature: Very weak

Lithology: The sample is a fresh-looking, well-indurated, laminated, fine-grained dolomite (Fig. 278). There is some oxidation on the surface, as well as along ~8-10 laminae. I did not observe any clasts, sand-sized grains, cherty material or sulfide crystals. Two thin (<1 mm wide), straight, sub-parallel dolomite veinlets are approximately perpendicular to the laminae. The sample does not attract a pencil magnet.



Figure 278: Carawine context sample X68-1 that is a well-indurated, laminated, finegrained dolomite. Sample number: 104141

Sample notes by Dr. Bruce M. Simonson: The sample is from the Ripon Hills southeast (RE) site, and it is a dolomitic laminite that is typical of the basinal strata that enclose the spherule layer (dolomixtite). The sample is \sim 5 m below the dolomixtite.

Number of pieces: One

Original weight of piece: 385.9 g

Size: ~7 by 6 by 3.5 cm

Shape: Like a shoebox

Colors: The rock is medium gray (N5) to medium dark gray (N4) on a fresh surface, and dark yellowish brown (10YR 4/2) to moderate brown (5YR 4/4) on the weathered surface.

Effervescence in 10% HCl at room temperature: Very weak

Lithology: The sample is a fresh-looking, well-indurated, well-laminated, fine-grained dolomite (Fig. 279). The sample encompasses ~7 cm of stratigraphic section. The laminae are more prominent on the weathered surface. I did not observe any clasts, sand-sized grains, cherty material or sulfide crystals. One thin (<1 mm wide), straight, slightly resistant veinlet traverses the sample, and it is approximately perpendicular to the laminae. The veinlet does not react with 10% HCl, and it is probably quartz. The sample does not attract a pencil magnet.



Figure 279: Carawine context sample 104141 that is a well-indurated, laminated, finegrained dolomite. Sample number: 104175

Sample notes by Dr. Bruce M. Simonson: The sample is from the Ripon Hills south (RS) site, and it is a dolomitic laminite that is typical of the basinal strata that enclose the spherule layer (dolomixtite). The sample occurs ~20 m above the dolomixtite. Number of pieces: Two (sawn as received)

Original weight of pieces: 24.1 g (smaller piece); 272.6 g (larger piece);

total weight = 296.7 g

Size: ~2.9 by 2.8 by 1.5 cm (smaller piece); 8.3 by 4.2 by 3.5 cm (larger piece)

Shape: Blocky (smaller piece); blocky (larger piece)

Colors: The pieces are medium light gray (N6) to medium gray (N5) on the sawn surfaces, and pale brown (5YR 5/2) to dark yellowish brown (10YR 4/2) on weathered surfaces. About 8 laminae in the larger piece and 6 laminae in the smaller piece are medium dark gray (N4).

Effervescence in 10% HCl at room temperature: Variable; stronger on weathered surfaces Lithology: The sample is a fresh-looking, well-indurated, laminated, fine-grained sugary crystalline dolomite (Fig. 280). The grain size appears to be very uniform. The laminae (\leq 2 mm thick) can have flat bases and parallel contacts, or the contacts can be a little wavy. There is some preferred weathering along the darker laminae. The smaller piece encompasses ~2.9 cm of stratigraphic section. I did not observe any clasts, sand-sized grains, cherty material, sulfide crystals, veinlets, or significant fractures.



Figure 280: The two pieces of Carawine context sample 104175. The sample is a well-indurated, laminated, fine-grained dolomite.

Appendix C

DESCRIPTIONS OF JEERINAH SPHERULE LAYER HAND SAMPLES

Sample number: W94-1Q

Sample notes by Dr. Bruce M. Simonson: This is a float sample that is pretty rich in spherules, and it is heavily oxidized.

Number of pieces: One

Original weight of piece: 88.2 g

Size: ~6.6 by 5.8 by 2.1 cm

Shape: Blocky

Colors: The matrix is very dusky red (10R 2/2) to moderate reddish orange (10R 6/6), and the oxidized coating on >80% of the surface is moderate reddish orange (10R 6/6) to light brown (5YR 5/6).

Effervescence in 10% HCl at room temperature: None

Lithology: About 30-35 vol% of the rock consists of very fine-grained, oxidized, matrix material that slightly flakes off with a needle. Spherical-to-ovoid spherules ($D \le 1 \text{ mm}$) are evenly dispersed through the matrix, and they comprise ~10 vol% of the sample. There are light gray (N7) to white (N9), elongate, angular grains (chert?), up to ~2 mm in diameter, that show a preferred orientation, and they do not scratch with the needle. A few very dark red (5R 2/6), hard, elongate, angular, fine-grained clasts (argillite?), up to ~6 mm long, are dispersed through the sample, and they show the same preferred orientation as the light-colored sand-sized grains (Fig. 281). There are two irregular melt

particles, ~2-3 mm in size, that have a different appearance than the other components in the sample. One of the irregular melt particles is light gray (N7) and the other is dark gray (N3), and they both appear to have a very fine faint banding or layering.



Figure 281: Jeerinah spherule layer sample W94-1Q with very dark red (5R 2/6), elongate, angular, fine-grained, lithic fragments (lf). The long axes of the indicated lithic fragments show a preferred orientation.

Sample number: X21-1

Sample notes by Dr. Bruce M. Simonson: This is a float sample that was collected on the slope in front of the outcrop.

Number of pieces: Two

Original weight of pieces: 136.6 g (smaller piece); 312.2 g (larger piece);

total weight = 448.8 g

Size: ~7.5 by 5 by 2 cm (smaller piece); no data for the larger piece

Shape: Blocky (smaller piece); no data for the larger piece

Colors: The sample is pale red (5R 6/2) to grayish red (5R 4/2) on a fresh surface, and it is moderate reddish orange (10R 6/6) on a weathered surface.

Effervescence in 10% HCl at room temperature: None

Lithology: The sample has a fine-grained ferruginous matrix, and it does not attract a pencil magnet. Light gray (N7), spherical-to-ovoid spherules and possible spherule fragments (D \leq 1 mm) comprise ~40-50 vol% of the sample. Very light gray (N8), irregular blocky fragments, up to ~4 mm in size, comprise <1 vol% of the sample. Dark reddish brown (10R 3/4), ferruginous, fine-grained clasts, up to 4 mm long, comprise ~10-15 vol% of the sample. The clasts are tabular and elongate, and they show a preferred orientation (Fig. 282).



Figure 282: The smaller piece of Jeerinah spherule layer sample X21-1 showing a few dark reddish brown (10R 3/4), elongate, fine-grained, lithic fragments (lf). The long axes of the indicated lithic fragments show a preferred orientation.

Appendix D

DESCRIPTIONS OF BEE GORGE (WITTENOOM) HAND SAMPLES

Sample numbers: 96714A and 96714B

Note on sample labeling: As noted by Dr. Simonson (see below), the samples are two slabs from the same rock (sample 96714). Since the two slabs were processed separately, they are considered two samples, and I refer to these samples as 96714A and 96714B. Sample notes by Dr. Bruce M. Simonson: The two slabs are from the same sample. The spherule layer is unusual in this sample in that it consists of a lower, thinner spherule-rich part (rippled, I believe), and a thicker (cm-scale) upper part with finer spherules and spherule fragments dispersed in a finer, shaly matrix. The rest of the sample is probably a mix of ambient lutite that consists of a combination of shale and carbonate. Number of pieces: 96714A (One); 96714B (One); both pieces were sawn as received Original weight of pieces: 96714A (184.0 g); 96714B (177.3 g); total weight = 361.3 g Size: 96714A (Cone); 96714B (Blocky)

Effervescence in 10% HCl at room temperature: Weak to moderate Lithologies: Samples 96714A and 96714B are essentially identical, adjoining slabs that are mirror images of one another. They both have stratigraphic "up" arrows, and they both encompass the same stratigraphic section. Each sample consists of a cm-scale, basal carbonate lutite context layer (Bcl; see Figs. 283 and 284) that is sharply overlain by a spherule layer. In each sample, the spherule layer consists of a set (~1.3-2.1 cm thick) of six sublayers that were sawn into the following three subdivisions (see Figs. 283 and 284): lowermost spherule-rich sublayer (Lspsl), spherule-bearing lutite sublayer (Splsl), and an upper spherule/lutite sublayers (Usplsl) subdivision that consists of four sublayers. I described sample 96714A, and for sample 96714B, I recorded the thicknesses of the basal carbonate lutite context layer and the six sublayers of the spherule layer.

Basal carbonate lutite (Bcl) context layer

This layer comprises the lower halves of samples 96714A and 96714B. It consists of medium dark gray (N4), fine-grained carbonate lutite. The layer is ~24 mm thick (20-23 mm thick in sample 96714B), and it contains about seven grayish red (5R 4/2), thin (\leq 1 mm) laminae that contain some brown spots that probably represent oxidized pyrite crystals. No spherules, irregular melt particles, clasts, sand-sized grains or veinlets are visible, and the layer does not attract a pencil magnet.

Spherule layer

The three subdivisions are described in ascending stratigraphic order. The lowermost spherule-rich sublayer (Lspsl) is 2-5 mm thick (3-6 mm thick in sample 96714B), and its basal contact is sharp with a relief of ~1 mm. A very thin layer of brown oxidized material occurs along the basal contact. This sublayer is moderate brown (5YR 4/4) on a fresh surface, and grayish red (5R 4/2) on a weathered surface. Light gray (N7) to medium dark gray (N4), spherical-to-ovoid spherules (D \leq 1 mm) occur in a lutite matrix, and they comprise 40-50 vol% of the sublayer. The cores of some of the spherules are replaced by fine-grained brown material. The lowermost spherule-rich sublayer (Lspsl) appears to be rippled (B. M. Simonson, personal communication, 2002).

The spherule-bearing lutite sublayer (SplsI) is 7-9 mm thick in both samples. It is medium gray (N5) on a fresh surface, and yellowish gray (5Y 7/2) on a weathered surface. Spherules comprise ~10-15 vol% of this sublayer. The spherules are dispersed in the sublayer, and they may be a little smaller on average than the spherules in the lowermost spherule-rich sublayer (LspsI).

The spherule-bearing lutite sublayer (SplsI) is overlain by the upper spherule/lutite sublayers (UsplsI) subdivision that consists of four sublayers. The basal sublayer of this uppermost subdivision is a spherule-rich lutite that is ~1-2 mm thick in sample 96714A, and ~0.5-2 mm thick in sample 96714B. This sublayer is moderate yellowish brown (10YR 5/4) to grayish orange (10YR 7/4) on a fresh surface, and it is moderate brown (5YR 3/4) on a weathered surface. The contacts of this sublayer are fairly sharp and parallel. The spherules are generally smaller than those in the lowermost spherule-rich sublayer (LspsI), and they comprise ~30-35 vol% of the sublayer. The upper spherule/lutite sublayers (UsplsI) subdivision shows a stronger effervescence in 10% HCl than the lowermost spherule-rich (LspsI) and spherule-bearing lutite (SplsI) sublayers.

In the upper spherule/lutite sublayers (UsplsI) subdivision, a thin (~1 mm thick), medium gray (N5) lutite sublayer overlies the basal spherule-rich lutite sublayer. A medium gray (N5) to medium dark gray (N4) sandy sublayer (~1-2 mm thick) overlies this thin lutite sublayer. The sandy sublayer has sharp contacts, and it contains subangular-to-angular, silt-to-very fine sand-sized grains and spherule fragments. A light olive gray (5Y 6/1), faintly laminated lutite sublayer (~1-2 mm thick) overlies this sandy sublayer. A moderate reddish orange (10R 6/6) thin coating of secondary iron

643

oxide/oxyhydroxide is present on the upper and lower surfaces of samples 96714A and 96714B. Neither sample attracts a pencil magnet.



Figure 283: A sawn surface of Bee Gorge (Wittenoom Fm.) sample 96714A showing the following four subdivisions that were processed separately: basal carbonate lutite (Bcl) context layer, lowermost spherule-rich sublayer (Lspsl), spherule-bearing lutite sublayer (Splsl), and the upper spherule/lutite sublayers (Usplsl) subdivision. The arrow shows stratigraphic "up", and the "I" on the left shows the main spherule-bearing interval. Fm. = Formation.



Figure 284: Weathered surface of Bee Gorge (Wittenoom Fm.) sample 96714B showing the following four subdivisions that were processed separately: basal carbonate lutite (Bcl) context layer, lowermost spherule-rich sublayer (Lspsl), spherule-bearing lutite sublayer (Splsl), and the upper spherule/lutite sublayers (Usplsl) subdivision. The arrow shows stratigraphic "up", and the "I" on the left shows the main spherule-bearing interval. Fm. = Formation. Sample number: BB

Sample notes by Dr. Bruce M. Simonson: The sample is mostly the spherule-rich layer, probably representing a single ripple. There is some caliche admixed, but it is probably too intimately mingled to separate it out. The rest of the sample is the ambient lutite that is a mix of shale and carbonate.

Number of pieces: One

Original weight of piece: 105.3 g

Size: ~7 by 4 by 2.5 cm

Shape: Blocky

Colors: Light olive gray (5Y 6/1) to light brownish gray (5YR 6/1)

Effervescence in 10% HCl at room temperature: Moderate

Lithologies: The sample consists of a spherule layer that is sandwiched between two carbonate lutite context layers. There is no stratigraphic "up" arrow on the sample, so the relative age of the three layers is unknown. The spherule layer is referred to as "BB (sl)". The thinner carbonate lutite context layer is named "context layer #1" and it is referred to as "BB (#1)". The other carbonate lutite context layer is named "context layer #2" and it is referred to as "BB (#2)".

The spherule layer (Fig. 285) is ~8-14 mm thick. Very light gray (N8) to medium gray (N5) spherules ($D \le 1 \text{ mm}$) occur in a light gray to brown, very fine-grained matrix. The spherules comprise >50 vol% of the spherule layer. There is no obvious gradation in the size of the spherules across the spherule layer. Some spherules are replaced by fine-grained iron oxide/oxyhydroxide.

Context layer #1 (Fig. 285) is laminated, and it is typically <7 mm thick. Solution cavities (up to ~1 cm in size) and caliche occur along the contact with the spherule layer.

This contact area weakly attracts a pencil magnet. Context layer #2 (Fig. 285) is laminated to thinly bedded, and it is ~6-11 mm thick. Context layer #2 contains a few fractures or partings that are subparallel to the bedding. Solution cavities and moderate orange pink (5YR 8/4) to light brown (5YR 6/4), clay-to-sand-sized caliche are present along fractures or partings. The caliche weakly attracts a pencil magnet.



Figure 285: A sawn surface of Bee Gorge (Wittenoom Fm.) sample BB showing the spherule layer (BB (sl)) that is sandwiched between two carbonate lutite context layers: context layer #1 (BB (#1)) and context layer #2 (BB (#2)). There is no stratigraphic "up" arrow on the sample, so the relative age of the three layers is unknown. Fm. = Formation.

Sample number: 92058 (Context sample)

Sample notes by Dr. Bruce M. Simonson: The sample is from the Wittenoom Gorge/Cathedral Pool site, and it occurs about 1 m above the spherule layer. The sample is a ripple cross-laminated fine calcarenite that is probably a carbonate turbidite. Number of pieces: Three Original weight of pieces: 479.2 g (total) Size: 6 by 3 by 2 cm (smallest piece); 5 by 3.5 by 2.5 cm; 5.5 by 5 by 3.5 cm (largest piece) Shape: Blocky (smallest piece); blocky; blocky (largest piece) Colors: The matrix is medium gray (N5) to medium dark gray (N4), the three bands (see below) are dark gray (N3) to pale yellowish brown (10YR 6/2), and the weathered surfaces are light brown (5YR 5/6) to moderate yellowish brown (10YR 5/4). Effervescence in 10% HCl at room temperature: Moderate to strong Lithology: The sample is a well-indurated, fine-grained calcarenite with three distinct thin (\leq 3 mm thick) bands (Fig. 286). The bands appear to be a little coarser-grained than the matrix, and one of the bands contains disseminated dark brown to ochre spots that are <1 mm in size. There are no visible clasts, sand-sized siliciclastic grains, unoxidized sulfide crystals, or veinlets. It is very difficult to see a cross-lamination. The sample does not attract a pencil magnet.



Figure 286: The three pieces of Bee Gorge (Wittenoom Formation) context sample 92058. The sample is a well-indurated, fine-grained calcarenite with a few distinct bands.

Appendix E

DESCRIPTIONS OF MONTEVILLE SPHERULE LAYER HAND SAMPLES

Sample number: U63-1

Sample notes by Dr. Bruce M. Simonson: The sample is a slab that is rich in sugary carbonate, and it is from the coarse, intraclast- and spherule-rich lower part of the spherule layer.

Number of pieces: One (sawn slab as received)

Original weight of piece: 814.7 g

Size: ~ 21 by 8 by 2 cm

Shape: Elongate slab with two parallel sawn surfaces

Colors: The sample is grayish red (5R 4/2), dark reddish brown (10R 3/4), and medium gray (N5).

Effervescence in 10% HCl at room temperature: Moderate to strong

Lithology: About 50 vol% of the rock consists of medium-to-coarsely crystalline calcite that occurs as a sugary matrix and as pinkish gray (5YR 8/1) irregular veinlets that are <8 mm wide (Fig. 287). Grayish red (5R 4/2) to dark reddish brown (10R 3/4), cm-sized hematitic clasts comprise \sim 30 vol% of the sample. The clasts are subrounded-to-angular, and they are tabular, spherical, ovoid, and wedge-shaped. The clasts are very fine-grained, locally show a very fine lamination, and they may be shale intraclasts. Medium dark gray (N4), very fine-grained, massive clasts comprise \sim 1 vol% of the sample. These clasts are ovoid, up to \sim 5 mm in size, and they may be chert fragments.

Light-colored, spherical-to-ovoid spherules (D ~0.5-1 mm) that scratch to a hematitic red powder are evenly dispersed through the sample, and they comprise ~5 vol% of the sample. Gray, very fine-to-fine-grained, soft material that has a semimetallic luster and scratches to a dark gray (N3) powder comprises ~15 vol% of the sample. This material appears to be secondary manganese oxide(s). No irregular melt particles were observed with a hand lens. The sample does not attract a pencil magnet. The sample has an oily smell, and the oil came from the rock saw at Oberlin College.



Figure 287: Monteville spherule layer sample U63-1 with hematitic, lithic clasts (hlc), calcite (cc) veinlets, and dark gray (N3) secondary manganiferous (mangan) material.

Sample number: V111

Sample notes by Dr. Bruce M. Simonson: The sample is from the finer, spherule-poor upper part of the spherule layer, and originally, it probably consisted predominantly of carbonate sand. The sample contains finer spherule debris and some silicate crystals, and possibly, hummocky cross-stratification.

Number of pieces: One

Original weight of piece: 427.9 g

Size: ~15.5 by 6.5 by 2.5 cm

Shape: Blocky

Colors: The sample is medium gray (N5) on a fresh surface, and there is a thin pale red (10R 6/2) to moderate orange pink (10R 7/4) oxidation coating on the top and bottom surfaces.

Effervescence in 10% HCl at room temperature: Very weak along cracks and bedding planes

Lithology: The sample is a fine-to-medium-grained, homogeneous crystalline dolomite (Fig. 288). There are very thin (<0.5 mm thick) partings that are coated with iron oxide/oxyhydroxide, and the partings may represent hummocky cross-stratification. No clasts, siliciclastic grains, spherules, irregular melt particles, sulfide crystals, or veinlets were observed with a hand lens. The sample does not attract a pencil magnet, and the sample can be scratched with a penknife.



Figure 288: Monteville spherule layer sample V111 that is a fine-to-medium-grained dolomite. Partings coated by iron oxide/oxyhydroxide material may represent hummocky cross-stratification.

Appendix F

DESCRIPTIONS OF MONTEVILLE CONTEXT HAND SAMPLES

Sample number: T149-1

Sample notes by Dr. Bruce M. Simonson: The sample is from massive, carbonate-rich thin beds that underlie the spherule layer. The sample occurs ~1 m below the spherule layer. Impressions from small (pyrite?) nodules occur on the bedding planes.

Number of pieces: Five (all sawn as received)

Original weight of pieces: 251.1 g (total)

Size: ~3.5 by 1.2 by 1 cm (smallest piece); ~5 by 3 by 1.2 cm; ~8 by 1.5 by 1.5 cm;

~7 by 2.5 by 1.5 cm; ~7.5 by 3 by 1.5 cm (largest piece)

Shape: All the pieces are blocky.

Colors: The pieces are brownish gray (5YR 4/1), dark gray (N3), and medium dark gray (N4) on sawn surfaces. The top and bottom surfaces of the pieces typically coincide with bedding planes that show a pale brown (5YR 5/2) and moderate reddish brown (10R 4/6) oxidation.

Effervescence in 10% HCl at room temperature: Moderate to strong

Lithology: Three pieces have stratigraphic "up" arrows that indicate that the sample encompasses ~1.2-1.5 cm of stratigraphic section. The sample is a well-indurated, faintly laminated, fine-grained carbonate that appears to have some clastic texture (Fig. 289). Circular-to-elongate shallow depressions, typically 2-11 mm wide, that locally contain small nodules of oxidized pyrite (?), occur along the bedding planes that coincide with the top and bottom surfaces of the pieces. There are no visible clasts or veinlets, and the sample does not attract a pencil magnet.



Figure 289: Monteville context sample T149-1 that consists of five pieces of wellindurated, faintly laminated, fine-grained carbonate. Sample number: II67-1B

Sample notes by Dr. Bruce M. Simonson: The sample is from a carbonate layer that has "roll-up related clastic texture" that probably represents ripped-up microbial mats. The sample occurs ~20 cm above the spherule layer.

Number of pieces: One

Original weight of piece: ~700 g

Size: ~7.5 by 6 by 4.5 cm

Shape: Blocky

Colors: Dark gray (N3) to light brownish gray (5YR 6/1)

Effervescence in 10% HCl at room temperature: Weak

Lithology: A stratigraphic "up" arrow shows that the sample encompasses ~7.5 cm of stratigraphic section. The sample is a fresh-looking, well-indurated, fine-to-medium-grained crystalline dolomite that has indistinct layering (Fig. 290). The matrix is finely mottled. The light brownish gray material has an irregular shape, and it is locally associated with vugs that are up to 1-2 mm in size. White (N9) to pale yellowish brown (10YR 6/2) vein material forms a coating on the weathered top surface of the sample, but there are no visible veinlets that cross-cut the layering. No clasts or sulfide crystals are visible, and the sample does not attract a pencil magnet.



Figure 290: Monteville context sample II67-1B that is a well-indurated, fine-to-mediumgrained dolomite.

Appendix G

DESCRIPTIONS OF GRÆNSESØ SPHERULE LAYER HAND SAMPLES

Sample number: GL8904-1

Sample collection notes: Sample GL8904-1 (Fig. 291) is from the basal part of the northeast part of the Grænsesø spherule layer outcrop (Fig. 292). The piece had slightly separated from the outcrop, but it had not moved relative to the outcrop. The sample encompasses ~22 cm of stratigraphic section.

Number of pieces: One

Original weight of piece: ~2,900 g

Size: ~22 by 14.5 by 8 cm

Shape: Blocky

Colors: The sample is very pale orange (10YR 8/2) and grayish orange (10YR 7/4).

Effervescence in 10% HCl at room temperature: Variable

Lithology: The sample consists of spherules, chert grains, and chert and carbonate clasts that are dispersed in a dolomitic matrix. The dolomitic matrix comprises ~ 50 vol% of the sample, and like the carbonate clasts, it shows a variable effervescence in 10% HCl. Black (N1), spherical-to-ovoid spherules (D ~ 0.5 -1 mm) comprise ~ 5 vol% of the sample. Black (N1), subrounded-to-angular chert grains, up to ~ 7 -8 mm in size, comprise ~ 5 vol% of the sample, and several of the chert grains are elongate to wedge-shaped. Dark gray (N3) to grayish black (N2), subrounded-to-subangular chert clasts, up to ~ 3 by 6 cm in size, comprise ~ 30 vol% of the sample. About five or six chert clasts show

a weak preferred orientation that is roughly parallel to the contacts of the Grænsesø spherule layer. The chert clasts are typically fractured. Dolomitic matrix material occupies these fractures, and locally, it entirely traverses a clast.

Grayish orange (10YR 7/4), fine-grained, saccharoidal dolomite clasts comprise \sim 8-10 vol% of the sample. The dolomite clasts are subrounded, \sim 2.5-6 cm in diameter, more yellow than the dolomitic matrix, and they do not contain spherules, chert grains, or chert clasts. Moderate yellowish brown (10YR 5/4) siliceous veinlets that are typically <0.5 mm wide comprise \sim 1 vol% of the sample. The veinlets are commonly subvertical, and some veinlets cut across the clasts. The sample does not attract a pencil magnet.



Figure 291: Grænsesø spherule layer sample GL8904-1 that is a dolomixtite. The rock contains spherules, mm-sized chert fragments, dark gray (N3) chert (ch) clasts, and grayish orange (10YR 7/4) dolomite (dol) clasts in a dolomitic matrix. The dolomite clasts do not contain spherules or chert grains. The arrow (on left) shows stratigraphic "up".



Figure 292: The lower part of the Grænsesø spherule layer outcrop at the Midternæs locality showing samples GL8904-1 (lower right) and GL8904-2 (center). The white scale (center) is ~15 cm long.
Sample number: GL8904-2

Sample collection notes: Sample GL8904-2 (Fig. 293) occurs just above sample GL8904-1 (see Fig. 292). The piece had slightly separated from the outcrop, but it had not moved relative to the outcrop. The sample encompasses ~15 cm of stratigraphic section.

Number of pieces: One

Original weight of piece: ~3,300 g

Size: ~18 by 15 by 10.5 cm

Shape: Blocky

Colors: The sample is medium gray (N5) to medium dark gray (N4) on a fresh surface, and very pale orange (10YR 8/2) and grayish orange (10YR 7/4) on the weathered surface.

Effervescence in 10% HCl at room temperature: Variable

Lithology: The sample consists of spherules, chert grains, and chert and carbonate clasts that are dispersed in a dolomitic matrix. Black (N1), spherical-to-ovoid spherules (D ~0.5-1 mm) comprise ~5-10 vol% of the matrix. Medium dark gray (N4) to black (N1), subangular-to-angular chert grains, up to ~3-4 mm in size, comprise ~10-15 vol% of the matrix, and several of the chert grains are elongate. There are medium dark gray (N4) to grayish black (N2), subangular-to-angular chert clasts, ~0.5-8 cm in size, and the largest clast (~8 by 1 by 1.5 cm) is tabular. The long axes of the three or four largest chert clasts show a weak preferred orientation that is roughly parallel to the contacts of the Grænsesø spherule layer.

There are two very pale orange (10YR 8/2), fine-grained, saccharoidal dolomite clasts. The dolomite clasts are subangular-to-subrounded, and they are ~1 by 1.5 cm and

 \sim 1.8 by 2 cm in size. The dolomite clasts do not contain spherules, chert grains, or chert clasts. The chert and dolomite clasts are matrix-supported. Light-colored quartz ± calcite veinlets that are typically <1 mm wide comprise \sim 1 vol% of the sample. One prominent set of veinlets is subvertical, and the veinlets cut across both the matrix and the clasts. The sample does not attract a pencil magnet.



Figure 293: Grænsesø spherule layer sample GL8904-2 that is a dolomixtite. This view shows medium dark gray (N4) chert (ch) clasts in a dolomitic matrix that contains spherules and chert grains.

Sample number: GL8904-3

Sample collection notes: Sample GL8904-3 (Fig. 294) is from the northeast part of the Grænsesø spherule layer outcrop (Fig. 295), and it is ~50 cm stratigraphically above sample GL8904-2. The piece had slightly separated from the outcrop, but it had not moved relative to the outcrop. The sample encompasses ~13 cm of stratigraphic section. Number of pieces: One

Original weight of piece: ~1,600 g

Size: 13 by 8 by 7 cm

Shape: Blocky

Colors: The sample is dark gray (N3) to medium dark gray (N4) on a fresh surface, and very pale orange (10YR 8/2), grayish orange (10YR 7/4), and grayish orange pink (5YR 7/2) on the weathered surface.

Effervescence in 10% HCl at room temperature: Variable

Lithology: The sample consists of spherules, chert grains, and chert and carbonate clasts that are dispersed in a dolomitic matrix. Black (N1), spherical-to-ovoid spherules $(D \sim 0.5-1 \text{ mm})$ comprise $\sim 10 \text{ vol}\%$ of the sample. Dark gray (N3) to black (N1), subrounded-to-subangular chert grains, up to $\sim 2-3 \text{ mm}$ in size, comprise $\sim 20-25 \text{ vol}\%$ of the sample, and some of the chert grains are elongate. Dark gray (N3), subangular-to-angular chert clasts, 0.3-6.5 cm in size, comprise $\sim 15 \text{ vol}\%$ of the sample. There is no obvious preferred orientation of the chert clasts. There is no obvious size-grading of the chert clasts or spherules in the sample.

There are two grayish orange (10YR 7/4), fine-grained, saccharoidal dolomite clasts. The dolomite clasts are \sim 5.5 by 2 by 1 cm and \sim 0.7 by 0.5 by 0.5 cm in size, and they do not contain spherules, chert grains, or chert clasts. Light gray (N7), subangular,

coarse sand-sized quartz grains are dispersed in the dolomitic matrix, and they comprise <1 vol% of the rock. There are about six, brown, quartz veinlets (<0.5 mm wide), and one of the veinlets sharply cuts a dolomite clast. The sample does not attract a pencil magnet.



Figure 294: Grænsesø spherule layer sample GL8904-3 that is a dolomixtite. The rock contains dark gray (N3) chert (ch) clasts and two grayish orange (10YR 7/4) dolomite (dol) clasts (the larger one is shown in this view) in a dolomitic matrix that contains spherules, chert fragments, and siliciclastic grains.



Figure 295: The middle part of the Grænsesø spherule layer outcrop at the Midternæs locality showing sample GL8904-3. The larger dolomite (dol) clast (see Fig. 294) is visible at the top of the sample.

Sample number: GL8904-4

Sample collection notes: Sample GL8904-4 (Fig. 296) was collected from near the top of the Grænsesø spherule layer dolomixtite at the northeast margin of the outcrop (Fig. 297). The sample is ~50 cm stratigraphically above sample GL8904-3, and sample GL8904-4 encompasses ~10.5 cm of stratigraphic section.

Number of pieces: One

Original weight of piece: 975.6 g

Size: ~14.5 by 10.5 by 6.5 cm

Shape: Blocky

Colors: The sample is medium dark gray (N4) on a fresh surface, and it is very pale orange (10YR 8/2), grayish orange (10YR 7/4), and yellowish gray (5Y 8/1) on the weathered surface.

Effervescence in 10% HCl at room temperature: Strong (see below)

Lithology: The sample consists of spherules, chert grains, and chert clasts in a finegrained, crystalline, dolomitic matrix. The strong reaction of the sample with 10% HCl appears to be due to a very thin layer of secondary calcite on the surface of the sample. Black (N1), spherical-to-ovoid spherules (D ~0.5-1 mm) are evenly dispersed throughout the dolomitic matrix, and they comprise ~10 vol% of the sample. Dark gray (N3) to black (N1), subrounded-to-subangular chert grains, up to ~2 mm in size, comprise ~15-20 vol% of the sample.

Dark gray (N3) to grayish black (N2), subrounded-to-angular chert clasts, 0.5-2.7 cm in size, comprise ~10-15 vol% of the sample. Some of the chert clasts appear to be recrystallized. Several of the chert clasts are tabular, and four of the chert clasts have their long axes oriented subparallel to the contacts of the Grænsesø spherule layer. The

dimensions of these four chert clasts are as follows: ~ 1.5 by 0.8 by 0.6 cm, ~ 1.8 by 1 by 0.5 cm, ~ 1.4 by 0.9 by 0.6 cm, and ~ 2.7 by 1.5 by 0.4 cm.

Subangular, coarse sand-sized quartz grains are dispersed in the dolomitic matrix, and they comprise ~ 1 vol% of the rock. The sample contains a few quartz ± calcite veinlets (<0.5 mm wide) that occur in two sets, and the veinlets in the subvertical set are spaced $\sim 2-5$ mm apart. The veinlets cut both the matrix and the clasts. The sample does not attract a pencil magnet.



Figure 296: Grænsesø spherule layer sample GL8904-4 that is a dolomixtite. There are dark gray (N3) chert (ch) clasts in a dolomitic matrix that contains spherules, chert fragments, and siliciclastic grains.



Figure 297: Grænsesø spherule layer sample GL8904-4 near the top of the exposed dolomixtite at the Midternæs locality. The pick is ~33 cm long.

Appendix H

DESCRIPTIONS OF GRÆNSESØ CONTEXT HAND SAMPLES

Sample number: SP3; the Denmark and Greenland Geological Survey (GEUS) sample number is 476418.

Sample notes by Dr. Mark T. Hutchison: The sample site is ~18 m northeast of, and slightly downhill from, the spherule layer outcrop. The sample should be a few meters stratigraphically below the spherule layer. The sample outcrop consists of ~5-15 cm-thick bands of massive dolomite that are alternately tan and blue-gray in color. No spherules or clasts are visible. There are carbonate veins that are approximately perpendicular to the bedding. The outcrop exhibits shallow open folds with ~1.5 m periodicity.

Number of pieces: Two

Original weight of pieces: 504.3 g (smaller piece); 600.0 g (larger piece);

total weight = 1104.3 g

Size: ~9 by 7 by 6 cm (smaller piece); 13 by 6 by 5 cm (larger piece)

Shape: Wedge-to-triangular-shaped (smaller piece); elongate and irregular (larger piece) Colors: The pieces are medium gray (N5) to medium dark gray (N4) on a fresh surface, and dark yellowish orange (10YR 6/6), light gray (N7), and moderate yellowish brown (10YR 5/4) on the weathered surfaces.

Effervescence in 10% HCl at room temperature: Generally weak to very weak Lithology: The sample is a fine-grained, saccharoidal, crystalline dolomite (Fig. 298) that contains darker, harder, mm-to-cm-sized areas that may be siliceous. The sample is massive: it contains no visible laminations or bedding. There are numerous very thin fractures, and at least two sets of white (N9), thin ($\leq 2 \text{ mm wide}$), slightly resistant, subparallel quartz veinlets. Minor white (N9) calcite occurs along fractures, in mm-sized patches, and in veinlets that are <1 cm wide. No spherules, clasts, siliciclastic grains, or sulfide crystals were observed with a hand lens. The sample does not attract a pencil magnet.



Figure 298: The larger piece of Grænsesø context sample SP3 that is a massive, finegrained, saccharoidal dolomite.

Sample number: GL8904-6

Sample collection notes: Sample GL8904-6 is from a dolomite layer that is <1 m above the top of the Grænsesø spherule layer dolomixtite. The sample site is ~3 m southeast of the top of the Grænsesø spherule layer outcrop, and the site is just southwest of the cairn that I erected.

Number of pieces: One

Original weight of piece: 650.6 g

Size: ~12.5 by 8.5 by 5 cm

Shape: Blocky

Colors: The sample is medium gray (N5) to medium dark gray (N4) on a fresh surface, and yellowish gray (5Y 8/1) to grayish orange (10YR 7/4) on a weathered surface. Effervescence in 10% HCl at room temperature: The medium gray areas show a strong reaction, and the medium dark gray areas show a weak reaction. The weathered surfaces show no reaction.

Lithology: The sample is a well-indurated, homogeneous, fine-grained dolomite with no obvious lamination or bedding (Fig. 299). There are three sets of thin (<0.5 mm wide) quartz + calcite veinlets. The veinlets have a spacing of ~4-15 mm. The veinlets and small patches of quartz and calcite comprise ~2-3 vol% of the sample. No spherules, clasts, siliciclastic grains, or sulfide crystals were observed with a hand lens. The sample does not attract a pencil magnet.



Figure 299: Grænsesø context sample GL8904-6 that is a well-indurated, massive, finegrained dolomite.

Appendix I

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE CARAWINE SPHERULE LAYER SAMPLES

Carawine spherule layer sample X38-2

| Date | Preparation step(s) |
|---|---|
| 11/4/03 | The original three pieces (sawn as received) were sawn into several pieces. The pieces were trimmed, washed with soap and warm water, and underwent ultrasonic agitation for a few minutes. The pieces were rinsed and put in the oven. |
| 11/8/03 | Subsamples 85.0879 g (three pieces) and 144.3 g (one piece) were weighed on the Sartorius analytical balance and Triple Beam balance, respectively. |
| 11/8/03 to 11/9/03 | Subsamples 85.0879 g and 144.3 g each went through a warm bath of concentrated HCl for a total of 6.5 hours. |
| Middle November/03 | The HCl-insoluble material for subsamples 85.0879 g and 144.3 g went through the dilution and decantation process for 8 and ~5 days, respectively. |
| 12/19/03 to 12/20/03 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions, and all the $<$ 38 μ m material was recovered. |
| Late December/03 to early January/04 | For each subsample, the 38-63 μ m, 125-250 μ m, and >250 μ m size fractions each went through one heavy liquid separation, and the 63-125 μ m size fraction went through three heavy liquid separations. |
| Early February/04 | For each subsample, the $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| 2/9/04 | For subsample 85.0879 g, the <38 µm material was weighed. |
| No data | For subsample 144.3 g, the <38 µm material was weighed. |
| No data | For each subsample, the heavy mineral separates for the 63-125 μ m, 125-250 μ m, and >250 μ m size fractions were transferred to cavity slides. |

| Date | Preparation step(s) |
|------------------|---|
| 2/8/05 to 2/9/05 | For each subsample, spherules and irregular melt particles were handpicked from the >250 μ m-sized light fraction, and they were weighed. |
| 2/1/06 to 2/2/06 | For subsample 144.3 g, the spherules and irregular melt particles were each dry sieved through 500 μ m and 1000 μ m sieves, and the three size fractions were weighed. |
| 3/1/08 to 3/4/08 | For subsample 85.0879 g, the spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. |

Subsample 85.0879 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 2.8176 | 2.7575 | 0.0601 |
| 125-250 μm | 0.5502 | 0.5489 | 0.0013 |
| 63-125 μm | 1.4404 | 1.4374 | 0.0030 |
| 38-63 μm | 0.4601 | 0.3552 | 0.1049 |
| <38 μm | 1.4922 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >250 µm | 0.0334 | 0.6555 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|------------------|-------------------------|--|
| >1000 µm | 0.0209 | 0.6255 |
| 500-1000 μm | 0.0131 | 0.0246 |
| 250-500 μm | 0.0024 | 0.0038 |
| $<250 \ \mu m^1$ | negligible | 0.0020 |

Subsample 144.3 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 2.0681 | 2.0492 | 0.0189 |
| 125-250 μm | 1.8062 | 1.8043 | 0.0019 |
| 63-125 μm | 2.9183 | 2.9119 | 0.0064 |
| 38-63 µm | 0.3909 | 0.3855 | 0.0054 |
| <38 μm | 2.0689 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >250 µm | 0.0652 | 0.4522 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >1000 µm | 0.0381 | 0.3844 |
| 500-1000 μm | 0.0224 | 0.0543 |
| 250-500 μm | 0.0035 | 0.0129 |

Carawine spherule layer sample W85-2

| Date | Preparation step(s) |
|---------------------------------------|---|
| 11/4/03 | The sample (one piece) was sawn into a few pieces. The pieces were trimmed, washed with soap and warm water, and underwent ultrasonic agitation for a few minutes. The pieces were rinsed and put in the oven. |
| November/03 | Subsamples 277.7 g (one piece) and 371.7 g (one piece) were weighed on the Triple Beam balance. |
| November/03 | Subsamples 277.7 g and 371.7 g each went through a warm bath of concentrated HCl for a total of 36.7 and 30.2 hours, respectively. |
| Late November to early December/03 | The HCl-insoluble material for subsamples 277.7 g and 371.7 g went through the dilution and decantation process for 13 and 15 days, respectively. |
| 1/6/04 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \ \mu m$ material was recovered. |
| No data | For each subsample, the $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| Early to middle January/04 | For each subsample, the 38-63 µm and 125-250 µm size fractions each went through one heavy liquid separation, and the 63-125 µm size fraction went through three heavy liquid separations. Using a binocular microscope, malachite (laboratory contamination) and pyrite were observed in the heavy mineral separates. |
| March and April/04 | For each subsample, the 63-125 μ m and 125-250 μ m heavy mineral separates each went through a warm bath of concentrated HNO ₃ in order to dissolve the malachite and pyrite. Each acid-insoluble heavy mineral separate went through the dilution and decantation process. The acid-insoluble heavy mineral separates were recovered by rinsing them into filters, and the heavy mineral separates were transferred to cavity slides. |
| October/04 | For each subsample, spherules and irregular melt particles were handpicked from the >250 µm size fraction. |
| 2/28/08 | For each subsample, the spherules and irregular melt particles were weighed. |
| 3/1/08 to 3/4/08 | For each subsample, the spherules and irregular particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. |

Subsample 277.7 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 24.9539 | | |
| 125-250 μm | 0.1907 | 0.1822 | 0.0085 |
| 63-125 μm | 0.6689 | 0.6645 | 0.0044 |
| 38-63 µm | 0.8512 | 0.8453 | 0.0059 |
| <38 μm | 2.3419 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >250 µm | 0.3106 | 7.5114 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.2248 | 7.2407 |
| 500-1000 μm | 0.0764 | 0.1492 |
| 250-500 μm | 0.0027 | 0.0178 |
| $<250 \ \mu m^{1}$ | 0.0051 | 0.0827 |

Subsample 371.7 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 30.7915 | | |
| 125-250 μm | 0.4075 | 0.4069 | 0.0006 |
| 63-125 μm | 1.0363 | 0.9570 | 0.0793 |
| 38-63 µm | 0.9458 | 0.9327 | 0.0131 |
| <38 μm | 2.4020 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >250 µm | 0.5205 | 11.8932 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.3574 | 11.2876 |
| 500-1000 μm | 0.1459 | 0.4655 |
| 250-500 μm | 0.0084 | 0.0529 |
| $<250 \ \mu m^{1}$ | 0.0101 | 0.1402 |

Carawine spherule layer sample 84-1

| Date | Preparation step(s) | | |
|---|--|--|--|
| 11/5/03 | The sample (one piece) was sawn into a few pieces. The pieces were trimmed, washed with soap and warm water, and underwent ultrasonic agitation for a few minutes. The pieces were rinsed and put in the oven. | | |
| 11/19/03 and 11/21/03 | Subsamples 268.1 g (one piece), 388.8 g (one piece), and 430.8 g (one large piece and five small fragments) were weighed on the Triple Beam balance. | | |
| Late November/03 | Subsamples 268.1 g, 388.8 g, and 430.8 g each went through a warm bath of concentrated HCl for a total of 14.9, 19.1, and 24.5 hours, respectively. | | |
| December/03 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for 7-9 days. | | |
| Middle January to middle February/04 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions. For subsample 268.1 g, all the $<38 \mu m$ material was recovered. For subsamples 388.8 g and 430.8 g, only a part of the $<38 \mu m$ material was recovered. | | |
| 2/9/04 to 2/22/04 | For each subsample, the 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. | | |
| Middle February to middle March/04 | For subsamples 268.1 g and 388.8 g, spherules and irregular melt particles were handpicked from the >250 μ m size fractions. | | |
| Late February to middle March/04 | For each subsample, the $<38 \ \mu m$ material was centrifuged and dried in the oven. | | |
| Middle March/04 | For each subsample, the $<38 \ \mu m$ material was weighed. | | |
| 1/11/05 to 1/14/05 | For subsample 268.1 g, the 63-125 μ m heavy mineral separate was transferred to a cavity slide. The other heavy mineral separates contained very abundant secondary iron oxide/oxyhydroxide grains, and these heavy mineral separates were put in vials. | | |
| No data | Using a binocular microscope, I handpicked grains from the 63-125 µm and 125-250 µm heavy mineral separates of subsample 268.1 g that were not obvious secondary iron oxide/oxyhydroxide grains. The handpicked grains were transferred to cavity slides. | | |
| 2/1/06 to 2/2/06 | For subsample 268.1 g, the spherules were dry sieved through 500 μ m and 1000 μ m sieves, and the three size fractions were weighed. | | |

| Date | Preparation step(s) |
|----------------------|---|
| 2/28/08 | For subsample 388.8 g, the spherules and irregular melt particles were weighed. |
| 3/1/08 | For subsample 268.1 g, the irregular melt particles were dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. |
| 3/1/08 | For subsample 388.8 g, the spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. |
| 11/13/11 to 11/17/11 | For subsample 268.1 g, the >250 μ m size fraction was rechecked, and a few more spherules and irregular melt particles were handpicked. |
| 12/29/11 | For subsample 268.1 g, these additional spherules and irregular melt particles were dry sieved and weighed. |

Subsample 268.1 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 29.8697 ¹ | | |
| 125-250 μm | 2.3810 | 2.4006 | -0.0196 |
| 63-125 μm | 2.2774 | 2.2871 | -0.0097 |
| 38-63 µm | 0.9694 | | |
| <38 μm | 20.8851 | | |

¹A little material from this size fraction was lost during wet sieving and weighing.

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.1636 | 11.5557 |
| 500-1000 μm | 0.1584 | 1.7741 |
| 250-500 μm | 0.0051 | 0.4198 |
| $<250 \ \mu m^{1}$ | No data | 0.1935 |

Subsample 388.8 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 40.9155 | | |
| 125-250 μm | 2.3614 | 2.3486 | 0.0128 |
| 63-125 μm | 3.0325 | 3.0441 | -0.0116 |
| 38-63 µm | 3.0219 | | |
| <38 μm | 3.9394 ¹ | | |

¹This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >250 µm | 0.4236 | 17.6552 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|------------------|-------------------------|--|
| >1000 µm | 0.2457 | 15.9661 |
| 500-1000 μm | 0.1745 | 1.4566 |
| 250-500 μm | 0.0029 | 0.1038 |
| $<250 \ \mu m^1$ | negligible | 0.0609 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Subsample 430.8 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 16.6899 | | |
| 125-250 μm | 1.0241 | 1.0047 | 0.0194 |
| 63-125 μm | 1.8101 | 1.7221 | 0.0880 |
| 38-63 µm | 2.3880 | | |
| <38 μm | 4.7573 ¹ | | |

¹This is a minimum weight, since only part of the $<38 \mu$ m material was recovered during wet sieving.

Carawine spherule layer sample X24-1

| Date | Preparation step(s) |
|-----------------------------------|--|
| 11/5/03 | The two slabs (sawn as received) were sawn and trimmed. |
| 11/8/03 | The pieces were washed with soap and warm water, rinsed, and put in the oven. |
| Middle November/03 | Six subsamples were weighed on the Triple Beam balance: 217.2 g (one piece), 247.9 g (two pieces), 290.4 g (one piece), 293.7 g (one piece), 413.0 g (one piece), and 475.5 g (one piece). |
| Late November/03 | Each subsample went through a warm bath of concentrated HCl for 3-4 days. |
| December/03 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for 7-11 days. |
| 1/7/04 to 1/14/04 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. |
| Late January to early March/04 | For each subsample, the $<38 \ \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| 1/12/04 to 2/6/04 and April/04 | For each subsample, the 38-63 μ m and 125-250 μ m size fractions each went through one heavy liquid separation, and the 63-125 μ m size fraction went through three heavy liquid separations. |
| No data | Prior to weighing, the 38-63 μ m, 63-125 μ m, and 125-250 μ m-sized light fractions of subsamples 413.0 g and 475.5 g were accidently spilled in the plastic baggies that held the filters that contained these light fractions. The spilled material in the baggies was recombined with the heavy mineral separates from the two subsamples, and this material was relabeled subsample 888.5 g. |
| 4/24/04 | Subsample 888.5 g was wet sieved using 125 μ m, 63 μ m, and 38 μ m sieves. Any <38 μ m material derived from the wet sieving was not recovered. |
| 4/24/04 to 5/1/04 | The 63-125 µm size fraction of subsample 888.5 g went through three heavy liquid separations. |
| No data | Using a binocular microscope, malachite (laboratory contamination) and abundant pyrite were observed in the heavy mineral separates. |
| 10/8/04 to 10/12/04 | For subsamples 217.2 g, 247.9 g, 290.4 g, 293.7 g, and 888.5 g, the 63-125 μ m heavy mineral separates each went through a warm bath of concentrated HNO ₃ for 4-5 hours in order to dissolve the malachite and pyrite. |

| Date | Preparation step(s) | |
|--|--|--|
| Middle to late October/04 | Each acid-insoluble heavy mineral separate went through the dilution and decantation process for 6-9 days. | |
| Middle to late October/04 | The acid-insoluble heavy mineral separates were recovered by rinsing them into filters. | |
| 10/15/04 to 1/11/05 | The 63-125 μ m acid-insoluble heavy mineral separates were transferred to cavity slides. | |
| 1/7/05 to 1/11/05 | The heavy mineral separates for the 125-250 μ m size fractions were transferred to cavity slides. | |
| 4/6/05 | The 63-125 μ m light fraction of subsample 888.5 g was combined with a little remnant material from the filters for the first and third heavy liquid separations, and this material was weighed (3.5098 g). This material went through a warm bath of concentrated HNO ₃ for three hours. | |
| 4/7/05 to 4/11/05 | This acid-insoluble material went through the dilution and decantation process for five days. | |
| 4/19/05 | This acid-insoluble material was wet sieved using a 63 μ m sieve, and the <63 μ m material was not recovered. This acid-insoluble 63-125 μ m size fraction was weighed (0.2311 g). | |
| 4/26/05 to 4/27/05 | This acid-insoluble 63-125 μ m size fraction went through one heavy liquid separation. | |
| 2/18/06 | The acid-insoluble 63-125 μ m heavy mineral separate obtained on 4/27/05 was transferred to a cavity slide. | |
| No data | The light fraction obtained on $4/27/05$ was combined with a little remnant material from the plastic baggie, and the combined material was weighed (~0.2718 g). | |
| Spring/04; February to March/05; March/08 | For each subsample, spherules and irregular melt particles were handpicked from the >250 μ m size fraction. | |
| 2/21/08 to 2/22/08 | For subsamples 217.2 g, 247.9 g, and 413.0 g, the spherules and irregular melt particles were weighed. | |
| 3/31/08 to 4/3/08 | For each subsample, the spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. | |

Subsample 217.2 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 21.9035 | | |
| 125-250 μm | 0.5613 | 0.5577 | 0.0036 |
| 63-125 μm | 0.9633 | 0.9589 | 0.0044 |
| 38-63 µm | 1.1670 | 1.1611 | 0.0059 |
| <38 μm | 2.4471 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >250 µm | 0.3605 | 7.6520 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.1779 | 6.7382 |
| 500-1000 μm | 0.1638 | 0.6956 |
| 250-500 μm | 0.0088 | 0.1202 |
| $<250 \ \mu m^{1}$ | 0.0046 | 0.0686 |

Subsample 247.9 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 16.7626 | | |
| 125-250 μm | 0.8198 | 0.8126 | 0.0072 |
| 63-125 μm | 1.1120 | 0.9282 | 0.1838 |
| 38-63 µm | 1.1402 | 1.1252 | 0.0150 |
| <38 μm | 2.4928 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|---------------|-------------------------|--|
| >250 µm | 0.4245 | 10.0465 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.2106 | 8.4932 |
| 500-1000 μm | 0.1976 | 1.1566 |
| 250-500 μm | 0.0131 | 0.2934 |
| $<250 \ \mu m^{1}$ | 0.0064 | 0.0887 |

Subsample 290.4 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 11.7850 | | |
| 125-250 μm | 0.5402 | 0.5369 | 0.0033 |
| 63-125 μm | 1.4687 | 1.4759 | -0.0072 |
| 38-63 µm | 1.9416 | 1.9232 | 0.0184 |
| <38 μm | 2.9838 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.2509 | 7.4297 |
| 500-1000 μm | 0.1727 | 1.0068 |
| 250-500 μm | 0.0063 | 0.1010 |
| $<250 \ \mu m^{1}$ | 0.0030 | 0.0415 |

Subsample 293.7 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 25.3688 | | |
| 125-250 μm | 0.5399 | 0.5305 | 0.0094 |
| 63-125 μm | 0.7517 | 0.7485 | 0.0032 |
| 38-63 µm | 0.7852 | 0.7855 | -0.0003 |
| <38 μm | 3.5206 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.1734 | 8.2914 |
| 500-1000 μm | 0.1589 | 1.0694 |
| 250-500 μm | 0.0029 | 0.1663 |
| $<250 \ \mu m^{1}$ | 0.0014 | 0.0647 |

Subsample 413.0 g

| Size Fraction | Weight (g) of HCl-Insoluble Material |
|---------------|--------------------------------------|
| >250 µm | 38.7038 |
| 125-250 μm | 0.9134 |
| 63-125 μm | 1.4565 |
| 38-63 µm | 1.2520 |
| <38 μm | 3.4238 |

| Size Fraction | Weight (g) of | Weight (g) of Spherules | Weight (g) of |
|---------------|-----------------|-------------------------|--------------------------|
| | Loose Spherules | in Matrix Material | Irregular Melt Particles |
| >250 µm | 0.4057 | 2.0595 | 13.1638 |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|------------------|-------------------------|--|
| >1000 µm | 0.2486 | 14.8180 |
| 500-1000 μm | 0.1452 | 1.0034 |
| 250-500 μm | 0.0074 | 0.1230 |
| $<250 \ \mu m^1$ | 0.0038 | 0.1696 |

Subsample 475.5 g

| Size Fraction | Weight (g) of HCl-Insoluble Material |
|---------------|--------------------------------------|
| >250 µm | 32.3294 |
| 125-250 μm | 1.5011 |
| 63-125 μm | 2.3584 |
| 38-63 µm | 2.1160 |
| <38 μm | 4.8668 ¹ |

¹A little material of this size fraction was lost during centrifuging on February 8, 2004.

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.4070 | 13.3074 |
| 500-1000 μm | 0.2972 | 2.1764 |
| 250-500 μm | 0.0125 | 0.2822 |
| $<250 \ \mu m^{1}$ | 0.0111 | 0.1929 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Subsample 888.5 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of HNO ₃ -Insoluble Light Fraction |
|---------------|---|---|
| 125-250 μm | 2.2550 | |
| 63-125 μm | 3.5775 | ~0.2718 |
| 38-63 µm | 2.9995 | |

Carawine spherule layer sample 43-1

Initial Preparation

| Date | Preparation step(s) | |
|---------|---|--|
| 9/20/02 | The sample (one piece with a sawn surface) was sawn into a few large pieces, and the pieces were trimmed. The pieces were broken down to fist-sized chunks with a rock hammer. The chunks underwent ultrasonic agitation, and they were rinsed and put in the oven. | |
| 9/21/02 | Twelve subsamples (283.8 g, 495.5 g, 535.3 g, 584.7 g, 599.2 g, 819.5 g, 893.3 g, 987.4 g, 1046.2 g, 1078.1 g, 1114.1 g, and 1136.4 g) totaling 9,573.5 g were weighed on the Triple Beam balance. | |

Subsample 283.8 g

| Date | Preparation step(s) | |
|--|---|--|
| 9/23/02 | The subsample went through a room-temperature bath of 20% HCl for one day. | |
| Late September to early November/02 | The subsample went through a warm bath of concentrated HCl for three days, and it sat in the acid for 37 days at room temperature. | |
| Early November/02 | The HCl-insoluble material went through the dilution and decantation process for seven days. | |
| 11/14/02 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. | |
| 11/14/02 to 11/15/02 | The 63-125 µm size fraction went through one heavy liquid separation. | |
| Late November/02 | Using a binocular microscope, pyrite was observed in the heavy mineral separate. | |
| 1/9/03 | The 63-125 μ m heavy mineral separate went through a warm bath of concentrated HNO ₃ in order to dissolve the pyrite. | |
| Middle January/03 | The acid-insoluble heavy mineral separate went through the dilution and decantation process for five days. The acid-insoluble heavy mineral separate was recovered by rinsing it into a filter. | |

Subsample 283.8 g, continued

| Date | Preparation step(s) |
|---|---|
| 1/21/03 | The HCl-insoluble 63-125 μ m light fraction was wet sieved using 38 μ m and 63 μ m sieves. The 38-63 μ m material derived from this wet sieving was recovered, but only some of the <38 μ m material was recovered. |
| Late January/03 | The $<38 \ \mu m$ material that was recovered on $11/14/02$ and $1/21/03$ was centrifuged and dried in the oven. |
| 1/28/03 | The <38 µm material was weighed. |
| 2/14/03 | The acid-insoluble 63-125 μ m heavy mineral separate was transferred to a cavity slide. |
| 2/24/03 to 2/25/03 | The HCl-insoluble 125-250 μ m material went through a warm bath of concentrated HNO ₃ . |
| 2/25/03 to early March/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| 3/4/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| 3/11/03 to 3/12/03 | The acid-insoluble 63-125 μ m material that was derived from the HNO ₃ dissolution of the HCl-insoluble 125-250 μ m material went through one heavy liquid separation. |
| 3/12/03 to 3/13/03 | The acid-insoluble 125-250 μm material went through one heavy liquid separation. |
| 3/14/03 | After being dried in the oven, the $<38 \mu m$ material that was recovered on $3/4/03$ was weighed. |
| 3/18/03 | The two heavy mineral separates that were obtained on $3/12/03$ and $3/13/03$ were transferred to cavity slides. |
| May, September, and early October/04 | Spherules and irregular melt particles were handpicked from the $>250 \ \mu m$ size fraction. |
| 3/14/05 to 3/21/05 | The HCl-insoluble 63-125 μ m light fraction that was wet sieved on 1/21/03 went through a warm bath of concentrated HNO ₃ for one day, and it went through the dilution and decantation process for seven days. |
| 3/22/05 | This acid-insoluble material was wet sieved through a 63 μ m sieve, and the <63 μ m material was not saved. |

Subsample 283.8 g, continued

| Date | Preparation step(s) | |
|-------------|--|--|
| November/11 | The $>250 \ \mu\text{m}$ size fraction was rechecked for spherules and irregular melt particles, and the spherules and irregular melt particles were resorted. | |
| 12/30/11 | The spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. | |

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Acid-Insoluble ¹ Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|--|---|
| >250 µm | 8.2280 | | |
| 125-250 μm | 0.4226 | | |
| 63-125 μm | 0.3522 | 0.0200 | < 0.3322 |
| 38-63 µm | 0.5017 | | |
| <38 μm | 2.3319 | | |

¹HCl and HNO₃ digestion

| Weights after | HNO ₃ digestion | and sieving of the | HCl-insoluble | 125-250 u | m material |
|---------------|----------------------------|--------------------|---------------|-----------|------------|
| | | | | | |

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.0171 | 0.0158 | 0.0013 |
| 63-125 μm | 0.0222 | 0.0096 ² | < 0.0126 |
| 38-63 µm | 0.0297 | | |
| <38 μm | 0.2343 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Subsample 283.8 g, continued

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.0416 | 0.2222 |
| 500-1000 μm | 0.1157 | 0.1412 |
| 250-500 μm | 0.0105 | 0.0729 |
| $<250 \ \mu m^{1}$ | 0.0000 | 0.0005 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Subsample 495.5 g

| Date | Preparation step(s) |
|--------------------------------------|---|
| 9/23/02 | The subsample went through a room-temperature bath of 20% HCl for one day. |
| Late September to late October/02 | The subsample went through a warm bath of concentrated HCl for six days, and it sat in the acid for 28 days at room temperature. |
| Late October to early November/02 | The HCl-insoluble material went through the dilution and decantation process for five days. |
| 12/30/02 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. |
| January to early February/03 | The $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| 2/5/03 | The <38 μm material was weighed. |
| 2/24/03 to 2/25/03 | The HCl-insoluble 125-250 μ m material went through a warm bath of concentrated HNO ₃ for two days. |
| 2/26/03 to 3/2/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| 3/3/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| March/03 | The $<38 \mu m$ material that was recovered on $3/3/03$ was centrifuged and dried in the oven. |

| Subsample | 495.5 | g, | continued |
|-----------|-------|----|-----------|
| | | | |

| Date | Preparation step(s) |
|--------------------------|---|
| 3/11/03 to 3/12/03 | The acid-insoluble 63-125 μ m material that was derived from the HNO ₃ dissolution of the HCl-insoluble 125-250 μ m material went through one heavy liquid separation. |
| 3/12/03 to 3/13/03 | The acid-insoluble 125-250 μ m material went through one heavy liquid separation. |
| 3/18/03 to 3/19/03 | The two heavy mineral separates were transferred to cavity slides. |
| 3/26/03 | The $<38 \mu m$ material that was recovered on $3/3/03$ was weighed. |
| 10/10/04 to 10/11/04 | Spherules and irregular melt particles were handpicked from the $>250 \ \mu m$ size fraction. |
| November/11 and 12/27/11 | The >250 μ m size fraction was rechecked for spherules and irregular melt particles. |
| 12/31/11 | The spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. |

| Size Fraction | Weight (g) of HCl-Insoluble Material |
|---------------|--------------------------------------|
| >250 µm | 21.4662 |
| 125-250 μm | 0.8832 |
| 63-125 μm | 0.5720 |
| 38-63 µm | 0.5674 |
| <38 μm | 4.7689 |

Subsample 495.5 g, continued

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.0204 | 0.0201 | 0.0003 |
| 63-125 μm | 0.0363 | 0.0246 ² | < 0.0117 |
| 38-63 µm | 0.0556 | | |
| <38 μm | 0.5687 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.0267 | 0.3116 |
| 500-1000 μm | 0.1845 | 0.3048 |
| 250-500 μm | 0.0175 | 0.1186 |
| $<250 \ \mu m^{1}$ | 0.0000 | 0.0025 |
Subsample 819.5 g

| Date | Preparation step(s) |
|---------------------------------------|--|
| 9/22/02 | The subsample went through a warm bath of 20% HCl for one day. |
| Late September to early October/02 | The subsample went through a warm bath of concentrated HCl for one day, and it sat in the acid for 15 days at room temperature. |
| October/02 | The HCl-insoluble material went through the dilution and decantation process for ten days. |
| 1/1/03 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \ \mu m$ material was recovered. |
| January to early February/03 | The <38 μm material was centrifuged and dried in the oven. |
| 2/7/03 | The <38 μm material was weighed. |
| February/03 | The HCl-insoluble 125-250 μ m material went through a warm bath of concentrated HNO ₃ for two days. |
| February/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| 2/28/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| March/03 | The $<38 \ \mu m$ material that was recovered on $2/28/03$ was centrifuged and dried in the oven. |
| 3/2/03 to 3/3/03 | The acid-insoluble 63-125 μ m material that was derived from the HNO ₃ dissolution of the HCl-insoluble 125-250 μ m material went through one heavy liquid separation. |
| 3/2/03 to 3/3/03 | The acid-insoluble 125-250 µm material went through one heavy liquid separation. |
| 3/15/03 | The <38 µm material that was recovered on 2/28/03 was weighed. |
| 3/25/03 | The two heavy mineral separates were transferred to cavity slides. |
| 10/25/04 to 10/27/04 | Spherules and irregular melt particles were handpicked from the $>250 \ \mu m$ size fraction. |
| 12/28/11 | The >250 μ m size fraction was rechecked for spherules and irregular melt particles. |
| 1/1/12 | The spherules and irregular melt particles were each dry sieved through $250 \ \mu\text{m}$, $500 \ \mu\text{m}$, and $1000 \ \mu\text{m}$ sieves, and the four size fractions were weighed. |

| Size Fraction Weight (g) of HCl-Insoluble Mater | |
|---|---------|
| >250 µm | 21.7408 |
| 125-250 μm | 0.6707 |
| 63-125 μm | 0.4682 |
| 38-63 µm | 0.3300 |
| <38 μm | 8.0362 |

Subsample 819.5 g, continued

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.0263 | 0.0254 | 0.0009 |
| 63-125 μm | 0.0388 | 0.0204^2 | < 0.0184 |
| 38-63 µm | 0.0460 | | |
| <38 μm | 0.2895 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.0431 | 0.9581 |
| 500-1000 μm | 0.3230 | 0.3677 |
| 250-500 μm | 0.0255 | 0.0670 |
| $<250 \ \mu m^{1}$ | 0.0000 | 0.0018 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Subsample 1078.1 g

| Date | Preparation step(s) | |
|---------------------------------------|--|--|
| 9/21/02 | The subsample went through a warm bath of muriatic acid (31.45% HCl) for one day. | |
| 9/22/02 | The subsample went through a warm bath of 20% HCl for one day. | |
| Late September to early October/02 | The subsample went through a warm bath of concentrated HCl for five days, and it sat in the acid for 11 days at room temperature. | |
| Middle October/02 | The HCl-insoluble material went through the dilution and decantation process for ten days. | |
| 1/8/03 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. | |
| January and February/03 | The <38 µm material was centrifuged and dried in the oven. | |
| January/03 | The HCl-insoluble 125-250 μ m material went through a warm bath of concentrated HNO ₃ for four days. | |
| January/03 | This acid-insoluble material went through the dilution and decantation process for four days. | |
| 1/31/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. | |
| February/03 | The $<38 \mu m$ material that was recovered on $1/31/03$ was centrifuged and dried in the oven before it was weighed. | |
| 2/4/03 to 2/7/03 | The acid-insoluble 63-125 μ m material that was derived from the HNO ₃ dissolution of the HCl-insoluble 125-250 μ m material, and the acid-insoluble 125-250 μ m material, each went through one heavy liquid separation. | |
| 2/26/03 | The $<38 \mu m$ material that was recovered on $1/8/03$ was weighed. | |
| 4/3/03 and 4/11/03 | The heavy mineral separates were transferred to cavity slides. | |
| 1/1/12 to 1/31/12 | Spherules and irregular melt particles were handpicked from the $>250 \ \mu m$ size fraction. | |
| 1/31/12 | The spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. | |

| Size Fraction | Weight (g) of HCl-Insoluble Material | |
|---------------|--------------------------------------|--|
| >250 µm | 28.7144 | |
| 125-250 μm | 0.9935 | |
| 63-125 μm | 0.6663 | |
| 38-63 µm | 0.6405 | |
| <38 μm | 10.4335 | |

Subsample 1078.1 g, continued

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.0362 | 0.0185 ² | < 0.0177 |
| 63-125 μm | 0.1228 | 0.0919 ² | < 0.0309 |
| 38-63 µm | 0.2003 | | |
| <38 μm | 0.4390 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|--------------------|-------------------------|--|
| >1000 µm | 0.0998 | 0.9646 |
| 500-1000 μm | 0.3992 | 0.7100 |
| 250-500 μm | 0.0405 | 0.2568 |
| $<250 \ \mu m^{1}$ | 0.0007 | 0.0075 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Preparation steps and weight data for the HNO₃ digestion of the combined HCl-insoluble $63-125 \mu m$ size fractions of subsamples 495.5 g, 819.5 g, and 1078.1 g.

| Date | Preparation step(s) | |
|--------------------------------------|--|--|
| Middle January/03 | The HCl-insoluble 63-125 μ m size fractions of subsamples 495.5 g, 819.5 g, and 1078.1 g were combined (total weight = 1.7065 g), and this material went through a warm bath of concentrated HNO ₃ for five days. | |
| Middle January/03 | This acid-insoluble material went through the dilution and decantation process for five days. | |
| 1/21/03 | This acid-insoluble material was wet sieved using 38 μm and 63 μm sieves, and all the material was recovered. | |
| Late January to early February/03 | The $<38 \ \mu m$ material was centrifuged and dried in the oven. | |
| 1/31/03 to 2/3/03 | The acid-insoluble 63-125 μ m size fraction went through one heavy liquid separation. | |
| 2/7/03 | The <38 μm material was weighed. | |
| 4/4/03 | The heavy mineral separate was transferred to a cavity slide. | |

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.2812 | 0.2684 ² | <0.0128 |
| 38-63 µm | 0.3353 | | |
| <38 μm | 0.8123 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Subsample 535.3 g

| Date | Preparation step(s) |
|--------------------------------------|---|
| 9/22/02 | The subsample went through a room-temperature bath of 20% HCl for one day. |
| Late September to late October/02 | The subsample went through a warm bath of concentrated HCl for nine days, and it sat in the acid for 28 days at room temperature. |
| Late October to early November/02 | The HCl-insoluble material went through the dilution and decantation process for seven days. |
| 12/28/02 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. |
| January and early February/03 | The $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| 2/7/03 | The <38 μm material was weighed. |
| 2/22/03 to 2/23/03 | The HCl-insoluble 125-250 μ m material went through a warm bath of concentrated HNO ₃ for two days. |
| 2/24/03 to 2/28/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| Early March/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| March/03 | The acid-insoluble $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| 3/5/03 to 3/6/03 | The acid-insoluble 63-125 μ m size fraction went through one heavy liquid separation. |
| 3/6/03 to 3/7/03 | The acid-insoluble 125-250 μ m size fraction went through one heavy liquid separation. |
| 3/20/03 to 3/21/03 | The heavy mineral separates were transferred to cavity slides. |
| 3/24/03 | The acid-insoluble <38 µm material was weighed. |

| Size Fraction | Weight (g) of HCl-Insoluble Material |
|---------------|--------------------------------------|
| >250 µm | 23.2842 |
| 125-250 μm | 1.0340 |
| 63-125 μm | 0.9327 |
| 38-63 µm | 0.9286 |
| <38 μm | 3.4227 |

Subsample 535.3 g, continued

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.0614 | 0.0633 | -0.0019^3 |
| 63-125 μm | 0.1973 | 0.1874^2 | <0.0099 |
| 38-63 µm | 0.2503 | | |
| <38 μm | 0.3804 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount. ³The heavy mineral separate contains some rust particles from the fume hood.

Subsample 893.3 g

| Date | Preparation step(s) |
|--|---|
| 9/21/02 to 9/22/02 | The subsample went through a warm bath of muriatic acid (31.45% HCl) for two days. |
| Late September to middle October/02 | The subsample went through a warm bath of concentrated HCl for four days, and it sat in the acid for 15 days at room temperature. |
| Middle October/02 | The HCl-insoluble material went through the dilution and decantation process for eight days. |
| 12/31/02 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. |
| January to early February/03 | The $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| 2/6/03 | The <38 μm material was weighed. |
| February/03 | The HCl-insoluble 125-250 μ m material went through a warm bath of concentrated HNO ₃ for two days. |
| February/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| 2/23/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| 2/26/03 to 3/4/03 | The acid-insoluble 125-250 μ m size fraction went through one heavy liquid separation. |
| 3/2/03 to 3/3/03 | The acid-insoluble 63-125 μ m size fraction went through one heavy liquid separation. |
| Early March/03 | The acid-insoluble $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| 3/14/03 | The acid-insoluble <38 μm material was weighed. |
| Late March/03 | The heavy mineral separates were transferred to cavity slides. |

| Size Fraction | Weight (g) of HCl-Insoluble Material |
|---------------|--------------------------------------|
| >250 µm | 31.3299 |
| 125-250 μm | 0.9553 |
| 63-125 μm | 1.1692 |
| 38-63 µm | 1.1991 |
| <38 μm | 7.0995 |

Subsample 893.3 g, continued

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.0459 | 0.0456 | 0.0003 |
| 63-125 μm | 0.0650 | 0.0467^2 | < 0.0183 |
| 38-63 µm | 0.0690 | | |
| <38 μm | 0.5522 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Subsample 1046.2 g

| Date | Preparation step(s) |
|--|---|
| 9/22/02 | The subsample went through a room-temperature bath of 20% HCl for one day. |
| Late September to middle October/02 | The subsample went through a warm bath of concentrated HCl for ten days, and it sat in the acid for 15 days at room temperature. |
| Late October/02 | The HCl-insoluble material went through the dilution and decantation process for four days. |
| 1/3/03 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. |
| January to early February/03 | The $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| 1/29/03 and 2/5/03 | The <38 μm material was weighed. |
| January/03 | The HCl-insoluble 125-250 μ m material went through a warm bath of concentrated HNO ₃ for four days. |
| January/03 | This acid-insoluble material went through the dilution and decantation process for four days. |
| 2/4/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| Early February/03 | The acid-insoluble $\leq 38 \ \mu m$ material was centrifuged and dried in the oven. |
| 2/11/03 | The acid-insoluble $<38 \ \mu m$ material was weighed. |
| 2/11/03 to 2/12/03 | The acid-insoluble 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. |
| 4/3/03 | The heavy mineral separates were transferred to cavity slides. |

| Size Fraction | Weight (g) of HCl-Insoluble Material |
|---------------|--------------------------------------|
| >250 µm | 35.7317 |
| 125-250 μm | 1.1779 |
| 63-125 μm | 1.3814 |
| 38-63 µm | 1.3820 |
| <38 μm | 8.4913 |

Subsample 1046.2 g, continued

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.0964 | 0.0818 ² | < 0.0146 |
| 63-125 μm | 0.1512 | 0.1331 ² | <0.0181 |
| 38-63 µm | 0.1614 | | |
| <38 μm | 0.5112 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Preparation steps and weight data for the HNO₃ digestion of the combined HCl-insoluble $63-125 \mu m$ size fractions of subsamples 535.3 g, 893.3 g, and 1046.2 g.

| Date | Preparation step(s) |
|-------------------|---|
| Early January/03 | The HCl-insoluble 63-125 μ m size fractions of subsamples 535.3 g, 893.3 g, and 1046.2 g were combined (total weight = 3.4833 g), and this material went through a warm bath of concentrated HNO ₃ for seven days. |
| Middle January/03 | This acid-insoluble material went through the dilution and decantation process for three days. |
| 1/21/03 | This acid-insoluble material was wet sieved using 38 μ m and 63 μ m sieves, and all the material was recovered. |
| Early February/03 | The <38 µm material was centrifuged and dried in the oven. |
| 1/31/03 to 2/3/03 | The acid-insoluble 63-125 μ m size fraction went through one heavy liquid separation. |
| 2/7/03 | The <38 μm material was weighed. |
| 4/7/03 to 4/10/03 | The heavy mineral separate was transferred to a cavity slide. |

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | No data | 0.5945^2 | < 0.0179 ³ |
| 38-63 µm | 0.6058 | | |
| <38 μm | 2.2651 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount. ³This value was obtained in the following manner: 3.4833 g - 0.5945 g - 0.6058 g - 2.2651 g = 0.0179 g.

Subsample 584.7 g

| Date | Preparation step(s) |
|--|---|
| 9/22/02 | The subsample went through a room-temperature bath of 20% HCl for one day. |
| Late September to middle October/02 | The subsample went through a warm bath of concentrated HCl for nine days, and it sat in the acid for 17 days at room temperature. |
| Middle October/02 | The HCl-insoluble material went through the dilution and decantation process for four days. |
| 11/8/02 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. |
| 11/8/02 to 11/9/02 | The HCl-insoluble 63-125 μ m size fraction went through one heavy liquid separation. |
| No data | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| 1/9/03 | The HCl-insoluble 63-125 μ m heavy mineral separate went through a warm bath of concentrated HNO ₃ for one day. |
| 1/10/03 to 1/13/03 | This acid-insoluble heavy mineral separate went through the dilution and decantation process for four days. |
| 1/22/03 | This material was wet sieved using 38 μ m and 63 μ m sieves, and some of the <38 μ m material was recovered. The acid-insoluble 63-125 μ m heavy mineral separate was recovered using a filter. |
| 2/14/03 | The acid-insoluble 63-125 μ m heavy mineral separate was transferred to a cavity slide. |
| 2/22/03 to 2/23/03 | The HCl-insoluble 125-250 μ m size fraction went through a warm bath of concentrated HNO ₃ for two days. |
| 2/24/03 to 2/28/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| 3/1/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| Early March/03 | The acid-insoluble $<38 \ \mu m$ material that was obtained from the wet sieving of $3/1/03$ was centrifuged and dried in the oven. |
| 3/10/03 | This acid-insoluble <38 µm material was weighed. |

Subsample 584.7 g, continued

| Date | Preparation step(s) |
|---------------------|--|
| 3/5/03 to 3/6/03 | The acid-insoluble 63-125 μ m and 125-250 μ m size fractions that were obtained from the wet sieving of 3/1/03 each went through one heavy liquid separation. |
| 3/21/03 and 3/24/03 | The two heavy mineral separates were transferred to cavity slides. |
| 3/4/05 | The HCl-insoluble 63-125 μ m light fraction went through a warm bath of concentrated HNO ₃ for one day. |
| 3/5/05 to 3/11/05 | This acid-insoluble light fraction went through the dilution and decantation process for seven days. |
| 3/19/05 | This acid-insoluble light fraction was wet sieved using a 63 μ m sieve, and the <63 μ m material was not recovered. The 63-125 μ m size fraction was weighed (0.1200 g). |

| Size Fraction | Weight (g) of HCl-Insoluble Material |
|---------------|--------------------------------------|
| >250 µm | 12.5532 |
| 125-250 μm | 0.5498 |
| 63-125 μm | 0.8434 |
| 38-63 µm | 0.8499 |
| <38 μm | 4.4160 |

Subsample 584.7 g, continued

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|------------------|---|---------------------------------|---|
| 125-250 μm | 0.0402 | 0.0404 | -0.0002 |
| 63-125 μm 0.0506 | | 0.0345 ² | < 0.0161 |
| 38-63 μm | 0.0564 | | |
| <38 μm | 0.2958 | | |

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Subsample 599.2 g

| Date | Preparation step(s) | |
|---------------------------------------|--|--|
| 9/22/02 | The subsample went through a room-temperature bath of 20% HCl for one day. | |
| Late September/02 | The subsample went through a warm bath of concentrated HCl for five days. During this step, a little material was spilled and lost. | |
| Late September to early October/02 | The HCl-insoluble material went through the dilution and decantation process for seven days. | |
| 11/10/02 | The HCl-insoluble material was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. | |
| 11/10/02 to 11/14/02 | The HCl-insoluble 63-125 μ m size fraction went through one heavy liquid separation. | |
| 1/9/03 | The HCl-insoluble 63-125 μ m heavy mineral separate was combine with the acid-insoluble heavy mineral separates of subsamples 987.4 g, 1114.1 g, and 1136.4 g (see below), and the combined heavy mineral separates went through a warm bath of concentrated HNO ₃ for one day. | |
| 1/10/03 to 1/14/03 | This acid-insoluble heavy mineral separate (combined) went through the dilution and decantation process for five days. | |
| No data | This acid-insoluble heavy mineral separate (combined) was wet sieved using 38 μ m and 63 μ m sieves, and some of the <38 μ m material was recovered. The acid-insoluble 63-125 μ m heavy mineral separate (combined) was recovered using a filter. | |
| January/03 | The HCl-insoluble $<38 \ \mu m$ material that was recovered on $11/10/02$ was centrifuged and dried in the oven. | |
| 1/27/03 | The HCl-insoluble <38 μm material was weighed. | |
| 2/15/03 | The acid-insoluble 63-125 μ m heavy mineral separate (combined) was transferred to a cavity slide. | |
| 2/22/03 | The $<38 \mu m$ material that was obtained by wet sieving the acid- insoluble heavy mineral separate (combined) was weighed (0.0026 g). | |
| 2/20/03 to 2/21/03 | The HCl-insoluble 125-250 μ m size fraction went through a warm bath of concentrated HNO ₃ for two days. | |

Subsample 599.2 g, continued

| Date | Preparation step(s) |
|----------------------|--|
| 2/22/03 to 2/26/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| 2/28/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| Early March/03 | The acid-insoluble $<$ 38 μ m material obtained from the wet sieving of 2/28/03 was centrifuged and dried in the oven. |
| 3/10/03 | This acid-insoluble <38 μm material was weighed. |
| 3/3/03 to 3/4/03 | The acid-insoluble 63-125 μ m and 125-250 μ m size fractions that were obtained from the wet sieving of 2/28/03 each went through one heavy liquid separation. |
| 3/24/03 to 3/25/03 | The two heavy mineral separates were transferred to cavity slides. |
| 10/24/04 to 10/25/04 | Spherules and irregular melt particles were handpicked from the $>250 \ \mu m$ size fraction. |
| 3/14/05 | The HCl-insoluble 63-125 μ m light fraction went through a warm bath of concentrated HNO ₃ for one day. |
| 3/15/05 to 3/21/05 | This acid-insoluble light fraction went through the dilution and decantation process for seven days. |
| Late March/05 | This acid-insoluble light fraction was wet sieved using a 63 μ m sieve, and the <63 μ m material was not recovered. The 63-125 μ m size fraction was weighed (0.0312 g). |
| 12/28/11 | The >250 μ m size fraction was rechecked for spherules and irregular melt particles. |
| 12/31/11 | The spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. |

Subsample 599.2 g, continued

| Size Fraction | Weight (g) of HCl-Insoluble Material ¹ |
|---------------|---|
| >250 µm | 15.7651 |
| 125-250 μm | 0.4743 |
| 63-125 μm | 0.5140 |
| 38-63 µm | 0.7299 |
| <38 μm | 5.4888 |

¹A little material was spilled and lost during acid digestion.

Weights after HNO3 digestion and sieving of the HCl-insoluble 125-250 μm material

| Size Fraction Weight (g) of Acid-Insoluble Material ¹ | | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---|--------|---------------------------------|---|
| 125-250 μm 0.0260 | | 0.0267 | -0.0007 |
| 63-125 μm 0.0352 | | 0.0233 ² | < 0.0119 |
| 38-63 µm | 0.0325 | | |
| <38 μm | 0.2285 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|------------------|-------------------------|--|
| >1000 µm | 0.0755 | 0.8689 |
| 500-1000 μm | 0.2383 | 0.3074 |
| 250-500 μm | 0.0221 | 0.0495 |
| $<250 \ \mu m^1$ | 0.0000 | 0.0000 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Subsample 987.4 g

| Date | Preparation step(s) | |
|----------------------|---|--|
| 9/22/02 to 9/30/02 | The subsample went through a room-temperature bath of 20% HCl for nine days. | |
| Early October/02 | The subsample went through a warm bath of concentrated HCl for three days. | |
| Early October/02 | The HCl-insoluble material went through the dilution and decantation process for five days. | |
| 10/13/02 to 10/25/02 | The HCl-insoluble material was divided into four groups (A, B, C, and D). Each group was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. | |
| No data | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. | |
| 11/4/02 to 11/6/02 | For each of the four groups, the HCl-insoluble 63-125 μ m size fraction went through one heavy liquid separation. Most of the heavy mineral separate for Group D was accidently lost. | |
| 11/8/02 to 11/9/02 | Each of the 63-125 µm heavy mineral separates went through a room-temperature bath of concentrated HNO ₃ for two days. | |
| 11/9/02 to 11/11/02 | The acid-insoluble heavy mineral separates each went through the dilution and decantation process for two days. | |
| 11/30/02 to 12/3/02 | The acid-insoluble heavy mineral separates were combined, and this material went through a room-temperature bath of concentrated HNO ₃ for four days. | |
| 12/4/02 to 12/8/02 | This acid-insoluble heavy mineral separate (combined) went through the dilution and decantation process for five days. | |
| 1/9/03 | This acid-insoluble heavy mineral separate (combined) was combined with those of subsamples 1114.1 g and 1136.4 g (see below), and the HCl-insoluble 63-125 μ m heavy mineral separate of subsample 599.2 g (see above). This heavy mineral separate (combined) went through a warm bath of concentrated HNO ₃ for one day. | |
| 1/10/03 to 1/14/03 | The acid-insoluble heavy mineral separate (combined) went through the dilution and decantation process for five days. | |

Subsample 987.4 g, continued

| Date | Preparation step(s) |
|--------------------|---|
| No data | The acid-insoluble heavy mineral separate (combined) was wet sieved using 38 μ m and 63 μ m sieves, and some of the <38 μ m material was recovered. The acid-insoluble 63-125 μ m heavy mineral separate (combined) was recovered using a filter. |
| 2/15/03 | The acid-insoluble 63-125 μ m heavy mineral separate (combined) was transferred to a cavity slide. |
| Middle February/03 | The HCl-insoluble 125-250 μ m size fractions of Groups A, B, C, and D were combined (total weight = 1.2427 g), and this material went through a warm bath of concentrated HNO ₃ for two days. |
| Middle February/03 | This acid-insoluble material went through the dilution and decantation process for five days. |
| 2/22/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. |
| 2/26/03 to 2/27/03 | The acid-insoluble 63-125 μ m and 125-250 μ m size fractions that were obtained from the wet sieving of 2/22/03 each went through one heavy liquid separation. |
| Early March/03 | The acid-insoluble $<38 \ \mu m$ material that was obtained from the wet sieving of 2/22/03 was centrifuged and dried in the oven. |
| 3/10/03 | The acid-insoluble $<38 \ \mu m$ material that was obtained from the wet sieving of 2/22/03 was weighed. |
| 3/27/03 and 4/2/03 | The two heavy mineral separates were transferred to cavity slides. |
| 3/11/05 to 3/13/05 | The HCl-insoluble 63-125 μ m light fractions of Groups A, B, C, and D each went through a warm bath of concentrated HNO ₃ for one day. |
| 3/12/05 to 3/20/05 | These acid-insoluble light fractions went through the dilution and decantation process for 6-7 days. |
| 3/19/05 to 3/22/05 | Each of the four acid-insoluble light fractions was wet sieved using a 63 μ m sieve, and the <63 μ m material was not recovered. The acid-insoluble 63-125 μ m light fractions were weighed. |

Subsample 987.4 g, continued

| Size Fraction | Group A | Group B | Group C | Group D | Total (g) |
|---------------|---------|---------|---------|---------|-----------|
| >250 µm | 9.1324 | 8.8045 | 3.4416 | 10.4969 | 31.8754 |
| 125-250 μm | 0.2670 | 0.2686 | 0.3229 | 0.3842 | 1.2427 |
| 63-125 μm | 0.2279 | 0.2155 | 0.3704 | 0.3305 | 1.1443 |
| 38-63 µm | 0.3062 | 0.2653 | 0.6297 | 0.5728 | 1.7740 |
| <38 μm | 1.7602 | 1.4655 | 1.5823 | 5.5458 | 10.3538 |

Weights (g) of HCl-insoluble Material

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size FractionWeight (g) of Acid-Insoluble Material1 | | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|--|--------|---------------------------------|---|
| 125-250 μm | 0.0404 | 0.0400 | 0.0004 |
| 63-125 μm 0.0720 | | 0.0435 ² | < 0.0285 |
| 38-63 μm | 0.1293 | | |
| <38 µm | 0.6258 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Weights of acid-insoluble¹ 63-125 µm Light Fractions

| Group | Weight (g) |
|-------|------------|
| А | 0.0167 |
| В | 0.0101 |
| С | 0.0167 |
| D | 0.0235 |

¹HCl and HNO₃ digestion

Subsample 1114.1 g

| Date | | Preparation step(s) | | |
|---------|------------------------------------|--|--|--|
| 9/21/02 | | The subsample went through a warm bath of muriatic acid (31.45% HCl) for two days. | | |
| | Late September/02 | The subsample went through a warm bath of concentrated HCl for five days, and it sat in the acid for two days at room temperature. | | |
| | Early October/02 | The HCl-insoluble material went through the dilution and decantation process for six days. | | |
| | 10/19/02, 10/27/02, and 11/4/02 | The HCl-insoluble material was divided into four groups (A, B, C, and D). Each group was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. | | |
| | No data | The $<38 \ \mu m$ material was centrifuged and dried in the oven before it was weighed. | | |
| | 11/4/02 to 11/6/02 | For each of the four groups, the HCl-insoluble 63-125 µm size fraction went through one heavy liquid separation. | | |
| | 11/9/02 | The four 63-125 μ m heavy mineral separates were combined, and this material went through a room-temperature bath of concentrated HNO ₃ for one day. | | |
| | 11/10/02 to 11/14/02 | This acid-insoluble heavy mineral separate (combined) went through the dilution and decantation process for five days. | | |
| | 1/9/03 | This acid-insoluble heavy mineral separate (combined) was combined with those of subsamples 987.4 g (see above) and 1136.4 g (see below), and the HCl-insoluble 63-125 μ m heavy mineral separate of subsample 599.2 g (see above). This heavy mineral separate (combined) went through a warm bath of concentrated HNO ₃ for one day. | | |
| | 1/10/03 to 1/14/03 | The acid-insoluble heavy mineral separate (combined) went through the dilution and decantation process for five days. | | |
| | No data | The acid-insoluble heavy mineral separate (combined) was wet sieved using 38 μ m and 63 μ m sieves, and some of the <38 μ m material was recovered. The acid-insoluble 63-125 μ m heavy mineral separate (combined) was recovered using a filter. | | |
| 2/15/03 | | The acid-insoluble 63-125 µm heavy mineral separate (combined) was transferred to a cavity slide. | | |

Subsample 1114.1 g, continued

| Date | Preparation step(s) | | |
|--------------------|--|--|--|
| 2/12/03 to 2/13/03 | The HCl-insoluble 125-250 μ m size fractions of Groups A, B, C, and D were combined (total weight = 1.2735 g), and this material went through a warm bath of concentrated HNO ₃ for two days. | | |
| Middle February/03 | This acid-insoluble material went through the dilution and decantation process for five days. | | |
| Middle February/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. | | |
| 2/24/03 to 2/25/03 | The acid-insoluble 63-125 μ m and 125-250 μ m size fractions that were obtained from this wet sieving each went through one heavy liquid separation. | | |
| Early March/03 | The acid-insoluble $<$ 38 μ m material that was obtained from this wet sieving was centrifuged and dried in the oven. | | |
| 3/4/03 | This acid-insoluble <38 µm material was weighed. | | |
| 4/15/03 | The two heavy mineral separates were transferred to cavity slides. | | |
| 3/7/05 to 3/9/05 | The HCl-insoluble 63-125 μ m light fractions of Groups A, B, C, and D each went through a warm bath of concentrated HNO ₃ for one day. | | |
| Middle March/05 | These acid-insoluble light fractions went through the dilution and decantation process for 5-7 days. | | |
| 3/18/05 to 3/19/05 | Each of the four acid-insoluble light fractions was wet sieved using a 63 μ m sieve, and the <63 μ m material was not recovered. The acid-insoluble 63-125 μ m light fractions were weighed. | | |

Subsample 1114.1 g, continued

| Size Fraction | Group A | Group B | Group C | Group D | Total (g) |
|---------------|---------|---------|---------|---------|-----------|
| >250 µm | 4.9413 | 8.4248 | 10.0311 | 10.0653 | 33.4625 |
| 125-250 μm | 0.5227 | 0.3764 | 0.2035 | 0.1709 | 1.2735 |
| 63-125 μm | 0.4599 | 0.4163 | 0.1433 | 0.1467 | 1.1662 |
| 38-63 µm | 0.4656 | 0.7141 | 0.1933 | 0.1190 | 1.4920 |
| <38 μm | 1.6761 | 5.2934 | 1.0402 | 0.8720 | 8.8817 |

Weights (g) of HCl-insoluble Material

Weights after HNO3 digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.1239 | 0.1192 | 0.0047 |
| 63-125 μm | 0.3245 | 0.3121 ² | < 0.0124 |
| 38-63 μm | 0.2524 | | |
| <38 µm | 0.3561 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Weights of acid-insoluble¹ 63-125 µm Light Fractions

| Group | Weight (g) |
|-------|------------|
| А | 0.0500 |
| В | 0.0100 |
| С | 0.0030 |
| D | 0.0064 |

¹HCl and HNO₃ digestion

Subsample 1136.4 g

| Date | Preparation step(s) | | |
|---|---|--|--|
| 9/27/02 | The subsample went through a room-temperature bath of 20% HCl for one day. | | |
| Late September/02 and early October/02 | The subsample went through a warm bath of concentrated HCl for seven days, and it sat in the acid for one day at room temperature. | | |
| Early October/02 | The HCl-insoluble material went through the dilution and decantation process for six days. | | |
| 11/4/02 and 11/5/02 | The HCl-insoluble material was divided into four groups (A, B, C, and D). Each group was wet sieved into five size fractions, and all the $<38 \mu m$ material was recovered. However, most of the $<38 \mu m$ material for Group D was accidently lost before this size fraction was weighed. | | |
| No data | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. | | |
| 11/5/02 to 11/6/02 | For each of the four groups, the HCl-insoluble 63-125 μ m size fraction went through one heavy liquid separation. | | |
| 11/10/02 | The four 63-125 μ m heavy mineral separates were combined, and this material went through a room-temperature bath of concentrated HNO ₃ for one day. | | |
| 11/11/02 to 11/15/02 | This acid-insoluble heavy mineral separate (combined) went through the dilution and decantation process for five days. | | |
| 1/9/03 | This acid-insoluble heavy mineral separate (combined) was combined with those of subsamples 987.4 g and 1114.1 g, and the HCl-insoluble 63-125 μ m heavy mineral separate of subsample 599.2 g (see above). This heavy mineral separate (combined) went through a warm bath of concentrated HNO ₃ for one day. | | |
| 1/10/03 to 1/14/03 | The acid-insoluble heavy mineral separate (combined) went through the dilution and decantation process for five days. | | |
| No data | The acid-insoluble heavy mineral separate (combined) was wet sieved using 38 μ m and 63 μ m sieves, and some of the <38 μ m material was recovered. The acid-insoluble 63-125 μ m heavy mineral separate (combined) was recovered using a filter. | | |

Subsample 1136.4 g, continued

| Date | Preparation steps(s) | | |
|--------------------|--|--|--|
| 2/15/03 | The acid-insoluble 63-125 μ m heavy mineral separate (combined) was transferred to a cavity slide. | | |
| 2/12/03 to 2/13/03 | The HCl-insoluble 125-250 μ m size fractions of Groups A, B, C, and D were combined (total weight = 1.3348 g), and this material went through a warm bath of concentrated HNO ₃ for two days. | | |
| 2/14/03 to 2/18/03 | This acid-insoluble material went through the dilution and decantation process for five days. | | |
| 2/21/03 | This acid-insoluble material was wet sieved using 38 μ m, 63 μ m, and 125 μ m sieves, and all the material was recovered. | | |
| 2/24/03 to 2/26/03 | The acid-insoluble 63-125 μ m and 125-250 μ m size fractions that were obtained from the wet sieving of 2/21/03 each went through one heavy liquid separation. | | |
| Early March/03 | The acid-insoluble $<38 \ \mu m$ material that was obtained from the wet sieving of $2/21/03$ was centrifuged and dried in the oven. | | |
| 3/4/03 | This acid-insoluble <38 μm material was weighed. | | |
| 4/14/03 to 4/15/03 | The two heavy mineral separates were transferred to cavity slides. | | |
| 3/5/05 to 3/6/05 | The HCl-insoluble 63-125 μ m light fractions of Groups A, B, C, and D each went through a warm bath of concentrated HNO ₃ for one day. | | |
| Middle March/05 | These acid-insoluble light fractions went through the dilution and decantation process for 5-6 days. | | |
| 3/18/05 to 3/19/05 | Each of the four acid-insoluble light fractions was wet sieved using a 63 μ m sieve, and the <63 μ m material was not recovered. The acid-insoluble 63-125 μ m light fractions were weighed. | | |

Subsample 1136.4 g, continued

| Size Fraction | Group A | Group B | Group C | Group D | Total (g) |
|---------------|---------|---------|---------|---------------------|---------------------|
| >250 µm | 3.9459 | 5.5498 | 9.1231 | 11.0154 | 29.6342 |
| 125-250 μm | 0.4470 | 0.2897 | 0.2860 | 0.3121 | 1.3348 |
| 63-125 μm | 0.4772 | 0.2607 | 0.3121 | 0.3578 | 1.4078 |
| 38-63 µm | 0.3741 | 0.2454 | 0.6324 | 0.5260 | 1.7779 |
| <38 μm | 1.2496 | 0.9012 | 3.6798 | 0.4063 ¹ | 6.2369 ² |

Weights (g) of HCl-insoluble Material

¹A minimum weight, since most of this size fraction was accidently lost prior to weighing. ²A minimum weight

Weights after HNO₃ digestion and sieving of the HCl-insoluble 125-250 µm material

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 125-250 μm | 0.1185 | 0.1197 | -0.0012 |
| 63-125 μm | 0.2009 | 0.1849 ² | < 0.0160 |
| 38-63 µm | 0.2376 | | |
| <38 μm | 0.5721 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since the light fraction was weighed after some material was used to make a grain mount.

Weights of acid-insoluble¹ 63-125 µm Light Fractions

| Group | Weight (g) |
|-------|------------|
| А | 0.1427 |
| В | 0.0177 |
| С | 0.0364 |
| D | 0.0280 |

¹HCl and HNO₃ digestion

Carawine spherule layer sample 42-1A

| Date | Preparation step(s) | |
|---------------------|---|--|
| 1/26/11 | The sample (one piece with two sawn surfaces) was sawn into three pieces, and the pieces were trimmed. The three pieces were quickly dipped in concentrated HCl, rinsed with distilled water, and put in the oven at a temperature of ~65 °C. | |
| 1/28/11 | Three subsamples (216.1 g, 341.4 g, and 460.0 g), each consisting of one piece, were weighed on the Triple Beam balance. | |
| 1/28/11 to 2/1/11 | Subsample 341.4 g went through a warm bath of concentrated HNO_3 for a total of 53 hours. | |
| 1/28/11 to 2/4/11 | Subsample 460.0 g went through a warm bath of concentrated HNO_3 for a total of 84.5 hours. | |
| 2/2/11 to 2/5/11 | Subsample 216.1 g went through a warm bath of concentrated HNO_3 for a total of 44 hours. | |
| 2/1/11 to 2/10/11 | For subsample 341.4 g, the HNO ₃ -insoluble material went through the dilution and decantation process seven times using only distilled water. | |
| 2/4/11 to 2/12/11 | For subsample 460.0 g, the HNO ₃ -insoluble material went through the dilution and decantation process seven times using only distilled water. | |
| 2/5/11 to 2/13/11 | For subsample 216.1 g, the HNO ₃ -insoluble material went through the dilution and decantation process eight times using only distilled water. | |
| 2/11/11 and 2/13/11 | For subsample 341.4 g, the HNO ₃ -insoluble material was wet sieved into five size fractions using only distilled water. All the $<$ 38 μ m material was recovered. | |
| 2/13/11 to 2/14/11 | For subsample 216.1 g, the HNO ₃ -insoluble material was wet sieved into five size fractions using only distilled water. All the $<38 \mu m$ material was recovered. | |
| 2/17/11 | For subsample 460.0 g, the HNO ₃ -insoluble material was wet sieved into five size fractions using only distilled water. All the $<38 \mu m$ material was recovered. | |

| | Date | Preparation step(s) |
|------------------------------------|------------------------------------|--|
| | Late February to early March/11 | For subsamples 216.1 g and 341.4 g, the 63-125 μ m and 125-250 μ m size fractions each went through three and two heavy liquid separations, respectively. |
| | 3/6/11 to 3/14/11 | The light fractions and heavy mineral separates were weighed. |
| | Early March/11 | For all the heavy mineral separates, I handpicked grains that were not obvious secondary iron or manganese oxide/oxyhydroxide grains using a binocular microscope. The handpicked grains were transferred to cavity slides. |
| Late February to early April/11 | | For each subsample, the $<38 \ \mu m$ material was centrifuged and dried in the oven. |
| | 4/14/11 | For each subsample, the $<38 \ \mu m$ material was weighed. |
| | October/11 | For subsamples 216.1 g and 341.4 g, spherules and irregular melt particles were handpicked from the >250 μ m size fractions. |
| | 12/29/11 to 12/30/11 | For subsamples 216.1 g and 341.4 g, the spherules and irregular melt particles were each dry sieved through 250 μ m, 500 μ m, and 1000 μ m sieves, and the four size fractions were weighed. |

Subsample 216.1 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 13.4204 | | |
| 125-250 μm | 0.7634 | 0.7294 | 0.0365 |
| 63-125 μm | 0.4943 | 0.4795 | 0.0140 |
| 38-63 µm | 0.4775 | | |
| <38 μm | 4.4920 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|------------------|-------------------------|--|
| >1000 µm | 0.0819 | 0.4768 |
| 500-1000 μm | 0.3976 | 0.1790 |
| 250-500 μm | 0.0618 | 0.0331 |
| $<250 \ \mu m^1$ | 0.0000 | 0.0000 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Subsample 341.4 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 14.5884 | | |
| 125-250 μm | 1.1432 | 1.1327 | 0.0073 |
| 63-125 μm | 0.7975 | 0.7890 | 0.0048 |
| 38-63 µm | 0.7020 | | |
| <38 μm | 5.0049 | | |

| Size Fraction | Weight (g) of Spherules | Weight (g) of Irregular Melt Particles |
|------------------|-------------------------|--|
| >1000 µm | 0.0761 | 0.7810 |
| 500-1000 μm | 0.6758 | 0.7859 |
| 250-500 μm | 0.1919 | 0.3956 |
| $<250 \ \mu m^1$ | 0.0009 | 0.0040 |

¹This material was derived during dry sieving of the >250 μ m size fractions.

Subsample 460.0 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material |
|---------------|--|
| >250 µm | 13.0717 |
| 125-250 μm | 1.3338 |
| 63-125 μm | 0.7048 |
| 38-63 µm | 0.7553 |
| <38 μm | 8.7077 |

Appendix J

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE CARAWINE CONTEXT SAMPLES

Carawine context sample X68-1

| Date | Preparation step(s) |
|--------------------|--|
| Early January/07 | The sample (one piece) was sawn into a few pieces. Two large pieces were trimmed, rinsed, and put in the oven. The two pieces were removed from the oven, quickly dipped in concentrated HCl, rinsed with tap water, and put back in the oven for about three days. |
| 1/15/07 | Subsamples 300.0 g and 304.7 g, each consisting of one piece, were weighed on the Triple Beam balance. |
| 1/15/07 to 1/16/07 | Subsamples 300.0 g and 304.7 g each went through a warm bath of concentrated HNO ₃ for 18.9 and 19.8 hours, respectively. |
| 1/16/07 to 2/8/07 | For each subsample, the HNO ₃ -insoluble material went through the dilution and decantation process 7-8 times. |
| 2/11/07 to 2/12/07 | For each subsample, the HNO ₃ -insoluble material was wet sieved into five size fractions. All the $<38 \mu m$ material was recovered. |
| No data | In subsample 304.7 g, some small chunks in the >250 μ m size fraction appeared to consist of grains cemented by clay and secondary quartz when they were viewed using a binocular microscope. The small chunks were crushed with a steel mortar and pestle. The crushed material was dry sieved through a 250 μ m sieve, and all the material was recovered. This material was recombined with the >38 μ m material of subsample 304.7 g, and the combined material was wet sieved into five size fractions. The <38 μ m material that was derived from this wet sieving step was not recovered. |
| 2/16/07 to 2/23/07 | For each subsample, the $<38 \mu m$ material was centrifuged. |
| 2/23/07 | For each subsample, the $<38 \ \mu m$ material was put in the oven. |
| No data | For each subsample, the $<38 \ \mu m$ material was weighed. |

Carawine context sample X68-1, continued

| Date | Preparation step(s) |
|--|---|
| 4/19/07 to 4/23/07, and 5/23/07 to 5/25/07 | For each subsample, the 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. |
| 6/13/07 to 6/15/07 | For subsample 300.0 g, the two heavy mineral separates were transferred to cavity slides. |
| 10/23/07 to 10/29/07 | For subsample 304.7 g, the heavy mineral separate of the 63-125 μ m size fraction was put in a vial, and the heavy mineral separate of the 125-250 μ m size fraction was transferred to two cavity slides. |
| 1/29/10 to 1/30/10 | Using a binocular microscope, I handpicked the grains that were not obvious secondary iron or manganese oxide/oxyhydroxide phases from the heavy mineral separate of the 63-125 μ m size fraction of subsample 304.7 g. The handpicked grains were transferred to a cavity slide. |

Carawine context sample X68-1, continued

Subsample 300.0 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0004 | | |
| 125-250 μm | 0.0011 | 0.0010 | 0.0001 |
| 63-125 μm | 0.0489 | 0.0473 | 0.0016 |
| 38-63 µm | 0.1309 | | |
| <38 μm | 2.3623 | | |

Subsample 304.7 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0331 | | |
| 125-250 μm | 0.2574 | 0.2542 | 0.0032 |
| 63-125 μm | 0.2069 | 0.1830 | 0.0239 |
| 38-63 µm | 0.2198 | | |
| <38 μm | 3.6088 | | |

Carawine context sample 104141

| Date | Preparation step(s) |
|-----------------------------------|--|
| 1/11/07 | The sample (one piece) was weighed on the Triple Beam balance (385.9 g), and it was trimmed with the rock saw. The piece was rinsed and put in the oven. |
| 1/12/07 | The piece was removed from the oven, quickly dipped in concentrated HCl, rinsed, and returned to the oven. |
| 1/16/07 | Subsample 357.2 g (one piece) was weighed on the Triple Beam balance and returned to the oven. |
| 1/17/07 to 1/18/07 | Subsample 357.2 g went through a warm bath of concentrated HNO ₃ for a total of 19.4 hours. |
| 1/19/07 to 2/5/07 | The HNO ₃ -insoluble material went through the dilution and decantation process eight times. |
| 2/9/07 | The HNO ₃ -insoluble material was wet sieved into five size fractions. All the $<38 \mu m$ material was recovered. |
| 2/15/07 to 2/23/07 | The <38 µm material was centrifuged. |
| 2/23/07 | The <38 μm material was put in the oven. |
| 3/17/07 | The <38 µm size fraction was weighed. |
| 5/26/07 to 5/28/07 | The 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. |
| 6/16/07, and 10/24/07 to 10/26/07 | The heavy mineral separates were transferred to cavity slides. |

Subsample 357.2 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.3437 | | |
| 125-250 μm | 0.0987 | 0.0971 | 0.0016 |
| 63-125 μm | 0.0958 | 0.0915 | 0.0043 |
| 38-63 µm | 0.1349 | | |
| <38 μm | 5.8437 | | |

Carawine context sample 104175

| Date | Preparation step(s) |
|--------------------|---|
| 5/14/10 | The two pieces (sawn as received) were trimmed, and they were rinsed with tap water. The two pieces were dipped in concentrated HCl for a few seconds, rinsed with distilled water, and put in the oven at a temperature (T) of ~ 62 °C. |
| 5/17/10 | The two pieces were weighed on the Triple Beam balance (18.0 g and 217.4 g), and they were combined to form subsample 235.4 g. |
| 5/17/10 to 5/19/10 | Subsample 235.4 g went through a warm (T \sim 70 °C) bath of concentrated HNO ₃ for a total of 29 hours. |
| 5/19/10 to 5/31/10 | The HNO ₃ -insoluble material went through the dilution and decantation process eight times using only distilled water. |
| 5/31/10 | The HNO ₃ -insoluble material was wet sieved into five size fractions. All the $<38 \mu m$ material was recovered. |
| 6/2/10 to 6/4/10 | The 63-125 μ m size fraction went through two heavy liquid separations. |
| 6/4/10 to 6/5/10 | The 125-250 μ m size fraction went through one heavy liquid separation. |
| 6/11/10 | The heavy mineral separates were weighed, and they were transferred to cavity slides. The grains were aligned in the cavity slides. The light fractions were weighed. |
| No data | The <38 µm material was centrifuged and dried in the oven. |
| 4/15/11 | The <38 μm material was weighed. |

Subsample 235.4 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0019 | | |
| 125-250 μm | 0.0008 | 0.0008 | 0.0000 |
| 63-125 μm | 0.0052 | 0.0048 | 0.0004 |
| 38-63 µm | 0.0252 | | |
| <38 μm | 1.1986 | | |
Appendix K

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE JEERINAH SPHERULE LAYER SAMPLES

Jeerinah spherule layer sample W94-1Q

| Date | Preparation step(s) | |
|--------------------|--|--|
| 5/29/02 | The sample (one piece) was sawn into two pieces, and the pieces were trimmed. The pieces underwent ultrasonic agitation for a few minutes. The pieces were dipped in 20% HCl for a few minutes, rinsed with water, dried under the heat lamp, and put in the oven. | |
| 5/30/02 | The two pieces were weighed on the Triple Beam balance: the smaller piece (\sim 6.5 by 1.9 by 1.2 cm) is 32.2 g, and the larger piece (\sim 6.3 by 4.0 by 1.8 cm) is 50.5 g. The smaller piece was held in reserve. The larger piece was put in a plastic baggie, and the baggie was put in a larger sample bag, and the piece was broken up with a rock hammer. The fragments were then crushed with a steel mortar and pestle to very coarse sand-to-granule-sized material. The material was put in the oven. | |
| Early June/02 | Four subsamples (9.5938 g, 10.3210 g, 13.0639 g, and 15.3415 g) were weighed on the Sartorius analytical balance, and they were put in the oven. | |
| 6/10/02 to 6/13/02 | Subsample 9.5938 g was slowly crushed with a steel mortar and pestle so that most of the material would pass through a 250 μ m sieve. It was dry sieved using 250 μ m, 125 μ m, and 63 μ m sieves. All the material was recovered. | |
| June/02 | In order to disaggregate the clay material, the 125-250 μ m size fraction and the <125 μ m size fractions were each boiled in a saturated solution of sodium pyrophosphate (Na ₄ P ₂ O ₇ ·10H ₂ O) for two days and one day, respectively. | |

| Jeerinah spherule l | ayer sample | W94-1Q, continued |
|---------------------|-------------|-------------------|
|---------------------|-------------|-------------------|

| Date | Preparation step(s) | |
|--------------------------------|---|--|
| June/02 | The 125-250 μ m size fraction and the <125 μ m size fractions each went through the dilution and decantation process for several days, and they were wet sieved. All the <38 μ m material was recovered. | |
| June/02 | All the size fractions of subsample 9.5938 g were recombined, and the material went through a warm bath of 1,2,4 trichlorobenzene for four days in an unsuccessful attempt to dissolve plastic fibers. The material was repeatedly rinsed with hexane in order to remove the 1,2,4 trichlorobenzene, and it was wet sieved into five size fractions. All the <38 μ m material was recovered. | |
| 6/27/02 to 6/29/02 | Subsamples 10.3210 g, 13.0639 g, and 15.3415 g were each slowly crushed with a steel mortar and pestle so that most of the material would pass through a 250 μ m sieve. | |
| July/02 | Subsamples 10.3210 g, 13.0639 g, and 15.3415 g were each boiled in a saturated solution of sodium pyrophosphate for 0.5-1 day. | |
| July/02 | Subsamples 10.3210 g, 13.0639 g, and 15.3415 g each went through the dilution and decantation process for several days, and they were wet sieved into five size fractions. All the $<38 \mu m$ material was recovered. | |
| No data | For each subsample, the $<38 \ \mu m$ material was centrifuged and dried in the oven. | |
| 8/11/02 | The 63-125 μ m size fraction of subsample 15.3415 g went through one heavy liquid separation. There was abundant secondary iron oxide/oxyhydroxide material in the heavy mineral separate. The heavy mineral separate was recombined with the light fraction. | |
| August/02 | For subsamples 9.5938 g, 10.3210 g, 13.0639 g, and 15.3415 g, the $>$ 38 µm size fractions each went through a warm bath of muriatic acid (31.45% HCl) for three days. | |
| August/02 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for 3-4 days. | |
| 8/28/02 to 8/29/02, and 9/3/02 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions, and the $<38 \mu m$ material that was derived from the acid-dissolution process was not saved. | |

| Jeerinah | spherule | layer | sample | W94-1Q, | continued |
|----------|----------|-------|--------|---------|-----------|
|----------|----------|-------|--------|---------|-----------|

| Date | Preparation step(s) |
|----------------------|--|
| 8/29/02 to 9/5/02 | For subsamples 9.5938 g, 13.0639 g, and 15.3415 g, the 38-63 μ m, 63-125 μ m, and 125-250 μ m size fractions each went through one heavy liquid separation. Subsample 10.3210 g was held in reserve. |
| 4/21/03 to 4/28/03 | The heavy mineral separates were transferred to cavity slides. |
| 3/22/08 to 3/26/08 | For subsample 10.3210 g, the 63-125 μ m size fraction went through two heavy liquid separations. |
| 3/28/08 to 4/1/08 | For subsample 10.3210 g, the 125-250 µm size fraction went through one heavy liquid separation. |
| 4/3/08 to 4/4/08 | For subsample 10.3210 g, the heavy mineral separates were transferred to cavity slides. |
| 12/16/08 to 12/19/08 | For each subsample, the $<38 \ \mu m$ size fraction went through a warm bath of concentrated HCl for 6-8 hours. |
| Late December/08 | For each subsample, the $<38 \mu m$ HCl-insoluble material went through the dilution and decantation process 5-6 times. |
| No data | For each subsample, the $<38 \ \mu m$ HCl-insoluble material was dried in the oven before it was weighed. |

Subsample 9.5938 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0639 | | |
| 125-250 μm | 1.7289 | 1.6872 | 0.0417 |
| 63-125 μm | 1.0682 | 1.0120 | 0.0562 |
| 38-63 µm | 0.3925 | 0.38441 | <0.0081 |
| <38 μm | 2.4228 | | |

¹A minimum weight, since a small amount of this size fraction was accidently lost prior to weighing.

Subsample 10.3210 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0471 | | |
| 125-250 μm | 2.0322 | 2.0348 | -0.0026 |
| 63-125 μm | 0.9551 | 0.9511 | 0.0040 |
| 38-63 µm | 0.3732 | | |
| <38 μm | 1.6643 | | |

Subsample 13.0639 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.1316 | | |
| 125-250 μm | 2.7037 | 2.6984 | 0.0053 |
| 63-125 μm | 1.3621 | 1.2922 | 0.0699 |
| 38-63 µm | 0.4152 | 0.4016 | 0.0136 |
| <38 μm | 2.5659 | | |

Subsample 15.3415 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0939 | | |
| 125-250 μm | 4.0548 | 4.0469 | 0.0079 |
| 63-125 μm | 0.7956 | 0.7881 | 0.0075 |
| 38-63 μm | 1.2178 | 1.1873 | 0.0305 |
| <38 μm | 1.6039 | | |

Jeerinah spherule layer sample X21-1

| | Date | Preparation step(s) |
|--|----------------------------------|--|
| | 11/5/03 | The two pieces were sawn and trimmed. The pieces underwent ultrasonic agitation for ~ 0.3 hour. The pieces were air-dried and put in the oven. |
| | 11/24/03 | A piece was weighed on the Triple Beam balance (240.4 g), and it went through a warm bath of concentrated HCl for \sim 0.6 hour. The piece did not react with the HCl, so it was removed from the acid, rinsed, and returned to the oven. |
| | No data | The pieces were put in double plastic baggies, and the pieces were broken down to mm-to-cm-sized fragments with a small sledge hammer. |
| | No data | Sixteen subsamples (see below) were weighed on the Sartorius analytical balance. |
| | 2/11/04 to 3/23/04 | For each subsample, the fragments were gently crushed with a steel mortar and pestle so that most of the material would pass through a 250 µm sieve. I forgot to weigh the subsamples after the dry sieving process and prior to the acid dissolution process. |
| Middle February to late March/04 | | Each subsample went through a warm bath of concentrated HCl for two days, and it went through the dilution and decantation process for 4-8 days. |
| | Middle March to late April/04 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions. All the <38 µm material was recovered. |
| No data Late March to May/04, and February to April/05 | | For each subsample, the $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| | | For subsamples 7.5830 g and 15.8285 g, the 63-125 μ m size fractions each went through two heavy liquid separations. The 63-125 μ m size fractions of the other 14 subsamples each went through three heavy liquid separations. |
| | 10/13/04 to 2/15/06 | All the heavy mineral separates were transferred to cavity slides. |

Subsample 7.5830 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0154 | | |
| 125-250 μm | 1.7986 | | |
| 63-125 μm | 1.0915 | 1.0940 | -0.0025 |
| 38-63 µm | 0.5103 | | |
| <38 μm | 1.4865 | | |

Subsample 15.1772 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.2352 | | |
| 125-250 μm | 5.4998 | | |
| 63-125 μm | 2.8423 | 2.8427 | -0.0004 |
| 38-63 µm | 1.1393 | | |
| <38 μm | 1.8481 | | |

Subsample 15.4470 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.4584 | | |
| 125-250 μm | 4.4276 | | |
| 63-125 μm | 2.6783 | 2.6458 | 0.0325 |
| 38-63 µm | 1.0549 | | |
| <38 μm | 2.2158 | | |

Subsample 15.6521 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.4674 | | |
| 125-250 μm | 4.9195 | | |
| 63-125 μm | 2.9212 | 2.9134 | 0.0078 |
| 38-63 µm | 1.0061 | | |
| <38 μm | 1.8426 | | |

Subsample 15.8285 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.3177 | | |
| 125-250 μm | 5.1733 | | |
| 63-125 μm | 2.9427 | 2.9402 | 0.0025^{1} |
| 38-63 μm | 1.0808 | | |
| <38 μm | 2.0528 | | |

¹On July 6, 2008 (after weighing), all the heavy mineral grains recovered from the second heavy liquid separation were accidently lost while aligning them in the cavity slide.

Subsample 16.1938 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.2301 | | |
| 125-250 μm | 4.4109 | | |
| 63-125 μm | 3.1214 | 3.1042 | 0.0172 |
| 38-63 µm | 1.2105 | | |
| <38 μm | 2.3495 | | |

Subsample 17.3884 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.2577 | | |
| 125-250 μm | 5.8223 | | |
| 63-125 μm | 3.0233 | 2.9166 ¹ | < 0.1067 |
| 38-63 µm | 1.0925 | | |
| <38 μm | 2.3623 | | |

¹This is a minimum weight, since a little of this size fraction was spilled and lost prior to weighing.

Subsample 21.7690 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.6288 | | |
| 125-250 μm | 7.2691 | | |
| 63-125 μm | 3.7947 | 3.7935 | 0.0012 |
| 38-63 µm | 1.1505 | | |
| <38 µm | 2.6742 | | |

| Subsamp | le 22. | 3758 g |
|---------|--------|--------|
|---------|--------|--------|

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.1068 | | |
| 125-250 μm | 7.0223 | | |
| 63-125 μm | 3.8443 | 3.7965 ¹ | 0.0478 |
| 38-63 µm | 1.6404 | | |
| <38 μm | 2.6715 | | |

¹After the third heavy liquid separation, one of the two filters that contained the light fraction may have been contaminated with an Ocean Drilling Program (ODP) sample while the filter was in the fume hood. Upon completion of the acetone rinse to remove the heavy liquid from the filter, the contents of this filter were weighed (1.5377 g), and this weight is included in the above weight (3.7965 g), but the contents of this filter were then discarded.

Subsample 22.6439 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.2101 | | |
| 125-250 μm | 6.0536 | | |
| 63-125 μm | 3.2115 | 3.5636 | -0.3521 |
| 38-63 µm | 1.4959 | | |
| <38 µm | 3.5178 | | |

Subsample 22.7851 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0970 | | |
| 125-250 μm | 5.3975 | | |
| 63-125 μm | 2.8951 | 2.6887 | 0.2064 |
| 38-63 µm | 1.2778 | | |
| <38 μm | 3.9897 | | |

Subsample 29.9445 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.4289 | | |
| 125-250 μm | 8.6197 | | |
| 63-125 μm | 4.8181 | 4.8324 ¹ | No data |
| 38-63 μm | 1.8362 | | |
| <38 μm | 2.7070 | | |

¹A very small amount of this material did not go through heavy liquid separation.

Subsample 30.7247 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.9058 | | |
| 125-250 μm | 10.3442 | | |
| 63-125 μm | 4.9169 | 4.9009 ¹ | ~0.0160 |
| 38-63 µm | 1.7239 | | |
| <38 μm | 2.9952 | | |

¹A very small amount of this material did not go through heavy liquid separation.

Subsample 32.5125 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.3360 | | |
| 125-250 μm | 10.9111 | | |
| 63-125 μm | 5.4753 | 5.4765 ¹ | No data |
| 38-63 µm | 2.2310 | | |
| <38 μm | 3.3436 | | |

¹A very small amount of this material did not go through heavy liquid separation.

Subsample 32.9150 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.2934 | | |
| 125-250 μm | 8.1338 | | |
| 63-125 μm | 4.5391 | 4.5208 ¹ | No data |
| 38-63 μm | 2.2775 | | |
| <38 µm | 6.0644 | | |

¹A very small amount of this material did not go through heavy liquid separation, and a small amount of the light fraction was spilled and not weighed.

Subsample 34.2206 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.5694 | | |
| 125-250 μm | 10.3386 | | |
| 63-125 μm | 4.4205 | 4.4281 ¹ | No data |
| 38-63 µm | 1.6762 | | |
| <38 μm | 4.5503 | | |

¹A very small amount of this material did not go through heavy liquid separation.

Appendix L

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE BEE GORGE (WITTENOOM) SAMPLES

Bee Gorge samples 96714A and 96714B

Initial Preparation

| Date | Preparation step(s) |
|------------------|---|
| 6/1/02 | Samples 96714A and 96714B (each sawn as received) were each sawn into four subdivisions, and each subdivision was processed separately. In ascending stratigraphic order, the four subdivisions consist of a basal carbonate lutite (Bcl) context layer, a lowermost spherule-rich sublayer (Lspsl; ~2-6 mm thick), a spherule-bearing lutite sublayer (Splsl; 7-9 mm thick), and an upper spherule/lutite sublayers subdivision (Usplsl; ~4-7 mm thick). In ascending stratigraphic order, the upper spherule/lutite sublayers subdivision (Usplsl) for each sample consists of a spherule-rich lutite sublayer, a lutite sublayer, a sandy sublayer with spherule fragments, and a lutite sublayer. |
| 6/1/02 to 6/3/02 | For samples 96714A and 96714B, the pieces of each subdivision underwent ultrasonic agitation for \sim 0.7 hour. The pieces were quickly dipped in concentrated HCl, rinsed, and put in the oven. |

Basal carbonate lutite (Bcl) context layer

Sample 96714A

| Date | Preparation step(s) | | |
|----------------------------|--|--|--|
| 6/4/02 | The material was crushed a little with a steel mortar and pestle, and it was returned to the oven. | | |
| Late June/02 | Nine subsamples (6.8001 g, 9.5376 g, 10.0687 g, 10.1556 g, 10.5610 g, 10.9594 g, 11.1877 g, 11.4911 g, and 11.6547 g) were weighed on the Sartorius analytical balance, and each subsample went through a warm bath of 20% HCl for 7-9 days. | | |
| Late June to early July/02 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for 4-5 days. | | |
| July/02 | For each subsample, the HCl-insoluble material was wet sieved using a 250 μ m sieve. Each of the nine >250 μ m size fractions went through a warm bath of 20% HCl for ~2 days, and through the dilution and decantation process for ~3-4 days. | | |
| July/02 | For each subsample, the HCl-insoluble material was recombined and wet sieved. All the material was recovered. | | |
| July/02 | For each subsample, the >250 μ m size fraction was crushed below 250 μ m, and this material went through a warm bath of 20% HCl for 2-5 days. | | |
| Late July/02 | For each subsample, this material went through the dilution and decantation process for 4-5 days, and it was recombined with its respective subsample. | | |
| July to August/02 | Each of the nine subsamples was boiled in water for 3-4 days and wet sieved. All the material was recovered. | | |
| August/02 | For each subsample, the 125-250 μ m size fraction was crushed below 125 μ m, and this material went through a warm bath of 20% HCl for 3-4 days. | | |
| August/02 | For each subsample, this material went through the dilution and decantation process for 3-4 days, and it was recombined with its respective subsample. | | |

Sample 96714A, continued

| Date | Preparation step(s) |
|---|--|
| 8/29/02, and 6/16/03 to 7/6/03 | For each subsample, the $<125 \mu m$ HCl-insoluble material was wet sieved using 38 μm and 63 μm sieves. All the material was recovered. |
| No data | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| 9/9/02 to 9/11/02, and 6/23/03 to 7/12/03 | For each subsample, the 38-63 μ m and 63-125 μ m size fractions each went through one heavy liquid separation. |
| 2/2/05 to 2/6/05 | For each subsample, the heavy mineral separate for the 63-125 μ m size fraction was transferred to a cavity slide. |

Subsample 6.8001 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.9156 | 0.9141 | 0.0015 |
| 38-63 µm | 0.5719 | 0.5699 | 0.0020 |
| <38 μm | 2.8487 | | |

Subsample 9.5376 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.3558 | 1.3560 | -0.0002 |
| 38-63 µm | 0.6646 | 0.6606 | 0.0040 |
| <38 μm | 3.9593 | | |

Sample 96714A, continued

Subsample 10.0687 g

| Size Fraction | Weight (g) of HCl-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|--|---------------------------------|---|
| 63-125 μm | 1.2862 | 1.2857 | 0.0005 |
| 38-63 µm | 0.5956 | 0.5929 | 0.0027 |
| <38 μm | 4.5945 | | |

¹During the boiling process, some material from subsample 10.9594 g may have gotten into this subsample.

Subsample 10.1556 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.7452 | 1.7443 | 0.0009 |
| 38-63 µm | 0.8007 | 0.7984 | 0.0023 |
| <38 μm | 1.9244 | | |

Subsample 10.5610 g

| Size Fraction | Weight (g) of HCl-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|--|---------------------------------|---|
| 63-125 μm | 1.5446 | 1.5436 | 0.0010 |
| 38-63 µm | 0.8021 | 0.7985 | 0.0036 |
| <38 μm | 3.9567 | | |

¹A little material was lost during wet sieving.

Sample 96714A, continued

Subsample 10.9594 g

| Size Fraction | Weight (g) of HCl-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|--|---------------------------------|---|
| 63-125 μm | 1.2773 | 1.2778 | -0.0005 |
| 38-63 µm | 0.6398 | 0.6376 | 0.0022 |
| <38 μm | 3.4461 | | |

¹Some material was lost during the boiling process.

Subsample 11.1877 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.7619 | 1.7642 | -0.0023 |
| 38-63 µm | 0.9780 | 0.9742 | 0.0038 |
| <38 μm | 4.5196 | | |

Subsample 11.4911 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.8938 | 1.8976 | -0.0038 |
| 38-63 µm | 0.9387 | 0.9382 | 0.0005 |
| <38 μm | 4.5987 | | |

Sample 96714A, continued

Subsample 11.6547 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.8187 | 1.8155 ¹ | < 0.0032 |
| 38-63 µm | 0.9824 | 0.9808 | 0.0016 |
| <38 μm | 4.5039 | | |

¹This is a minimum weight, since a very small amount of this light fraction was lost during weighing.

Sample 96714B

| Date | Preparation step(s) | | |
|----------------------------|---|--|--|
| 6/5/02 | The material was crushed a little with a steel mortar and pestle, and it was returned to the oven. | | |
| June/02 | Five subsamples (9.5155 g, 10.3847 g, 10.7160 g, 11.0042 g, and 11.1367 g) were weighed on the Sartorius analytical balance, and each subsample went through a warm bath of 20% HCl for 4-10 days. | | |
| Late June to early July/02 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for four days. | | |
| 7/10/02 | The HCl-insoluble material for subsample 11.0042 g was boiled in a sodium pyrophosphate solution in order to break up the clay material, and then it went through the dilution and decantation process. | | |
| No data | For each subsample, the HCl-insoluble material was wet sieved using a 250 μ m sieve. | | |
| No data | For each subsample, the >250 μ m size fraction was crushed below 250 μ m, and this material went through a warm bath of 20% HCl for ~1-3 days. | | |

Sample 96714B, continued

| Date | Preparation step(s) | |
|--------------------|---|--|
| No data | For each subsample, this material went through the dilution and decantation process for 3-4 days, and it was recombined with its respective subsample. | |
| No data | Subsamples 10.3847 g and 11.1367 g were boiled in water for two days to break up the clay material. | |
| No data | For each subsample, the HCl-insoluble material was wet sieved using a 125 μ m sieve. | |
| No data | For each subsample, the 125-250 μ m size fraction was crushed below 125 μ m, and this material went through a warm bath of 20% HCl for 2-10 days. | |
| September/02 | For each subsample, this material went through the dilution and decantation process for \sim 3-5 days, and it was recombined with its respective subsample. | |
| 6/10/03 to 6/15/03 | For each subsample, the $<125 \mu m$ HCl-insoluble material was wet sieved using 38 μm and 63 μm sieves. All the material was recovered. | |
| No data | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. | |
| 6/11/03 to 6/20/03 | For each subsample, the 38-63 μ m and 63-125 μ m size fractions each went through one heavy liquid separation. | |
| 2/7/05 | For each subsample, the heavy mineral separate for the 63-125 μ m size fraction was transferred to a cavity slide. | |

Sample 96714B, continued

Subsample 9.5155 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.6186 | 1.6214 | -0.0028 |
| 38-63 µm | 0.8341 | 0.8336 | 0.0005 |
| <38 μm | 3.7958 | | |

Subsample 10.3847 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.8332 | 1.8341 | -0.0009 |
| 38-63 µm | 0.7781 | 0.7776 | 0.0005 |
| <38 μm | 4.2699 | | |

Subsample 10.7160 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.0687 | 1.0684 | 0.0003 |
| 38-63 µm | 0.8961 | 0.8957 | 0.0004 |
| <38 μm | 4.9494 | | |

Sample 96714B, continued

Subsample 11.0042 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.4269 | 1.4354 | -0.0085 |
| 38-63 µm | 0.8644 | 0.8622 | 0.0022 |
| <38 μm | 4.6023 | | |

Subsample 11.1367 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.8859 | 1.8864 | -0.0005 |
| 38-63 μm | 0.9464 | 0.9447 | 0.0017 |
| <38 μm | 4.2051 | | |

Lowermost spherule-rich sublayer (Lspsl)

Sample 96714A

| Date | Preparation step(s) |
|--------------------|--|
| 6/12/02 to 6/18/02 | Subsamples 7.3433 g and 8.5769 g were weighed on the Sartorius analytical balance, and each subsample went through a warm bath of 20% HCl for seven days. |
| Late June/02 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for five days. |
| No data | For each subsample, the HCl-insoluble material was wet sieved using a 250 µm sieve. |
| No data | For each subsample, the >250 μ m size fraction was crushed a little, and this material went through a warm bath of 20% HCl for two days, and then through the dilution and decantation process for five days. This material was boiled in water for 2-3 days in order to break up the clay material. |
| No data | Each subsample was recombined, and it was wet sieved. All the material was recovered. |
| No data | For each subsample, Joe Zullo handpicked spherules and spherule fragments from the >250 μ m size fraction. |
| No data | For each subsample, the >250 μ m and 125-250 μ m size fractions were crushed below 125 μ m, and this material went through a warm bath of concentrated HCl for two days. |
| No data | For each subsample, this material went through the dilution and decantation process for five days, and it was recombined with its respective subsample. |
| 5/25/03 to 5/26/03 | For each subsample, the $<125 \mu m$ HCl-insoluble material was wet sieved using 38 μm and 63 μm sieves. All the material was recovered. |
| 6/2/03 to 6/4/03 | For each subsample, the 38-63 µm and 63-125 µm size fractions each went through one heavy liquid separation. |
| June/03 | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| 2/2/05 | For each subsample, the heavy mineral separate for the 63-125 μ m size fraction was transferred to a cavity slide. |
| 2/14/08 | For each subsample, the spherules and spherule fragments that were handpicked from the >250 μ m size fraction were weighed. |

Lowermost spherule-rich sublayer (Lspsl), continued

Sample 96714A, continued

Subsample 7.3433 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.2723 | 0.0558 | 0.2165 |
| 38-63 µm | 0.2225 | 0.2181 | 0.0044 |
| <38 μm | 1.5615 | | |

| Size Fraction | Weight (g) of Spherules and Spherule Fragments | |
|---------------|--|--|
| >250 µm | 1.6837 | |

Subsample 8.5769 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.1861 | 0.1842 | 0.0019 |
| 38-63 µm | 0.1465 | 0.1416 | 0.0049 |
| <38 μm | 1.5576 | | |

| Size Fraction | Weight (g) of Spherules and Spherule Fragments | |
|---------------|--|--|
| >250 µm | 2.4281 | |

Lowermost spherule-rich sublayer (Lspsl), continued

Sample 96714B

| Date | Preparation step(s) | | |
|----------------------------|---|--|--|
| 6/19/02 to late June/02 | Subsample 13.8178 g was weighed on the Sartorius analytical balance, and the subsample went through a warm bath of 20% HCl for eight days. | | |
| Late June to early July/02 | The HCl-insoluble material went through the dilution and decantation process for four days. | | |
| No data | The HCl-insoluble material was wet sieved using a 250 µm sieve. | | |
| No data | The >250 μ m size fraction went through a warm bath of 20% HCl for two days, and then through the dilution and decantation process for four days. | | |
| No data | Subsample 13.8178 g was recombined, and it was wet sieved. All the material was recovered. | | |
| No data | Joe Zullo handpicked spherules from the $>250 \mu m$ size fraction. | | |
| No data | The >250 μ m and 125-250 μ m size fractions were crushed below 125 μ m, and this material went through a warm bath of concentrate HCl for two days. This material went through the dilution and decantation process for five days. | | |
| 5/28/03 | The subsample was recombined, and the $<125 \mu m$ HCl-insoluble material was wet sieved using 38 μm and 63 μm sieves. All the material was recovered. | | |
| No data | The $<38 \ \mu m$ material was centrifuged and dried in the oven before it was weighed. | | |
| 6/5/03 to 6/6/03 | The 38-63 µm and 63-125 µm size fractions each went through one heavy liquid separation. | | |
| 2/2/05 to 2/3/05 | The heavy mineral separate for the 63-125 μ m size fraction was transferred to a cavity slide. | | |
| 2/1/06 | The spherules were dry sieved using 500 µm and 1000 µm sieves. | | |
| 2/3/06 | The three size fractions of spherules were weighed. | | |

Lowermost spherule-rich sublayer (Lspsl), continued

Sample 96714B, continued

Subsample 13.8178 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.4055 | 0.4031 | 0.0024 |
| 38-63 μm | 0.3252 | 0.3211 | 0.0041 |
| <38 μm | 2.0481 | | |

| Size Fraction | Weight (g) of Spherules |
|---------------|-------------------------|
| >1000 µm | 0.1332 |
| 500-1000 μm | 3.0302 |
| 250-500 μm | 1.1490 |

Spherule-bearing lutite sublayer (Splsl)

Sample 96714A

| Date | Preparation step(s) | | |
|---|--|--|--|
| 6/4/02 | The material was crushed a little with a steel mortar and pestle, and it was returned to the oven. | | |
| 6/12/02 to late June/02 | Subsample 10.3574 g was weighed on the Sartorius analytical balance, and the subsample went through a warm bath of 20% HCl for seven days. | | |
| No data | The HCl-insoluble material went through the dilution and decantation process for five days. | | |
| 7/16/02 | The HCl-insoluble material was wet sieved using a 250 µm sieve. | | |
| 7/17/02 to 7/22/02 | The >250 μ m size fraction went through a warm bath of 20% HCl for two days, and then through the dilution and decantation process for three days. | | |
| 7/23/02 | Subsample 10.3574 g was recombined, and it was wet sieved. All the material was recovered. | | |
| No data The >250 μ m and 125-250 μ m size fractions were crushed l 125 μ m, and this material went through a warm bath of 20% three days. This material went through the dilution and deca process for two days. | | | |
| 9/26/02 The subsample was recombined, and the <125 μm HCl-ins material was wet sieved using 38 μm and 63 μm sieves. Al material was recovered. | | | |
| No data | The <38 µm material was centrifuged and dried in the oven. | | |
| 12/19/02 | The <38 μm material was weighed. | | |
| 5/28/03 to 5/29/03 | The 38-63 μm and 63-125 μm size fractions each went through one heavy liquid separation. | | |
| 2/4/05 | The heavy mineral separate for the 63-125 μ m size fraction was transferred to a cavity slide. | | |

Spherule-bearing lutite sublayer (Splsl), continued

Sample 96714A, continued

Subsample 10.3574 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.5507 | 1.5491 | 0.0016 |
| 38-63 μm | 1.1675 | 1.1569 | 0.0106 |
| <38 µm | 3.0160 | | |

Sample 96714B

| Date | Preparation step(s) | | |
|-------------------------|--|--|--|
| 6/19/02 to late June/02 | Subsamples 6.5066 g and 12.0772 g were weighed on the Sartorius analytical balance, and the subsamples went through a warm bath of 20% HCl for 7 and 9 days, respectively. | | |
| Early July/02 | The HCl-insoluble material for subsamples 6.5066 g and 12.0772 g went through the dilution and decantation process for 4 and 5 days, respectively. | | |
| No data | For each subsample, the HCl-insoluble material was wet sieved using a 250 μ m sieve. | | |
| No data | For each subsample, the >250 μ m size fraction went through a warm bath of 20% HCl for two days, and then through the dilution and decantation process for four days. | | |
| No data | Each subsample was recombined, and it was wet sieved. All the material was recovered. | | |
| No data | For each subsample, Joe Zullo handpicked spherules and spherule fragments from the >250 μ m size fraction. | | |
| No data | For each subsample, the >250 μ m and 125-250 μ m size fractions were crushed below 125 μ m. For each subsample, this material went through a warm bath of concentrated HCl for 2-3 days, and then through the dilution and decantation process for five days. Each subsample was recombined. | | |

Spherule-bearing lutite sublayer (Splsl), continued

Sample 96714B, continued

| Date | Preparation step(s) |
|-------------------|--|
| May and June/03 | For each subsample, the $<125 \mu m$ HCl-insoluble material was wet sieved using 38 μm and 63 μm sieves. All the material was recovered. |
| No data | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| 5/29/03 to 6/7/03 | For each subsample, the 38-63 μ m and 63-125 μ m size fractions each went through one heavy liquid separation. |
| 2/3/05 | For each subsample, the heavy mineral separate for the 63-125 μ m size fraction was transferred to a cavity slide. |
| 2/14/08 | For each subsample, the spherules and spherule fragments that were handpicked from the >250 μ m size fraction were weighed. |

Subsample 6.5066 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.5748 | 0.5756 | -0.0008 |
| 38-63 µm | 0.3621 | 0.3638 | -0.0017 |
| <38 μm | 1.9802 | | |

| Size Fraction | Weight (g) of Spherules and Spherule Fragments | |
|---------------|--|--|
| >250 µm | 0.8739 | |

Spherule-bearing lutite sublayer (Splsl), continued

Sample 96714B, continued

Subsample 12.0772 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.3368 | 1.3360 | 0.0008 |
| 38-63 µm | 0.6877 | 0.6848 | 0.0029 |
| <38 μm | 3.7861 | | |

| Size Fraction | Weight (g) of Spherules and Spherule Fragments |
|---------------|--|
| >250 µm | 1.6303 |

Upper spherule/lutite sublayers (Usplsl) subdivision

Sample 96714A

| Date | Preparation step(s) |
|-------------------------|--|
| 6/12/02 to late June/02 | Subsamples 8.4057 g and 8.7879 g were weighed on the Sartorius analytical balance, and each subsample went through a warm bath of 20% HCl for seven days. |
| Early July/02 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for five days. |
| July/02 | For each subsample, the HCl-insoluble material was dry and/or wet sieved using a 250 μm sieve. |
| July/02 | For each subsample, the >250 μ m size fraction went through a warm bath of 20% HCl for two days, and then through the dilution and decantation process for 3-5 days. |
| No data | Each subsample was recombined, and it was wet sieved. All the material was recovered. |
| No data | For each subsample, Joe Zullo handpicked spherules and spherule fragments from the >250 μ m size fraction. |
| No data | For each subsample, the >250 μ m and 125-250 μ m size fractions were crushed below 125 μ m. For each subsample, this material went through a warm bath of concentrated HCl for ~2-6 days, and then through the dilution and decantation process for 4-6 days. Each subsample was recombined. |
| No data | For each subsample, the $<125 \mu m$ HCl-insoluble material was wet sieved using 38 μm and 63 μm sieves. All the material was recovered. |
| No data | The $<38 \ \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| 5/28/03 to 6/10/03 | For each subsample, the 38-63 μ m and 63-125 μ m size fractions each went through one heavy liquid separation. |
| 2/1/05 | For each subsample, the heavy mineral separate for the 63-125 μm size fraction was transferred to a cavity slide. |
| No data | For subsample 8.4057 g, the spherules and spherule fragments that were handpicked from the >250 μ m size fraction were weighed. |
| No data | For subsample 8.7879 g, the spherules and spherule fragments that were handpicked from the >250 μ m size fraction were dry sieved using 250 μ m and 500 μ m sieves, and the three size fractions were weighed. |

Upper spherule/lutite sublayers (Usplsl) subdivision, continued

Sample 96714A, continued

Subsample 8.4057 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.6796 | 0.3411 | 0.3385 |
| 38-63 µm | 0.6269 | 0.6095 | 0.0174 |
| <38 μm | 2.1414 | | |

| Size Fraction | Weight (g) of Spherules and Spherule Fragments |
|---------------|--|
| >250 µm | 0.5981 |

Subsample 8.7879 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 0.8238 | 0.8196 | 0.0042 |
| 38-63 µm | 0.5311 | 0.5189 | 0.0122 |
| <38 μm | 2.2311 | | |

| Size Fraction | Weight (g) of Spherules and Spherule Fragments |
|---------------|--|
| >500 µm | 0.0857 |
| 250-500 μm | 0.4372 |
| <250 μm | 0.0319 |

Upper spherule/lutite sublayers (Usplsl) subdivision, continued

Sample 96714B

| Date | Preparation step(s) |
|-------------------------|---|
| 6/20/02 to late June/02 | Subsample 14.2225 g was weighed on the Sartorius analytical balance, and the subsample went through a warm bath of 20% HCl for nine days. |
| Early July/02 | The HCl-insoluble material went through the dilution and decantation process for five days. |
| No data | The HCl-insoluble material was wet sieved using a 250 µm sieve. |
| No data | The >250 μ m size fraction went through a warm bath of 20% HCl for two days, and then through the dilution and decantation process for four days. |
| No data | Subsample 14.2225 g was recombined, and it was wet sieved. All the material was recovered. |
| No data | Joe Zullo handpicked spherules and spherule fragments from the $>250 \ \mu m$ size fraction. |
| No data | The >250 μ m and 125-250 μ m size fractions were crushed below 125 μ m. This material went through a warm bath of concentrated HCl for three days, and then through the dilution and decantation process for five days. |
| 6/3/03 | Subsample 14.2225 g was recombined, and the $<125 \mu m$ HCl- insoluble material was wet sieved using 38 μm and 63 μm sieves. All the material was recovered. |
| No data | The $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. |
| 6/8/03 to 6/9/03 | The 38-63 μ m and 63-125 μ m size fractions each went through one heavy liquid separation. |
| 2/3/05 | The heavy mineral separate for the $63-125 \ \mu m$ size fraction was transferred to a cavity slide. |
| 2/14/08 | The spherules and spherule fragments that were handpicked from the $>250 \ \mu m$ size fraction were weighed. |

Upper spherule/lutite sublayers (Usplsl) subdivision, continued

Sample 96714B, continued

Subsample 14.2225 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| 63-125 μm | 1.0619 | 1.0576 | 0.0043 |
| 38-63 µm | 1.0019 | 0.9926 | 0.0093 |
| <38 μm | 4.6675 | | |

| Size Fraction | Weight (g) of Spherules and Spherule Fragments |
|---------------|--|
| >250 µm | 0.6326 |

Bee Gorge sample BB

Initial Preparation

| Date | Preparation step(s) |
|---------|---|
| 5/30/02 | The sample (one piece) consists of a spherule layer (BB (sl)) sandwiched between two carbonate lutite context layers. The thinner context layer is named "context layer #1" and it is referred to as "BB (#1)". The other context layer is named "context layer #2" and it is referred to as "BB (#2)". The layers were separated from each other by using a rock saw and a screwdriver. I trimmed off as much of the caliche and iron oxide/oxyhydroxide material as possible. The pieces underwent ultrasonic agitation. The pieces were dipped in 20% HCl for ~1-2 minutes, rinsed, and put in the oven. |
| 6/3/02 | The pieces from each of the three layers were crushed a little with a steel mortar and pestle. Six subsamples were weighed on the Sartorius analytical balance, and they were put in the oven. |

Bee Gorge sample BB, continued

Spherule layer (BB (sl))

| Date | Preparation step(s) |
|--------------------|--|
| June/02 | Subsamples 9.8364 g, 10.6019 g, and 10.7999 g each went through a warm bath of 20% HCl for seven days. |
| Late June/02 | For each subsample, the HCl-insoluble material went through the dilution and decantation process for 5-9 days. |
| 7/10/02 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions. All the $<38 \mu m$ material was recovered. The size fractions for subsample 10.6019 g were kept in reserve. |
| No data | For each subsample, the $<38 \ \mu m$ material was dried in the oven before it was weighed. |
| 8/11/02 to 9/9/02 | For subsamples 9.8364 g and 10.7999 g, the 38-63 μ m and 125-250 μ m size fractions each went through one heavy liquid separation, and the 63-125 μ m size fractions each went through two heavy liquid separations. |
| 4/29/03 to 4/30/03 | For subsamples 9.8364 g and 10.7999 g, the heavy mineral separates were transferred to cavity slides. |
| No data | For subsample 10.7999 g, spherules were handpicked from the $>250 \ \mu m$ size fraction. |
| 2/1/06 | The spherules were dry sieved through 500 µm and 1000 µm sieves. |
| 2/3/06 | For the spherules, the 250-500 $\mu m,$ 500-1000 $\mu m,$ and >1000 μm size fractions were weighed. |
| 3/11/08 to 3/15/08 | For subsample 10.6019 g, the 63-125 μ m and 125-250 μ m size fractions each went through two heavy liquid separations. |
| 3/21/08 to 3/22/08 | For subsample 10.6019 g, the heavy mineral separates were transferred to cavity slides. |

Bee Gorge sample BB, continued

Spherule layer (BB (sl)), continued

Subsample 9.8364 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 1.6903 | | |
| 125-250 μm | 0.3995 | 0.4003 | -0.0008 |
| 63-125 μm | 0.3375 | 0.3404 | -0.0029 |
| 38-63 µm | 0.2727 | 0.2635 | 0.0092 |
| <38 µm | 0.5120 | | |

Subsample 10.6019 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 1.6311 | | |
| 125-250 μm | $0.4354/0.4365^1$ | 0.4355 | 0.0010 |
| 63-125 μm | 0.3476 | 0.3473 | 0.0003 |
| 38-63 µm | 0.3218 | | |
| <38 µm | 0.4764 | | |

¹The 125-250 µm size fraction was weighed again (0.4365 g) just prior to the heavy liquid separation in March, 2008.

Bee Gorge sample BB, continued

Spherule layer (BB (sl)), continued

Subsample 10.7999 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 1.9822 | | |
| 125-250 μm | 0.3693 | 0.3458 ¹ | < 0.0235 |
| 63-125 μm | 0.3229 | 0.3235 | -0.0006 |
| 38-63 µm | 0.2798 | 0.2796 | |
| <38 µm | 0.6255 | | |

¹This is a minimum weight, since a little material was spilled and lost during the weighing process.

| Size Fraction | Weight (g) of Spherules |
|---------------|-------------------------|
| >1000 µm | 0.0113 |
| 500-1000 μm | 0.8240 |
| 250-500 μm | 1.1248 |
Context layer #1 (BB (#1))

| Date | Preparation step(s) | |
|----------------------------------|---|--|
| Early June/02 | Subsample 5.4035 g went through a warm bath of 20% HCl for about five days. | |
| Middle June/02 | The HCl-insoluble material went through the dilution and decantation process for five days. | |
| 7/9/02 | The HCl-insoluble material was wet sieved into five size fractions. All the $<38 \mu m$ material was recovered. | |
| 7/26/02 | Some of the $<38 \mu m$ material was lost when the beaker broke during transfer of this material to a smaller beaker. This size fraction may contain some glass fragments. | |
| August/02 | The <38 μm material was dried in the oven. | |
| 8/30/02 | The <38 µm material was weighed. | |
| Early August/02 | The >38 μ m HCl-insoluble material went through a warm bath of 1,2,4 trichlorobenzene for four days in an unsuccessful attempt to dissolve plastic fibers. This material was rinsed with hexane for several days in order to remove the 1,2,4 trichlorobenzene. | |
| 8/11/02 | The >38 μ m HCl-insoluble material was wet sieved into five size fractions. I did not record if any <38 μ m material was obtained during this wet sieving process, or if it was recovered. | |
| 8/19/02 to 9/9/02 | The 38-63 μ m, 63-125 μ m, and 125-250 μ m size fractions each went through one heavy liquid separation. | |
| Late April/03 to early May/03 | The heavy mineral separates were transferred to cavity slides. | |

Context layer #1 (BB (#1)), continued

Subsample 5.4035 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0211 | | |
| 125-250 μm | 0.0041 | 0.0043 | -0.0002 |
| 63-125 μm | 0.0221 | 0.0070 | 0.0151 |
| 38-63 μm | 0.0900 | 0.0890 | 0.0010 |
| <38 μm | 0.9272^{1} | | |

¹This is a minimum weight, since a little material was lost when the beaker broke.

Context layer #2 (BB (#2))

| | Date | Preparation step(s) | |
|---|--------------------|--|--|
| | June/02 | Subsamples 5.9409 g and 8.9479 g each went through a warm bath of 20% HCl for seven days. | |
| | Late June/02 | For subsamples 5.9409 g and 8.9479 g, the HCl-insoluble material went through the dilution and decantation process for five and nine days, respectively. | |
| | 7/11/02 | For each subsample, the HCl-insoluble material was wet sieved into five size fractions. All the <38 µm material was recovered. | |
| | 7/11/02 | The respective size fractions of subsamples 5.9409 g and 8.9479 g were combined into subsample 14.89 g (referred to as Group 1 in laboratory notes). | |
| Ī | July/02 | For subsample 14.89 g, the <38 µm material was dried in the oven. | |
| Ī | 7/25/02 | The <38 μm material was weighed. | |
| | Early August/02 | For subsample 14.89 g, the >38 μ m HCl-insoluble material went through a warm bath of 1,2,4 trichlorobenzene for four days in an unsuccessful attempt to dissolve plastic fibers. This material was rinsed with hexane for several days in order to remove the 1,2,4 trichlorobenzene. | |
| | 8/11/02 | The >38 μ m HCl-insoluble material was wet sieved into five size fractions. I did not record if any <38 μ m material was obtained during this wet sieving process, or if it was recovered. | |
| | 8/20/02 to 9/10/02 | The 38-63 μ m, 63-125 μ m, and 125-250 μ m size fractions each went through one heavy liquid separation. | |
| ſ | 5/13/03 to 5/21/03 | The heavy mineral separates were transferred to cavity slides. | |

Context layer #2 (BB (#2)), continued

Subsample 14.89 g (Subsamples 5.9409 g and 8.9479 g combined)

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0134 | | |
| 125-250 μm | 0.0114 | 0.0113 | 0.0001 |
| 63-125 μm | 0.0119 | 0.0118 | 0.0001 |
| 38-63 µm | 0.1027 | 0.0991 | 0.0036 |
| <38 μm | 1.7349 | | |

Bee Gorge context sample 92058

| Date | Preparation step(s) | |
|------------------------------|--|--|
| 1/11/07 | As received from Dr. Bruce M. Simonson, the sample consisted of three pieces that were weighed on the Triple Beam balance (total weight = 479.2 g). The three pieces were trimmed, rinsed, and put in the oven. | |
| 1/15/07 | The three pieces were removed from the oven, quickly dipped in concentrated HCl, rinsed, and returned to the oven. | |
| 1/16/07 | The three pieces were weighed on the Triple Beam balance (106.3 g, 110.1 g, and 236.3 g), and they were returned to the oven. | |
| 1/17/07 to 1/19/07 | Subsample 216.4 g (106.3 g + 110.1 g) went through a warm bath of concentrated HNO ₃ for a total of 28.8 hours. A small amount of coarse-grained material was removed from the acid bath, crushed twice with a steel mortar and pestle, sieved through a 250 μ m sieve, and all the material was returned to the acid bath. | |
| 1/19/07 to 1/20/07 | Subsample 236.3 g went through a warm bath of concentrated HNO_3 for a total of 16.4 hours. A small amount of coarse-grained material was removed from the acid bath, crushed with a steel mortar and pestle, sieved through a 250 µm sieve, and all the material was returned to the acid bath. | |
| 1/19/07 to early March/07 | For each subsample, the HNO ₃ -insoluble material went through the dilution and decantation process fifteen times. | |
| 2/28/07 to 3/2/07 | For subsample 216.4 g, the HNO ₃ -insoluble material was wet sieved into five size fractions, and only part of the $<38 \mu m$ material was recovered. | |
| 3/9/07 to 3/14/07 | For subsample 236.3 g, the HNO ₃ -insoluble material was wet sieved into five size fractions, and only part of the $<38 \mu m$ material was recovered. | |
| 3/14/07 to 4/3/07 | For each subsample, the <38 µm material was centrifuged. | |
| 4/3/07 to 4/4/07 | For each subsample, the $<38 \mu m$ material was put in the oven. | |
| 4/13/07 | For each subsample, the <38 µm material was weighed. | |
| 6/4/07 to 6/18/07 | For subsample 216.4 g, the 63-125 μ m and 125-250 μ m size fractions each went through two heavy liquid separations. | |

Bee Gorge context sample 92058, continued

| Date | Preparation step(s) | |
|---------------------|--|--|
| 6/6/07 to 6/30/07 | For subsample 236.3 g, the 63-125 μ m size fraction went through two heavy liquid separations, and the 125-250 μ m size fraction went through one heavy liquid separation. | |
| 10/26/07 to 11/7/07 | Most of the heavy mineral separates were transferred to cavity slides. For subsample 216.4 g, the heavy mineral separates of the 63-125 µm size fraction were combined and put in a vial. The heavy mineral separates contain abundant oxidized pyrite crystals. | |
| No data | Using a binocular microscope, I handpicked the grains that were not obvious secondary iron oxide/oxyhydroxide grains from the heavy mineral separates of subsample 236.3 g that were in cavity slides. The handpicked grains were transferred to other cavity slides. | |

Bee Gorge context sample 92058, continued

Subsample 216.4 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0988^{1} | | |
| 125-250 μm | 0.8780 | 0.8848 | -0.0068 |
| 63-125 μm | 2.7062 | 2.7361 | -0.0299 |
| 38-63 µm | 1.8835 | | |
| <38 μm | 16.5521 ² | | |

¹This is a minimum weight, since prior to weighing, a little material was accidently lost while drying the size fraction under the heat lamp. ²This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

Subsample 236.3 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0100 | | |
| 125-250 μm | 0.6275 | 0.6314 | -0.0039 |
| 63-125 μm | 2.7644 | 2.7947 | -0.0303 |
| 38-63 μm | 2.6683 | | |
| <38 μm | 20.4345 ¹ | | |

¹This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

Appendix M

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE MONTEVILLE SPHERULE LAYER SAMPLES

Monteville spherule layer sample U63-1

| Date | Preparation step(s) | |
|--------------------------------|---|--|
| 11/7/03 | The sample (one sawn slab as received) was sawn and trimmed. Two large pieces were rinsed and put in the oven. | |
| 11/28/03 | Subsamples 278.0 g (one piece) and 315.2 g (one piece) were weighed on the Triple Beam balance. | |
| 11/28/03 to 11/30/03 | Subsamples 278.0 g and 315.2 g each went through a warm bath of concentrated HCl for a total of 23.8 hours. | |
| Early to middle December/03 | For each subsample, the HCl-insoluble material went through the dilution and decantation process 7-8 times. | |
| 1/28/04 | For subsample 278.0 g, the HCl-insoluble material was wet sieved several times into five size fractions. All the $<38 \mu m$ material was recovered. | |
| 1/29/04 to 1/30/04 | For subsample 278.0 g, the >38 μ m size fractions went through ultrasonic agitation and acetone rinse in an unsuccessful attempt to remove the saw oil contamination. | |
| 1/30/04 | For subsample 278.0 g, the HCl-insoluble material was wet sieved into five size fractions. All the $<$ 38 μ m material was recovered. | |
| 1/30/04 to 1/31/04 | For subsample 315.2 g, the HCl-insoluble material was dried in a beaker on a hotplate in an unsuccessful attempt to remove the saw oil contamination. | |
| 2/6/04 to 2/11/04 | For subsample 315.2 g, the HCl-insoluble material was rinsed several times with acetone in an unsuccessful attempt to remove the saw oil contamination. | |

| Date | Preparation step(s) | |
|-------------------|---|--|
| 2/29/04 to 3/2/04 | For subsample 315.2 g, the HCl-insoluble material was wet sieved several times into five size fractions. All the $<38 \mu m$ material was recovered. | |
| No data | For each subsample, the $<38 \mu m$ material was centrifuged and dried in the oven before it was weighed. | |
| 3/8/04 to 3/9/04 | For subsample 278.0 g, the 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. | |
| 3/9/04 to 3/10/04 | For subsample 315.2 g, the 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. | |
| No data | For each subsample, the heavy mineral separates were put in vials. | |
| Early April/11 | For each subsample, I handpicked the grains from the heavy mineral separates that were not obvious secondary iron or manganese oxide/oxyhydroxide grains using a binocular microscope. The handpicked grains were transferred to cavity slides. | |

Monteville spherule layer sample U63-1, continued

Monteville spherule layer sample U63-1, continued

Subsample 278.0 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 31.7357 | | |
| 125-250 μm | 1.3474 | 1.2216 | 0.1258 |
| 63-125 μm | 1.6027 | 1.5368 | 0.0659 |
| 38-63 µm | 2.1045 | | |
| <38 μm | 13.3190 | | |

Subsample 315.2 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 32.6709 | | |
| 125-250 μm | 1.3665 | 0.9067 | 0.4598 |
| 63-125 μm | 1.3862 | 1.1891 | 0.1971 |
| 38-63 µm | 1.3934 | | |
| <38 μm | 21.0270 | | |

Monteville spherule layer sample V111

| Date | | Preparation step(s) | | |
|------|---------------------------------------|--|--|--|
| | 11/7/03 | The sample (one piece) was sawn into several pieces, and three pieces were selected for processing. | | |
| | 11/9/03 | The three pieces were trimmed, washed in soap and water, rinsed, and put in the oven. | | |
| | 11/24/03 | Subsamples 106.1 g (two pieces) and 219.9 g (one piece) were weighed on the Triple Beam balance. | | |
| | 11/24/03 to 11/27/03 | Subsamples 106.1 g and 219.9 g each went through a warm bath of concentrated HCl for a total of 24.8 and 22.5 hours, respectively. The material underwent ultrasonic agitation during the acid dissolution in an attempt to break up some remnant chunks. | | |
| | Late November to early December/03 | For each subsample, the HCl-insoluble material went through the dilution and decantation process 5-8 times. | | |
| | 2/14/04 to 2/15/04 | For subsample 106.1 g, the HCl-insoluble material was wet sieved into five size fractions. The >250 μ m size fraction contained remnant chunks, so this size fraction was ground with a steel mortar and pestle during the wet sieving process. By visual estimate, ~80-90% of the total <38 μ m material was recovered. | | |
| | 2/18/04 to 2/19/04 | For subsample 219.9 g, the HCl-insoluble material was wet sieved into five size fractions. The >38 μ m size fractions were boiled in water in an attempt to break up the material, and this material was wet sieved into five size fractions. By visual estimate, ~90% of the total <38 μ m material was recovered. | | |
| | 2/20/04 | For subsample 106.1 g, the >38 μ m size fractions were boiled in water in an attempt to break up the material, and this material was wet sieved into five size fractions. Very little additional <38 μ m material resulted from this wet sieving. | | |
| | No data | For each subsample, the $<38 \ \mu m$ material was centrifuged and dried in the oven before it was weighed. | | |
| | 2/26/04 to 2/28/04 | For subsample 106.1 g, the 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. | | |
| | 2/27/04 to 2/29/04 | For subsample 219.9 g, the 63-125 µm and 125-250 µm size fractions each went through one heavy liquid separation. | | |

Monteville spherule layer sample V111, continued

| Date | Preparation step(s) |
|--------------------|--|
| 8/11/06 to 8/16/06 | For subsample 219.9 g, the 63-125 μ m heavy mineral separate was transferred to a cavity slide. |
| Early September/06 | For subsample 219.9 g, the 125-250 μ m heavy mineral separate was transferred to a cavity slide. |

Subsample 106.1 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0018 ¹ | | |
| 125-250 μm | 0.6364 | 0.6368 | -0.0004 |
| 63-125 μm | 2.7734 | 2.1964 | 0.5770 |
| 38-63 µm | 1.4887 | | |
| <38 μm | 3.9369 ² | | |

¹This size fraction was ground during the wet sieving process. ²This is a minimum weight, since ~10-20% of the $<38 \mu m$ material was not recovered during wet sieving.

Subsample 219.9 g

| Size Fraction | Weight (g) of HCl-Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.1062 | | |
| 125-250 μm | 1.5783 | 1.5802 | -0.0019 |
| 63-125 μm | 5.3686 | 5.3672 ¹ | 0.0014 |
| 38-63 µm | 3.4572 | | |
| <38 μm | 12.3548 ² | | |

¹After weighing, some of the light fraction material was spilled and discarded. The remaining light fraction material was weighed (4.3973 g). ²This is a minimum weight, since ~10% of the <38 μ m material was not recovered during wet sieving.

Appendix N

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE MONTEVILLE CONTEXT SAMPLES

Monteville context sample T149-1

| Date | Preparation step(s) |
|--------------------|---|
| 1/11/07 | The sample consists of five pieces (all sawn as received) that were weighed on the Triple Beam balance (total weight = 251.1 g). The five pieces were trimmed, rinsed, and put in the oven. |
| 1/15/07 | The five pieces were removed from the oven, quickly dipped in concentrated HCl, rinsed, and returned to the oven. |
| 1/16/07 | The five pieces were individually weighed on the Triple Beam balance (7.7 g, 37.0 g, 38.1 g, 64.5 g, and 67.0 g), and they were returned to the oven. |
| 1/24/07 to 1/26/07 | Subsamples 105.1 g (38.1 g + 67.0 g) and 109.2 g (7.7 g + 37.0 g + 64.5 g) each went through a warm bath of concentrated HNO ₃ for a total of 5.8 and 6.2 hours, respectively. |
| 1/25/07 to 2/15/07 | For each subsample, the HNO ₃ -insoluble material went through the dilution and decantation process 6-7 times. |
| 2/21/07 to 2/24/07 | For each subsample, the HNO ₃ -insoluble material was wet sieved into five size fractions. For each subsample, the 38-63 μ m and 63-125 μ m size fractions were wet sieved several times, but it was difficult to achieve a good separation. For each subsample, most of the <38 μ m material was recovered. |
| 2/26/07 to 3/24/07 | For each subsample, the $<38 \ \mu m$ material was centrifuged. |
| 3/24/07 | For each subsample, the $<38 \ \mu m$ material was put in the oven. |
| 3/27/07 | For each subsample, the $<38 \ \mu m$ material was weighed. |

Monteville context sample T149-1, continued

| | Date | Preparation step(s) | |
|-------------------|-------------------|--|--|
| 7/23/07 to 8/5/07 | | For each subsample, the 63-125 μ m size fraction went through three heavy liquid separations, and the 125-250 μ m size fraction went through two heavy liquid separations. The heavy mineral separates contain abundant oxidized pyrite crystals. | |
| | 10/31/07 | The heavy mineral separates were weighed and put in vials. | |
| | Early February/10 | For each subsample, I handpicked grains from the heavy mineral separates that were not obvious secondary iron oxide/oxyhydroxide grains using a binocular microscope. The handpicked grains were transferred to cavity slides. | |

Monteville context sample T149-1, continued

Subsample 105.1 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0409 | | |
| 125-250 μm | 0.0680 | 0.0007 | 0.0671 |
| 63-125 μm | 0.1788 | 0.1015 | 0.0735 |
| 38-63 µm | 1.2526 | | |
| <38 μm | 8.6091 ¹ | | |

¹This is a minimum weight, since a little material was not recovered during wet sieving.

Subsample 109.2 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.0580 | | |
| 125-250 μm | 0.0901 | 0.0052 | 0.0865 |
| 63-125 μm | 0.7205 | 0.6219 | 0.0981 |
| 38-63 µm | 2.3368 | | |
| <38 µm | 8.3163 ¹ | | |

¹This is a minimum weight, since a little material was not recovered during wet sieving.

Monteville context sample II67-1B

| Date | Preparation step(s) | |
|---------------------|--|--|
| Early January/07 | The sample (one piece) was sawn into two large pieces, and the pieces were trimmed. The two pieces were rinsed and put in the oven. | |
| 1/15/07 | The two pieces were removed from the oven, quickly dipped in concentrated HCl, rinsed, and returned to the oven. | |
| 1/16/07 | Subsamples 286.9 g (one piece) and 329.8 g (one piece) were weighed on the Triple Beam balance, and the subsamples were returned to the oven. | |
| 1/23/07 to 1/25/07 | Subsamples 286.9 g and 329.8 g each went through a warm bath of concentrated HNO ₃ for a total of 15.8 and 12.7 hours, respectively. | |
| 1/24/07 to 2/14/07 | For each subsample, the HNO ₃ -insoluble material went through the dilution and decantation process seven times. | |
| 2/14/07 to 2/15/07 | For each subsample, the HNO ₃ -insoluble material was wet sieved into five size fractions. For each subsample, all the $<38 \mu m$ material was recovered. For subsample 329.8 g, the $>38 \mu m$ size fractions were wet sieved again. The small amount of $<38 \mu m$ material that was obtained during the second wet sieving was discarded. | |
| 2/21/07 to 3/17/07 | For each subsample, the $<38 \ \mu m$ material was centrifuged. | |
| 3/9/07 and 3/17/07 | For each subsample, the $<38 \ \mu m$ material was put in the oven. | |
| 3/17/07 and 3/19/07 | For each subsample, the $<38 \ \mu m$ material was weighed. | |
| 7/6/07 to 7/22/07 | For each subsample, the 63-125 µm size fraction went through three heavy liquid separations, and the 125-250 µm size fraction went through two heavy liquid separations. | |
| 10/31/07 | The heavy mineral separates were weighed and put in vials. | |
| Early February/10 | For each subsample, I handpicked the grains from the heavy mineral separates that were not obvious secondary iron or manganese oxide/oxyhydroxide grains using a binocular microscope. The handpicked grains were transferred to cavity slides. | |

Monteville context sample II67-1B, continued

Subsample 286.9 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.3006 | | |
| 125-250 μm | 0.0256 | 0.0178 | 0.0036 |
| 63-125 μm | 0.0959 | 0.0888 | 0.0061 |
| 38-63 µm | 0.4280 | | |
| <38 μm | 8.3146 | | |

Subsample 329.8 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 0.7425 | | |
| 125-250 μm | 0.1335 | 0.1240 | 0.0064 |
| 63-125 μm | 0.1894 | 0.1644 | 0.0212 |
| 38-63 µm | 0.5946 | | |
| <38 μm | 10.4286 | | |

Appendix O

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE GRÆNSESØ SPHERULE LAYER SAMPLES

Grænsesø spherule layer sample GL8904-1

| Date | | Preparation step(s) |
|------|----------------------------------|--|
| | 6/23/05 | The sample (one piece) was sawn into several pieces, and the pieces were trimmed. The pieces underwent ultrasonic agitation for ~ 1 hour. The pieces were quickly dipped in concentrated HCl, rinsed in distilled water, and put in the oven. |
| | 7/4/05 | Subsamples 331.3 g (one piece), 349.3 g (one piece), and 567.8 g (two pieces) were weighed on the Triple Beam balance. |
| | 7/4/05 to 7/6/05 | Each subsample went through a warm bath of concentrated HCl for 24.9 hours. |
| | 7/7/05 to 7/22/05 | For each subsample, the HCl-insoluble material went through the dilution and decantation process 8-9 times. |
| | 7/21/05 to 7/22/05 | For subsamples 331.3 g, 349.3 g, and 567.8 g, the HCl-insoluble material went through a warm bath of concentrated HNO ₃ for a total of 12.2, 6.6, and 11.2 hours, respectively. |
| | 7/21/05 to 8/28/05 | For each subsample, the acid-insoluble material went through the dilution and decantation process 7-10 times. |
| | 8/23/05 to early September/05 | For each subsample, the acid-insoluble material was wet sieved into seven size fractions. For each subsample, only a part of the $<38 \mu m$ material was recovered. |
| | 9/13/05 to 10/4/05 | For each subsample, the $<38 \mu m$ material was centrifuged. |
| | 9/26/05 and 10/4/05 | For each subsample, the $<38 \mu m$ material was put in the oven. |
| Ī | 10/4/05 and 10/9/05 | For each subsample, the $<38 \mu m$ material was weighed. |
| | 1/24/06 to 2/16/06 | For subsamples 331.3 g and 349.3 g, the 63-125 μ m size fractions went through three heavy liquid separations, and the 125-250 μ m size fractions went through two heavy liquid separations. |
| Γ | 6/13/06 to 6/15/06 | The heavy mineral separates were transferred to cavity slides. |

Grænsesø spherule layer sample GL8904-1, continued

Subsample 331.3 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|------------------|---|---------------------------------|---|
| >1000 µm 52.5559 | | | |
| 500-1000 μm | 5.7970 | | |
| 250-500 μm | 4.8493 | | |
| 125-250 μm | 11.8978 | 11.8843 | 0.0135 |
| 63-125 μm | 9.6974 | 9.5683 | 0.1291 |
| 38-63 µm | 2.1797 | | |
| <38 μm | 7.2922^{2} | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

Subsample 349.3 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >1000 µm | 35.8707 | | |
| 500-1000 μm | 5.0224 | | |
| 250-500 μm | 3.9747 | | |
| 125-250 μm | 7.1659 | 7.1651 | 0.0008 |
| 63-125 μm | 8.2451 | 8.2218 | 0.0233 |
| 38-63 µm | 2.5968 | | |
| <38 μm | 7.6738 ² | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu$ m material was recovered during wet sieving.

Grænsesø spherule layer sample GL8904-1, continued

Subsample 567.8 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | |
|---------------|--|--|
| >1000 µm | 100.3301 | |
| 500-1000 μm | 12.3629 | |
| 250-500 μm | 9.6507 | |
| 125-250 μm | 19.7337 | |
| 63-125 μm | 12.7524 | |
| 38-63 µm | 3.3086 | |
| <38 μm | 4.8318 ² | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

Grænsesø spherule layer sample GL8904-2

| Date | | Preparation step(s) | |
|--|---------------------|--|--|
| | 6/23/05 | The sample (one piece) was sawn into several pieces, and the pieces were trimmed. The pieces underwent ultrasonic agitation for ~ 1 hour. The pieces were quickly dipped in concentrated HCl, rinsed in distilled water, and put in the oven. | |
| | 7/7/05 | Subsamples 386.9 g (one piece), 421.4 g (one piece), and 694.2 g (two pieces) were weighed on the Triple Beam balance. | |
| | 7/7/05 to 7/11/05 | Subsamples 386.9 g, 421.4 g, and 694.2 g each went through a warm bath of concentrated HCl for a total of 20.1, 20.1, and 37.8 hours, respectively. | |
| | 7/10/05 to 7/25/05 | For each subsample, the HCl-insoluble material went through the dilution and decantation process 7-8 times. | |
| 7/23/05 to 7/25/05 7/23/05 to 8/28/05 | | For subsamples 386.9 g, 421.4 g, and 694.2 g, the HCl-insoluble material went through a warm bath of concentrated HNO ₃ for a total of 8, 10, and 7.6 hours, respectively. | |
| | | For each subsample, the acid-insoluble material went through the dilution and decantation process 8-10 times. | |
| | 8/26/05 to 9/6/05 | For each subsample, the acid-insoluble material was wet sieved into seven size fractions. For subsample 386.9 g, it was difficult to get a good separation of the size fractions. For each subsample, only a part of the <38 μ m material was recovered. | |
| | 9/16/05 to 9/28/05 | For each subsample, the $<38 \mu m$ material was centrifuged. | |
| ľ | 9/26/05 and 9/28/05 | For each subsample, the $<38 \mu m$ material was put in the oven. | |
| | 10/3/05 | For each subsample, the $<38 \mu m$ material was weighed. | |
| | 2/14/06 to 2/22/06 | For subsample 421.4 g, the 63-125 μ m size fraction went through three heavy liquid separations, and the 125-250 μ m size fraction went through two heavy liquid separations. | |
| ſ | 4/06 to 6/06 | The heavy mineral separates were transferred to cavity slides. | |

Grænsesø spherule layer sample GL8904-2, continued

Subsample 386.9 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | |
|---------------|--|--|
| >1000 µm | 48.6327 | |
| 500-1000 μm | 12.3151 | |
| 250-500 μm | 6.4990 | |
| 125-250 μm | 10.1343 | |
| 63-125 μm | 9.5892 | |
| 38-63 µm | 2.2922 | |
| <38 μm | 8.0082 ² | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

Subsample 421.4 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >1000 µm | 55.0616 | | |
| 500-1000 μm | 12.3211 | | |
| 250-500 μm | 6.9732 | | |
| 125-250 μm | 8.1381 | 8.1312 | 0.0069 |
| 63-125 μm | 9.8444 | 9.8070 | 0.0374 |
| 38-63 μm | 2.8265 | | |
| <38 μm | 8.4513 ² | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu$ m material was recovered during wet sieving.

Grænsesø spherule layer sample GL8904-2, continued

Subsample 694.2 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | |
|---------------|--|--|
| >1000 µm | 238.8017 ² | |
| 500-1000 μm | 13.6484 | |
| 250-500 μm | 6.6301 | |
| 125-250 μm | 10.1089 | |
| 63-125 μm | 11.3437 | |
| 38-63 µm | 3.1421 | |
| <38 μm | 5.2491 ³ | |

¹HCl and HNO₃ digestion; ²One silicified chunk in this size fraction weighs 166.2 g. ³This is a minimum weight, since only part of the <38 µm material was recovered during wet sieving.

Grænsesø spherule layer sample GL8904-3

| Date | | Preparation step(s) | |
|--|--|--|--|
| | 6/24/05 | The sample (one piece) was sawn into several pieces, and the pieces were trimmed. Three pieces underwent ultrasonic agitation for \sim 1 hour. The three pieces were rinsed and put in the oven. | |
| | 7/7/05 | The three pieces were removed from the oven, quickly dipped in concentrated HCl, rinsed in distilled water, and returned to the oven. | |
| | 7/11/05 | Subsample 487.8 g (two pieces) was weighed on the Triple Beam balance, and the subsample was started in a warm bath of concentrated HCl. | |
| | 7/15/05 | Subsample 320.6 g (one piece) was weighed on the Triple Beam balance, and the subsample was started in a warm bath of concentrated HCl. | |
| | Middle July/05 | Subsamples 320.6 g and 487.8 g went through the warm HCl baths for a total of 21.8 and 30.8 hours, respectively. | |
| 7/16/05 to 7/26/05 7/26/05 and 7/28/05 7/27/05 to 8/25/05 9/6/05 to 9/13/05 | | For each subsample, the HCl-insoluble material went through the dilution and decantation process 6-7 times. | |
| | | For subsamples 320.6 g and 487.8 g, the HCl-insoluble material went through a warm bath of concentrated HNO_3 for a total of 9 and 7.6 hours, respectively. | |
| | | For each subsample, the acid-insoluble material went through the dilution and decantation process 7-8 times. | |
| | | For each subsample, the acid-insoluble material was wet sieved into seven size fractions. For each subsample, only a part of the <38 μ m material was recovered. | |
| | 9/21/05 to 10/4/05 | For each subsample, the $<38 \mu m$ material was centrifuged. | |
| | 9/28/05 to 10/4/05 | For each subsample, the $<38 \mu m$ material was put in the oven. | |
| | 10/4/05 and 10/10/05 | For each subsample, the $<38 \mu m$ material was weighed. | |
| | 12/6/05 to 12/9/05, and 1/8/06 to 1/24/06 | For each subsample, the 63-125 μ m size fraction went through three heavy liquid separations, and the 125-250 μ m size fraction went through two heavy liquid separations. | |
| | Early May to middle June/06 | The heavy mineral separates were transferred to cavity slides. | |

Grænsesø spherule layer sample GL8904-3, continued

Subsample 320.6 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|------------------|---|---------------------------------|---|
| >1000 µm 19.1321 | | | |
| 500-1000 μm | 21.8255 | | |
| 250-500 μm | 17.0132 | | |
| 125-250 μm | 5.8938 | 5.8090 | 0.0848 |
| 63-125 μm | 4.7911 | 4.7821 | 0.0090 |
| 38-63 µm | 2.6576 | | |
| <38 μm | 6.8331 ² | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

Subsample 487.8 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >1000 µm | 18.3422 | | |
| 500-1000 μm | 24.9316 | | |
| 250-500 μm | 17.0184 | | |
| 125-250 μm | 5.3159 | 5.3145 | 0.0014 |
| 63-125 μm | 7.5839 | 7.5709 | 0.0130 |
| 38-63 µm | 5.6856 | | |
| <38 μm | 9.4330 ² | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu$ m material was recovered during wet sieving.

Grænsesø spherule layer sample GL8904-4

| _ | | | | |
|---|-----------------------|--|--|--|
| | Date | Preparation step(s) | | |
| 6/24/05 | | The sample (one piece) was sawn and trimmed. Two pieces underwent ultrasonic agitation for ~1 hour. The two pieces were rinsed and put in the oven. | | |
| | 7/7/05 | The two pieces were removed from the oven, quickly dipped in concentrated HCl, rinsed in distilled water, and returned to the oven. | | |
| | 7/15/05 | Subsample 294.1 g (one piece) was weighed on the Triple Beam balance, and the subsample was started in a warm bath of concentrated HCl. | | |
| | 7/17/05 | Subsample 187.9 g (one piece) was weighed on the Triple Beam balance, and the subsample was started in a warm bath of concentrated HCl. | | |
| | Middle July/05 | Subsamples 187.9 g and 294.1 g went through the warm HCl baths for a total of 15 and 21.6 hours, respectively. | | |
| 7/19/05 to 7/26/05 7/27/05 and 7/29/05 7/27/05 to 8/25/05 | | For each subsample, the HCl-insoluble material went through the dilution and decantation process six times. | | |
| | | For subsamples 187.9 g and 294.1 g, the HCl-insoluble material went through a warm bath of concentrated HNO_3 for a total of 3.8 and 11.3 hours, respectively. | | |
| | | For each subsample, the acid-insoluble material went through the dilution and decantation process 6-8 times. | | |
| | 9/16/05 to 9/21/05 | For each subsample, the acid-insoluble material was wet sieved into seven size fractions. For each subsample, only a part of the <38 μ m material was recovered. | | |
| | 10/5/05 to 10/21/05 | For each subsample, the $<38 \mu m$ material was centrifuged. | | |
| | 10/13/05 and 10/21/05 | For each subsample, the $<38 \mu m$ material was put in the oven. | | |
| | 10/24/05 | For each subsample, the $<38 \mu m$ material was weighed. | | |
| | 11/14/05 to 11/31/05 | For subsample 187.9 g, the 63-125 μ m and 125-250 μ m size fractions each went through three heavy liquid separations. For subsample 294.1 g, the 63-125 μ m size fraction went through three heavy liquid separations, and the 125-250 μ m size fraction went through two heavy liquid separations. | | |
| ľ | 11/27/05 to 4/5/06 | The heavy mineral separates were transferred to cavity slides. | | |

Grænsesø spherule layer sample GL8904-4, continued

Subsample 187.9 g

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >1000 µm | 52.0909 ² | | |
| 500-1000 μm | 8.6104 | | |
| 250-500 μm | 4.2755 | | |
| 125-250 μm | 1.0870 | 1.0864 | 0.0006 |
| 63-125 μm | 1.5948 | 1.5922 | 0.0026 |
| 38-63 µm | 1.0614 | | |
| <38 μm | 3.2451 ³ | | |

¹HCl and HNO₃ digestion; ²Some silicified chunks are present in this size fraction. ³This is a minimum weight, since only part of the <38 µm material was recovered during wet sieving.

| Subsamp | le 294.1 | g |
|---------|----------|---|
| | | |

| Size Fraction | Weight (g) of Acid-Insoluble Material ¹ | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >1000 µm | 10.8333 | | |
| 500-1000 μm | 13.7293 | | |
| 250-500 μm | 9.2721 | | |
| 125-250 μm | 3.2078 | 3.2075 | 0.0003 |
| 63-125 μm | 4.0213 | 4.0195 | 0.0018 |
| 38-63 µm | 2.4516 | | |
| <38 μm | 10.5980^2 | | |

¹HCl and HNO₃ digestion; ²This is a minimum weight, since only part of the $<38 \mu m$ material was recovered during wet sieving.

Appendix P

TABLES FOR PREPARATION STEPS AND SIZE FRACTION WEIGHT DATA FOR THE GRÆNSESØ CONTEXT SAMPLES

Grænsesø context sample SP3

| Date | Preparation step(s) | |
|--------------------|--|--|
| Middle January/07 | The two pieces (504.3 g and 600.0 g) were sawn into four pieces, and the four pieces were trimmed, rinsed, and put in the oven. Subsamples 155.0 g (one piece), 260.0 g (one piece), 276.0 g (one piece), and 286.3 g (one piece) were weighed on the Triple Beam balance, and the subsamples were returned to the oven. | |
| 1/20/07 | Each subsample was removed from the oven, quickly dipped in concentrated HNO ₃ , rinsed with tap water, and returned to the oven. | |
| 1/26/07 to 2/2/07 | Subsamples 155.0 g, 260.0 g, 276.0 g, and 286.3 g each went through a warm bath of concentrated HNO ₃ for a total of 11.1, 35.2, 14.8, and 34.2 hours, respectively. | |
| 1/27/07 to 3/4/07 | For each subsample, the HNO ₃ -insoluble material went through the dilution and decantation process 7-13 times. | |
| 3/19/07 to 4/5/07 | For each subsample, the HNO ₃ -insoluble material was wet sieved into five size fractions. For each subsample, all the $<38 \mu m$ material was recovered. | |
| 3/22/07 to 4/5/07 | For each subsample, the $<38 \ \mu m$ material was centrifuged. | |
| 3/30/07 to 4/13/07 | For each subsample, the $<38 \mu m$ material was put in the oven. | |
| 4/13/07 to 4/15/07 | For each subsample, the <38 µm material was weighed. | |

Grænsesø context sample SP3, continued

| Date | Preparation step(s) | |
|------------------------------|---|--|
| 8/12/07 to 9/17/07 | For subsample 155.0 g, the 63-125 μ m and 125-250 μ m size fractions each went through one heavy liquid separation. For subsamples 260.0 g, 276.0 g, and 286.3 g, the 63-125 μ m size fractions each went through two heavy liquid separations, and the 125-250 μ m size fractions each went through one heavy liquid separation. | |
| Early November/07 to 12/4/07 | The heavy mineral separates were transferred to cavity slides. | |

Subsample 155.0 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 4.3576 | | |
| 125-250 μm | 0.4038 | 0.4045 | -0.0007 |
| 63-125 μm | 0.4875 | 0.4845 | 0.0030 |
| 38-63 µm | 0.5400 | | |
| <38 μm | 4.4044 | | |

Subsample 260.0 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 34.4443 | | |
| 125-250 μm | 1.0507 | 1.0507 | 0.0000 |
| 63-125 μm | 1.0214 | 1.0168 | 0.0046 |
| 38-63 µm | 38-63 μm 0.8432 | | |
| <38 μm | 7.6840 | | |

Grænsesø context sample SP3, continued

Subsample 276.0 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 15.9287 | | |
| 125-250 μm | 0.5517 | 0.5518 | -0.0001 |
| 63-125 μm | 0.9037 | 0.9023 | 0.0014 |
| 38-63 µm | 1.0236 | | |
| <38 μm | 5.9132 | | |

Subsample 286.3 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >250 µm | 27.5527 | | |
| 125-250 μm | 1.5733 | 1.5736 | -0.0003 |
| 63-125 μm | 1.3838 | 1.3824 | 0.0014 |
| 38-63 µm | 0.9277 | | |
| <38 µm | 8.0545 | | |

Grænsesø context sample GL8904-6

| Date | Preparation step(s) | |
|---------------------|---|--|
| 6/24/05 | The sample (one piece) was sawn into two pieces, and the pieces were trimmed. | |
| 6/25/05 | The pieces underwent ultrasonic agitation for 1 hour. The pieces were rinsed and put in the oven. | |
| 7/7/05 | One piece was selected for further processing. This piece was removed from the oven, quickly dipped in concentrated HCl, rinsed in distilled water, and returned to the oven. | |
| 7/19/05 | Subsample 321.1 g was weighed on the Triple Beam balance. | |
| 7/19/05 to 7/21/05 | Subsample 321.1 g went through a warm bath of concentrated HNO ₃ for a total of 21.6 hours. | |
| 7/21/05 to 7/31/05 | The HNO ₃ -insoluble material went through the dilution and decantation process five times. | |
| 9/27/05 to 9/28/05 | The HNO ₃ -insoluble material was wet sieved into seven size fractions, and only a part of the $<38 \ \mu m$ material was recovered. | |
| 10/9/05 to 10/14/05 | The <38 µm material was centrifuged. | |
| 10/14/05 | The $<38 \mu m$ material was put in the oven. | |
| No data | The <38 µm material was weighed. | |
| 2/19/06 to 2/25/06 | The 63-125 μ m and 125-250 μ m size fractions each went through two heavy liquid separations. | |
| 5/10/06 to 5/11/06 | The heavy mineral separates were transferred to cavity slides. The heavy mineral separates from the second heavy liquid separations contained very little material. | |

Grænsesø context sample GL8904-6, continued

Subsample 321.1 g

| Size Fraction | Weight (g) of HNO ₃ -Insoluble Material | Weight (g) of Light Fraction | Derived Weight (g) of Heavy Mineral Fraction |
|---------------|---|---------------------------------|---|
| >1000 µm | 1.1174 | | |
| 500-1000 μm | 0.3351 | | |
| 250-500 μm | 0.3063 | | |
| 125-250 μm | 0.7473 | 0.7466 | 0.0007 |
| 63-125 μm | 1.1648 | 1.1615 | 0.0033 |
| 38-63 µm | 1.3199 | | |
| <38 μm | 5.6771 ¹ | | |

¹This is a minimum weight, since only part of the <38 µm material was recovered during wet sieving.

Appendix Q

HYDROFLUORIC ACID (HF) ETCHING AND TREATMENT PROCEDURES

Carawine spherule layer sample 43-1

A very small amount of material from the 63-125 µm-sized light fraction of subsample 987.4 g Group D of Carawine spherule layer sample 43-1 (Appendix I) was put in a 50 ml polypropylene centrifuge tube. About 5 ml of distilled water was added to the tube, and the tube was put in a plastic rack in a fume hood. About 5 ml of 48-50% HF solution from the bottle was added to the tube, and the grains were etched for four minutes with periodic hand agitation of the tube. The HF solution was neutralized by the alternate addition and decantation of small amounts of saturated sodium carbonate solution. The sodium carbonate solution was neutralized by the alternate addition and decantation of distilled water.

In order to remove colloidal silicates, ~5 drops of 20% HCl were added to the tube, and the tube was hand-agitated for ~2 minutes. The HCl solution was neutralized by the alternate addition and decantation of small amounts of distilled water. Throughout the various steps, the pH of the solution was monitored with Alkacid[®] test paper. The material was wet sieved using a 63 μ m sieve, and it underwent a final rinse with distilled water. The 63-125 μ m-sized grains were dried under a heat lamp, and they were put in a vial.

Grænsesø spherule layer samples GL8904-3 and GL8904-4

Using a binocular microscope, I handpicked the zircons, colorless translucent or transparent grains, and white translucent-to-opaque grains from the 63-125 μ m-sized heavy mineral separates of subsample 487.8 g of Grænsesø spherule layer sample GL8904-3, and subsamples 187.9 g and 294.1 g of Grænsesø spherule layer sample GL8904-4. The handpicked grains were put in cavity slides, and they did not undergo HF treatment. For each of the three subsamples, the remaining grains in the heavy mineral separate were put in a 50 ml polypropylene centrifuge tube, and a small amount of 48-50% HF solution from the bottle was added to the tube. The grains underwent HF treatment for ~1 hour.

The HF solution was neutralized by the alternate addition and decantation of small amounts of saturated sodium carbonate solution. The sodium carbonate solution was neutralized by the alternate addition and decantation of small amounts of distilled water. Throughout the various steps, the pH of the solution was monitored with Alkacid[®] test paper. For each subsample, the grains that underwent HF treatment were wet sieved using a 63 µm sieve. For each subsample, the 63-125 µm-sized grains were rinsed with distilled water, dried under a heat lamp, and transferred to cavity slides.

Appendix **R**

TABLES FOR ACID-INSOLUBLE WEIGHT DATA FOR THE SUBSAMPLESOF THE SPHERULE LAYER AND CONTEXT SAMPLES

Carawine spherule layer samples

| Sample | Subsample (g) | Weight (g) of Acid-Insoluble Material | Wt% of Acid-Insoluble Material |
|--------|---------------|--|-----------------------------------|
| X38-2 | 85.0879 | 6.7605 ¹ | 7.9 |
| | 144.3 | 9.2524 ¹ | 6.4 |
| 42-1A | 216.1 | 19.6476 ² | 9.1 |
| | 341.4 | 22.2360 ² | 6.5 |
| | 460.0 | 24.5733 ² | 5.3 |
| 43-1 | 283.8 | 11.8364 ¹ | 4.2 |
| | 495.5 | 28.2577 ¹ | 5.7 |
| | 535.3 | 29.6022 ¹ | 5.5 |
| | 584.7 | 19.2123 ¹ | 3.3 |
| | 599.2 | 22.9721 ^{1,3} | 3.8 |
| | 819.5 | 31.2459 ¹ | 3.8 |
| | 893.3 | 41.7530 ¹ | 4.7 |
| | 987.4 | 46.3902 ¹ | 4.7 |
| | 1046.2 | 48.1643 ¹ | 4.6 |
| | 1078.1 | 41.4482 ¹ | 3.8 |
| | 1114.1 | 46.2759 ¹ | 4.2 |
| | 1136.4 | 40.3916 ^{1,4} | 3.6 |
| X24-1 | 217.2 | 27.0422 ¹ | 12.4 |
| | 247.9 | 22.3274 ¹ | 9.0 |
| | 290.4 | 18.7193 ¹ | 6.4 |
| | 293.7 | 30.9662 ¹ | 10.5 |
| | 413.0 | 45.7495 ¹ | 11.1 |
| | 475.5 | 43.1717 ^{1,5} | 9.1 |

| Sample | Subsample (g) | Weight (g) of Acid-Insoluble Material | Wt% of Acid-Insoluble Material |
|--------|---------------|--|-----------------------------------|
| W85-2 | 277.7 | 29.0066 ¹ | 10.4 |
| | 371.7 | 35.5831 ¹ | 9.6 |
| 84-1 | 268.1 | 56.3826 ^{1,6} | 21.0 |
| | 388.8 | 53.2707 ^{1,7} | 13.7 |
| | 430.8 | 26.6694 ^{1,7} | 6.2 |

Carawine spherule layer samples, continued

¹HCl-insoluble material; ²HNO₃-insoluble material; ³A little material was spilled and lost during acid digestion. ⁴A little <38 μ m material was accidently lost prior to weighing. ⁵A little <38 μ m material was lost during centrifuging. ⁶A little >250 μ m material was lost during wet sieving. ⁷Only part of the <38 μ m material was recovered during wet sieving.

Carawine context samples

| Sample | Subsample (g) | Weight (g) of HNO ₃ -Insoluble Material | Wt% of HNO ₃ -Insoluble Material |
|--------|---------------|---|--|
| 104175 | 235.4 | 1.2317 | 0.5 |
| 104141 | 357.2 | 6.5168 | 1.8 |
| X68-1 | 300.0 | 2.5436 | 0.8 |
| | 304.7 | 4.3260 | 1.4 |
Jeerinah spherule layer samples

| | | Weight (g) of | Wt% (minimum) of |
|--------|---------------|-------------------------------------|------------------------|
| Sample | Subsample (g) | HCl-Insoluble Material ¹ | HCl-Insoluble Material |
| X21-1 | 7.5830 | 4.9023 | 64.6 |
| | 15.1772 | 11.5647 | 76.2 |
| | 15.4470 | 10.8350 | 70.1 |
| | 15.6521 | 11.1568 | 71.3 |
| | 15.8285 | 11.5673 | 73.1 |
| | 16.1938 | 11.3224 | 69.9 |
| | 17.3884 | 12.5581 | 72.2 |
| | 21.7690 | 15.5173 | 71.3 |
| | 22.3758 | 15.2853 | 68.3 |
| | 22.6439 | 14.4889 | 64.0 |
| | 22.7851 | 13.6571 | 59.9 |
| | 29.9445 | 18.4099 | 61.5 |
| | 30.7247 | 20.8860 | 68.0 |
| | 32.5125 | 22.2970 | 68.6 |
| | 32.9150 | 21.3082 | 64.7 |
| | 34.2206 | 21.5550 | 63.0 |
| W94-1Q | 9.5938 | 5.6763 | 59.2 |
| | 10.3210 | 5.0719 | 49.1 |
| | 13.0639 | 7.1785 | 54.9 |
| | 15.3415 | 7.7660 | 50.6 |

¹For each subsample, a little material was lost during crushing and dry sieving. After these steps, the material for each subsample was not reweighed prior to acid digestion. Therefore, these values represent minimum weights. Furthermore, for sample W94-1Q, the <38 μ m material that was derived from the acid digestion of the >38 μ m size fractions was not recovered (see Appendix K).

| Sample | Layer/ (Sublayer(s)) | Subsample (g) | Weight (g) of Acid-Insoluble Material | Wt% of Acid-Insoluble Material |
|--------|-------------------------|---------------|--|-----------------------------------|
| 96714A | (Usplsl) | 8.4057 | 4.0460 ¹ | 48.1 |
| | | 8.7879 | 4.1408 ¹ | 47.1 |
| | (Splsl) | 10.3574 | 5.7342 ¹ | 55.4 |
| | (Lspsl) | 7.3433 | 3.7400 ¹ | 50.9 |
| | | 8.5769 | 4.3183 ¹ | 50.3 |
| | Bcl | 6.8001 | 4.3362 ¹ | 63.8 |
| | | 9.5376 | 5.9797 ¹ | 62.7 |
| | | 10.0687 | 6.4763 ^{1,2} | 64.3 |
| | | 10.1556 | 4.4703 ¹ | 44.0 |
| | | 10.5610 | 6.3034 ^{1,3} | 59.7 |
| | | 10.9594 | 5.3632 ^{1,4} | 48.9 |
| | | 11.1877 | 7.2595 ¹ | 64.9 |
| | | 11.4911 | 7.4312 ¹ | 64.7 |
| | | 11.6547 | 7.3050^{1} | 62.7 |
| 96714B | (Usplsl) | 14.2225 | 7.3639 ¹ | 51.8 |
| | (Splsl) | 6.5066 | 3.7910 ¹ | 58.3 |
| | | 12.0772 | 7.4409^{1} | 61.6 |
| | (Lspsl) | 13.8178 | 7.0912 ¹ | 51.3 |
| | Bcl | 9.5155 | 6.2485 ¹ | 65.7 |
| | | 10.3847 | 6.8812 ¹ | 66.3 |
| | | 10.7160 | 6.9142 ¹ | 64.5 |
| | | 11.0042 | 6.8936 ¹ | 62.6 |
| | | 11.1367 | 7.0374 ¹ | 63.2 |

Bee Gorge (Wittenoom Formation) samples

| Sample | Layer | Subsample (g) | Weight (g) of Acid-Insoluble Material | Wt% of Acid-Insoluble Material |
|--------------------|---------|--------------------|--|-----------------------------------|
| BB | BB (sl) | 9.8364 | 3.2120^{1} | 32.6 |
| | | 10.6019 | 3.2123 ¹ | 30.3 |
| | | 10.7999 | 3.5797 ¹ | 33.1 |
| | BB (#1) | 5.4035 | 1.0645 ^{1,5} | 19.7 |
| | BB (#2) | 14.89 ⁶ | 1.8743 ¹ | 12.6 |
| 92058 (context) | | 216.4 | 22.1186 ^{7,8,9} | 10.2 |
| | | 236.3 | 26.5047 ^{7,8} | 11.2 |

Bee Gorge (Wittenoom Formation) samples, continued

¹HCl-insoluble material; ²During boiling, some material from subsample 10.9594 g may have gotten into subsample 10.0687 g. ³A little material was lost during wet sieving. ⁴Some material was lost during boiling. ⁵A little <38 μ m material was lost prior to weighing. ⁶This subsample is a combination of the original subsamples 5.9409 g and 8.9479 g (see Appendix L). ⁷HNO₃-insoluble material; ⁸This is a minimum weight, since only part of the <38 μ m material was recovered during wet sieving. ⁹A little of the >250 μ m material was lost prior to weighing.

Notes for sample BB: Sample BB consists of a spherule layer sandwiched between two context layers. There is no stratigraphic "up" arrow on the sample, so the relative age of the three layers is unknown. The spherule layer (sl) is referred to as "BB (sl)" in the table. One of the context layers is named "context layer #1" and it is referred to as "BB (#1)" in the table. The other context layer is named "context layer #2" and it is referred to as "BB (#2)" in the table.

Notes for samples 96714A and 96714B: The samples are from the same rock, and they are mirror images of one another. Each sample consists of a basal carbonate lutite (Bcl) context layer that is directly overlain by a spherule layer. The spherule layer consists of three subdivisions that were processed separately. In ascending stratigraphic order, the three subdivisions are as follows: 1) Lowermost spherule-rich sublayer (Lspsl) 2) Spherule-bearing lutite sublayer (Splsl) 3) Upper spherule/lutite sublayers (Usplsl).

Monteville spherule layer samples

| Sample | Subsample (g) | Weight (g) of HCl-Insoluble Material | Wt% of HCl-Insoluble Material |
|--------|---------------|---|----------------------------------|
| V111 | 106.1 | 8.8372 ¹ | 8.3 |
| | 219.9 | 22.8651 ¹ | 10.4 |
| U63-1 | 278.0 | 50.1093 | 18.0 |
| | 315.2 | 57.8440 | 18.4 |

¹This is a minimum weight, since some of the $<38 \mu$ m material was not recovered during wet sieving.

Monteville context samples

| Sample | Subsample (g) | Weight (g) of HNO ₃ -Insoluble Material | Wt% of HNO ₃ -Insoluble Material |
|---------|---------------|---|--|
| II67-1B | 286.9 | 9.1647 | 3.2 |
| | 329.8 | 12.0886 ¹ | 3.7 |
| T149-1 | 105.1 | 10.1494^2 | 9.6 |
| | 109.2 | 11.5217^2 | 10.6 |

¹A very small amount of $<38 \,\mu\text{m}$ material that was derived from re-wet sieving the $>38 \,\mu\text{m}$ material was not recovered. ²This is a minimum weight, since some of the $<38 \,\mu\text{m}$ material was not recovered during wet sieving.

Grænsesø spherule layer samples

| Sample | Subsample (g) | Weight (g) of Acid-Insoluble Material ¹ | Wt% (minimum) of Acid-Insoluble Material |
|----------|---------------|---|---|
| GL8904-4 | 187.9 | 71.9651 | 38.3 |
| | 294.1 | 54.1134 | 18.4 |
| GL8904-3 | 320.6 | 78.1464 | 24.4 |
| | 487.8 | 88.3106 | 18.1 |
| GL8904-2 | 386.9 | 97.4707 | 25.2 |
| | 421.4 | 103.6162 | 24.6 |
| | 694.2 | 288.9240 | 41.6 |
| GL8904-1 | 331.3 | 94.2693 | 28.4 |
| | 349.3 | 70.5494 | 20.2 |
| | 567.8 | 162.9702 | 28.7 |

¹All the samples went through both HCl and HNO₃ digestion, and for each sample, only part of the $<38 \mu m$ material was recovered during wet sieving.

Grænsesø context samples

| Sample | Subsample (g) | Weight (g) of HNO ₃ -Insoluble Material | Wt% of HNO ₃ -Insoluble Material |
|----------|---------------|---|--|
| GL8904-6 | 321.1 | 10.6679 ¹ | 3.3 |
| SP3 | 155.0 | 10.1933 | 6.6 |
| | 260.0 | 45.0436 | 17.3 |
| | 276.0 | 24.3209 | 8.8 |
| | 286.3 | 39.4920 | 13.8 |

¹This is a minimum weight, since only part of the $<38 \mu$ m material was recovered during wet sieving.

Appendix S

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE CARAWINE SPHERULE LAYER SAMPLES

Introductory Note: The following abbreviations are used in Appendix S:

Admntn = Adamantine; ID = Identification; n = number of grains; n.d. = no data;

Octhdl = Octahedral; Prsmtc = Prismatic; ShPrsm = Short Prism; SlElng = Slightly

Elongate; Subang = Subangular; Subeq = Subequant; Subrnd = Subrounded;

Wllrnd = Well-rounded; XRD ID = the identification number of a grain that was analyzed by XRD.

Carawine spherule layer sample 84-1

Subsample 268.1 g

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|--------------------------------------|---|----------------------------------|---|-----------------------|---------------------------|
| Actinolite | Green | Opaque | Subeq | Subrnd | |
| | Green | Opaque | Subeq | Subang | |
| | Olive green | Opaque | Subeq | Subrnd | |
| Anatase (n = 585) | Very light peach- to-peach Very light buff Light brownish golden Light pink-to- white Light-to-medium gray Beige Colorless with very light yellow or yellow-green tint | Mostly Opaque; Translucent | Mostly Subeq; Equant Irregular SlElng | Subrnd | Some Waxy |
| Anglesite | Clear with very light yellow tint | Opaque | Subeq | Subrnd | |
| Chrome spinel | Black | Opaque | Equant | Subang | |
| Clinozoisite/ Epidote (n = 32) | Very light green- yellow; white | Transparent- to-Opaque | Subeq Blocky | Subrnd-to- Angular | |
| Orthopyroxene | Clear with light yellow tint | Translucent | Subeq | Subrnd | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|------------------------------|--|---|---|-----------------------------|---------------------------|
| Rutile ± Anatase (n = 26) | Light peach-to- peach Very light buff- to-buff Light brownish or grayish red Light reddish brown Amber | Mostly Opaque; Translucent- to-Opaque for the reddish grains | Mostly Subeq; Equant Irregular SIElng | Mostly Subrnd; Subang | Some Waxy or Admntn |
| Rutile + Unidentified | White | Opaque | Equant | Subrnd | |
| | White | Opaque | n.d. | n.d. | |
| Tourmaline | Amber | Translucent | Subeq | Subrnd | |
| | Dark amber | Translucent- to-Opaque | Subeq | Subrnd | |
| | Dark green | Translucent | Subeq | Wllrnd | |
| | Dark green | Translucent- to-Opaque | ShPrsm | Subrnd | |
| Zircon ± Anatase | Pale pink | Translucent | Prsmtc | Euhedral/ Angular | 210 x 60 |
| | Pale pink | Translucent | ShPrsm | Subang | 120 x 80 |
| | Pale pink | Translucent | ShPrsm | Subang | 80 x 60 |
| | Pale pink with white matrix | Translucent- to-Opaque | ShPrsm | Subang | 120 x 60 |
| | Pale pink with white matrix | Translucent- to-Opaque | ShPrsm | Subang | 160 x 70 |
| | Pale pink with white matrix | Translucent- to-Opaque | ShPrsm | Subang | 100 x 80 |
| | Pale pink with white matrix | Translucent- to-Opaque | Equant | Subrnd | 80 x 80 |
| | Very pale pink with white matrix | Translucent- to-Opaque | Irregular | Subang | 100 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|-------------------------|---|-------------|------------------------|----------------------|---------------------------|
| Zircon ± Anatase | Very light pale pink | Transparent | Prsmtc | Euhedral/ Angular | 120 x 50 |
| | Very light pale pink | Transparent | Blocky | Angular | 140 x 90 |
| | Very light pale pink | Translucent | Blocky | Angular | 80 x 65 |
| | Champagne | Transparent | ShPrsm | Subang | 100 x 60 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subhedral | 120 x 80 |
| | Clear with light yellow tint | Translucent | Subeq | Subang | 120 x 80 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subrnd | 100 x 70 |
| | Colorless | Transparent | Blocky | Subrnd | 120 x 80 |
| | Colorless | Transparent | Subeq | Subrnd | 100 x 80 |
| | Colorless | Transparent | Subeq | Subrnd | 100 x 80 |
| | Colorless | Translucent | Prsmtc | Euhedral/ Angular | 90 x 50 |
| | Colorless | Translucent | Subeq | Subang | 80 x 60 |
| Unidentified (n = 2) | Dark gray with colorless-to- bright green matrix | Opaque | Subeq-to- Irregular | Subrnd | |

Subsample 268.1 g, continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster |
|---|---|-------------|--|--------------------------------|--------------|
| Actinolite | Forest green | Opaque | Subeq | Subrnd | |
| Anatase $(n = 51)$ | Very light peach- to-peach Light buff Light gray | Opaque | Mostly Subeq-to- Equant; SIEIng | Mostly Subrnd; Irregular | Some Waxy |
| Clinozoisite/ Epidote (n = 3) Very light yellow | | Opaque | Subeq Blocky | Subrnd | |
| Orthopyroxene $(n = 2)$ | Clear with light yellow tint | Transparent | ShPrsm | Subang | |
| Spessartine | Pale amber | Transparent | Subeq | Subang | |
| Tourmaline | Olive green | Translucent | Subeq | Subrnd | |

Carawine spherule layer sample W85-2

Subsamples 277.7 g and 371.7 g ($\Sigma = 649.4$ g)

Size Fraction: 63-125 μm

| Phase | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|----------------------|---|---|--|-----------------------|---------------------------------------|
| Actinolite | Light olive green | Transparent | Prsmtc | Angular | |
| | Light olive green | Transparent | Acicular | Angular | (1) |
| | Light olive green | Transparent | Elongate | Angular | |
| | Olive green | Transparent | Blocky | Subang | |
| | Light green | Transparent | Acicular | Angular | (2) |
| | Light green | Translucent | Blocky | Subang | |
| | Light green | Transparent | Blocky | Subang | |
| | Blue-green | Transparent | SlElng | Angular | |
| | Blue-green | Transparent | SlElng | Subang | (3) |
| | Green | Transparent | Elongate | n.d. | (4) |
| | n.d. | n.d. | n.d. | n.d. | |
| Almandine | Colorless | Transparent | Subeq | Angular | |
| | Colorless | Transparent | Blocky | Subang | |
| Anatase (n = 137) | Very light peach-to-peach Light brownish peach Very light buff-to-buff Very light gray-to-light medium gray Light grayish brown Beige-to-white | Mostly Opaque; a few Translucent | Subeq Irregular SIElng Equant | Subrnd-to- Angular | Some Waxy or Admntn |

| Phase | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|---------------|------------------------|---------------------------|-----------|-----------|---------------------------------------|
| Anglesite | Colorless-to- white | Translucent-to- Opaque | Blocky | Subrnd | (5) |
| | White | Translucent-to- Opaque | Subeq | Subrnd | (6) |
| | Colorless-to- white | Translucent | Equant | Wllrnd | (7) |
| | White | Opaque | n.d. | Subrnd | Admntn |
| | White | Opaque | Subeq | Subrnd | Waxy |
| Chrome spinel | Black | Opaque | Octhdl | n.d. | (8) |
| Rutile | Light peach | Opaque | Irregular | Subrnd | |
| Tourmaline | Light brown- amber | Transparent | Prsmtc | Subrnd | |
| Zircon | Pale pink | Translucent | ShPrsm | Subang | (9) 120 x 80 |
| | White | Translucent-to- Opaque | n.d. | Subang | (10) n.d. (for size) |

Subsamples 277.7 g and 371.7 g ($\Sigma = 649.4$ g), continued

Size Fraction: 125-250 µm

| Phase | Color(s) | Diaphaneity | Shape | Roundness | Luster or (XRD ID) |
|-------------------|-----------------------|-------------|--------|----------------------|-----------------------|
| Anatase $(n = 4)$ | Beige Light buff | Opaque | SlElng | Subrnd-to- Subang | |
| Corundum | Light golden brown | Translucent | ShPrsm | Subang | (11) Admntn |
| | Golden brown | Translucent | SlElng | Subang | (12) Admntn |

XRD ID: (1) G 4-7-04 (2) G 4-8-05 (3) G 4-11-05 (4) G 3-20-05 (5) G 3-25-04 (6) G 4-1-04 (7) D-S 4-8-04 (8) G 4-6-05 (9) D-S 7-26-04 (10) G 12-11-04/D-S 8-29-05 (11) D-S 7-27-04 (12) G 7-8-05. Carawine spherule layer sample X24-1

Subsamples 290.4 g, 293.7 g, and 888.5 g ($\Sigma = 1,472.6$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|----------------------|---|--|---|--|---------------------------------------|
| Actinolite | Light yellowish green | Transparent | Prsmtc | Subang | (1) |
| | Light olive green | Translucent | Elongate | Subrnd | |
| | Light green | Transparent | Subeq | Angular | |
| | Light medium green | Translucent | ShPrsm | Angular | |
| | Forest green | Translucent | Prsmtc | Subang | (2) |
| | Forest green | Transparent | Blocky | n.d. | |
| | Very light greenish yellow | Opaque | n.d. | Subrnd | |
| Almandine | Clear with light greenish yellow tint | Transparent | Subeq | Subang | |
| Anatase (n = 454) | Very light peach-to-peach Light buff-to- buff Light golden Clear with very light yellow tint Light grayish brown Light gray-to- medium dark gray Beige White | Mostly Opaque; Translucent- to-Opaque | Mostly Subeq; SIEIng Irregular Equant Blocky | Mostly Subrnd; Subang-to- Angular | Some are Waxy or Admntn |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|--------------------------------------|---|--|-------------------------------------|-----------------------|---------------------------------------|
| Anatase + K-feldspar (n = 25) | Very light yellow-to-white Colorless-to- white | Opaque | Subeq SIElng Irregular | Subrnd-to- Angular | |
| Chrome spinel | Black | Opaque | Octhdl | Subang | (3) |
| Clinopyroxene | Colorless | Translucent | n.d. | Subang | |
| | Clear with very light green tint | Translucent | SlElng | Subang | |
| Clinozoisite/ Epidote (n = 16) | Light green-to- yellow Colorless with light green and/or yellow tint Colorless-to- white | Mostly Translucent- to-Opaque; Transparent- to-Translucent | Subeq SIEIng Blocky Equant | Subang-to- Subrnd | Waxy |
| Rutile ± Anatase | Peach | Opaque | Subeq | Wllrnd | Waxy |
| | Peach | Opaque | Subeq | Subrnd | (4) Waxy |
| | Light peach | Opaque | Equant | Subrnd | |
| | Light peach | Opaque | Subeq | Subrnd | |
| | Very light peach | Opaque | Subeq | Subrnd | |
| | Light brownish peach | Opaque | Equant | Subrnd | |
| | Brown-medium gray | Opaque | Equant | Subrnd | |
| | Golden orange | Opaque | Subeq | Subrnd | Waxy |
| | Light amber | Opaque | Subeq | Subrnd | Waxy |
| | Light amber | Opaque | SlElng | Subrnd | |
| | Light amber | Translucent | Subeq | Subang | |
| | Reddish amber | Translucent | Subeq | Subrnd | |
| | Amber | Translucent | SlElng | Subrnd | (5) |
| | Amber | Translucent | Subeq | Subrnd | (6) |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|------------|------------------------------|-------------|--------|-----------|---------------------------------------|
| Tourmaline | Olive green | Translucent | Equant | Wllrnd | |
| | Olive green | Translucent | ShPrsm | Subrnd | (7) |
| | Olive green | Transparent | Subeq | Angular | |
| | Olive green | Transparent | Blocky | Subang | (8) |
| | Olive green | Transparent | ShPrsm | Subrnd | |
| | Dark olive green | Translucent | Subeq | Wllrnd | (9) |
| | Bluish green | Translucent | Subeq | Wllrnd | (10) |
| Zircon | Champagne | Transparent | Blocky | Angular | 140 x 70 |
| | Champagne | Transparent | ShPrsm | Subang | 140 x 80 |
| | Grayish champagne | Translucent | Blocky | Subang | 80 x 50 |
| | Clear with light yellow tint | Transparent | Subeq | Subang | 80 x 65 |
| | Clear with light yellow tint | Transparent | Equant | Angular | 80 x 80 |
| | Clear with light yellow tint | Transparent | Equant | Subang | 80 x 80 |
| | Clear with light yellow tint | Transparent | ShPrsm | Subang | 80 x 50 |
| | Clear with light yellow tint | Translucent | Blocky | Subrnd | (11) 80 x 80 |
| | Clear with light yellow tint | Transparent | Blocky | Subang | 120 x 80 |
| | Clear with light yellow tint | Translucent | Blocky | Subang | 100 x 80 |
| | Clear with light yellow tint | Transparent | Blocky | Subang | 100 x 80 |
| | Clear with light yellow tint | Transparent | Equant | Subang | 65 x 65 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|----------|-----------------------------------|--------------------------------|--------|-----------|---------------------------------------|
| Zircon | Clear with very light yellow tint | Transparent- to-Translucent | Prsmtc | Subhedral | (12) 140 x 60 |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | (13) 90 x 70 |
| | Clear with very light yellow tint | Translucent | ShPrsm | Subrnd | (14) 80 x 50 |
| | Clear with very light yellow tint | Transparent | ShPrsm | Subrnd | (15) 130 x 90 |
| | Clear with very light yellow tint | Transparent | Subeq | Subrnd | 80 x 80 |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | (16) 120 x 80 |
| | Clear with very light yellow tint | Transparent | Blocky | Subang | (17) 80 x 80 |
| | White | Translucent- to-Opaque | Equant | Wllrnd | 70 x 50 |

Subsamples 290.4 g and 293.7 g ($\Sigma = 584.1$ g)

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or (XRD ID) |
|-------------------------------------|--|---------------------------|------------------------------|-----------------------------|--|
| Anatase (n = 40) | Light peach Light gray Light medium gray Very light grayish brown Beige | Opaque | Subeq SIElng Irregular | Subrnd Subang Angular | Some Waxy |
| Anatase + K-feldspar (n = 22) | Colorless-to-white | Translucent- to-Opaque | Blocky Irregular | Subang Angular | |
| Tourmaline | Very light bluish green | Opaque | SIEIng | Subrnd | (18) Colorless- to-cream- colored matrix |

XRD ID: (1) G 7-25-05 (2) G 8-25-05 (3) G 8-29-05 (4) G 8-3-05 (5) G 8-9-05 (6) G 8-10-05 (7) G 7-29-05 (8) G 8-2-05 (9) G 7-27-05 (10) G 7-28-05 (11) G 9-3-05 (12) G 7-26-05 (13) G 8-4-05 (14) G 8-8-05 (15) G 8-31-05 (16) G 9-5-05 (17) G 9-6-05 (18) G 7-20-05. Carawine spherule layer sample 43-1

Subsamples 283.8 g, 495.5 g, 819.5 g, 1,078.1 g, 535.3 g, 893.3 g, and 1,046.2 g

$(\Sigma = 5,151.7 \text{ g})$

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|----------------------|--|--|--|--|---------------------------------------|
| Actinolite | Light forest green | Translucent | ShPrsm | Subrnd | |
| Anatase (n = 651) | Very light peach-to- peach Reddish peach Very light buff Light-to- medium grayish brown Light-to- medium gray Clear-to- white Clear with light yellow tint | Mostly Opaque; a few are Transparent- to-Translucent | Mostly Subeq and SIEIng; Equant Blocky Irregular | Mostly Subrnd; Wllrnd Subang-to- Angular | Typically Waxy |
| Brookite | Peach | Opaque | SlElng | Subrnd | Waxy |
| Chrome spinel | Black | Opaque | SlElng | Wllrnd | |
| | Black | Opaque | SlElng | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Octhdl | Subang | (1) |
| | Black | Opaque | n.d. | Subang | |
| Hemimorphite | White | Opaque | Subeq | Wllrnd | (2) |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|--------------------------|--|---------------------------|--------|-----------|---------------------------------------|
| Rutile ± Anatase | Light peach | Opaque | SlElng | Subrnd | |
| | Light peach | Opaque | Subeq | Subrnd | |
| | Peach | Opaque | Subeq | Subrnd | |
| | Peach | Opaque | Equant | Subrnd | Waxy |
| | Very light buff | Opaque | SlElng | Subrnd | |
| | Light buff | Opaque | Subeq | Subrnd | |
| | Orange | Opaque | Subeq | Subrnd | Waxy |
| | Light amber | Translucent | SlElng | Subrnd | |
| | Light amber | Translucent | Equant | Subrnd | |
| | Light amber | Translucent | Subeq | Subrnd | |
| | Amber | Translucent | SlElng | Subrnd | |
| | Amber | Translucent | Subeq | Subrnd | |
| | Reddish amber | Translucent- to-Opaque | Equant | Wllrnd | |
| | Reddish amber | Opaque | Equant | Subrnd | |
| Rutile + Unidentified | Light gray-to- white | Opaque | Subeq | Subrnd | (3) |
| Zircon | Pink | Transparent | Subeq | Subrnd | (4) 100 x 80 |
| | Pale pink | Transparent | Prsmtc | Subhedral | 160 x 70 |
| | Clear with very pale pink-yellow tint | Transparent | Blocky | n.d. | 80 x 80 |
| | Champagne | Transparent | Blocky | Subang | 90 x 80 |
| | Champagne | Transparent | Blocky | Subang | 120 x 110 |
| | Champagne | Transparent | ShPrsm | Subang | 120 x 100 |
| | Champagne | Transparent | Prsmtc | Subhedral | 120 x 50 |
| | Champagne | Transparent | SlElng | Angular | 120 x 70 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|----------|---|-------------|-----------|-----------|---------------------------------------|
| Zircon | Champagne | Transparent | ShPrsm | Subrnd | 100 x 60 |
| | Champagne | Transparent | Blocky | Subang | 100 x 60 |
| | Champagne | Transparent | Equant | Subang | 70 x 60 |
| | Champagne | Translucent | Blocky | Subang | 70 x 60 |
| | Champagne | Transparent | Blocky | Subang | 80 x 60 |
| | Champagne | Transparent | Irregular | Subang | 80 x 60 |
| | Champagne | Transparent | Blocky | Subrnd | 70 x 50 |
| | Champagne | Transparent | Subeq | Subrnd | 65 x 65 |
| | Champagne | Transparent | Blocky | Subang | 70 x 40 |
| | Champagne | Transparent | ShPrsm | Subrnd | 80 x 60 |
| | Champagne | Transparent | Subeq | Subrnd | 80 x 60 |
| | Champagne | Transparent | Blocky | Subang | 100 x 100 |
| | Clear with very light yellow tint | Transparent | ShPrsm | Subhedral | 120 x 80 |
| | Clear with very light yellow tint | Transparent | Blocky | Subrnd | 100 x 90 |
| | Clear with very light yellow tint | Transparent | Blocky | Subrnd | 110 x 60 |
| | Clear with very light yellow tint | Translucent | Subeq | Subrnd | 100 x 80 |
| | Clear with very light yellow tint | Translucent | Subeq | Subrnd | (5) 90 x 80 |
| | Clear with light yellow tint | Transparent | Blocky | Subang | 70 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|----------|------------------------|-------------|--------|-----------|---------------------------------------|
| Zircon | Clear with yellow tint | Transparent | Equant | Subrnd | 100 x 70 |
| | Clear with yellow tint | Transparent | Subeq | Subrnd | 80 x 80 |
| | Clear with yellow tint | Transparent | Subeq | Subang | 80 x 70 |
| | Clear with yellow tint | Transparent | Blocky | Subang | 100 x 50 |
| | Clear with yellow tint | Transparent | Blocky | Subang | 70 x 40 |
| | Clear with yellow tint | Transparent | Blocky | Subang | 80 x 60 |
| | Clear with yellow tint | Transparent | Blocky | Subang | 120 x 60 |
| | Clear with yellow tint | Translucent | Blocky | Subrnd | 80 x 65 |
| | Clear with yellow tint | Translucent | Blocky | Subang | 80 x 60 |
| | Clear with yellow tint | Transparent | ShPrsm | Subang | 100 x 60 |
| | Clear with yellow tint | Translucent | ShPrsm | Subrnd | 80 x 60 |
| | Clear with yellow tint | Transparent | Prsmtc | Subhedral | 100 x 40 |
| | Clear with yellow tint | Transparent | Prsmtc | Subhedral | 140 x 40 |
| | Clear with yellow tint | Translucent | Prsmtc | Subhedral | 130 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) or (XRD ID) |
|--------------|-----------------------------|--------------------------------|--------|----------------------|---------------------------------------|
| Zircon | Very light pink-to-white | Translucent- to-Opaque | Prsmtc | Euhedral/ Angular | (6) 160 x 90 |
| | White | Transparent- to-Translucent | Prsmtc | Euhedral/ Angular | (7) 120 x 70 |
| | White | Translucent | n.d. | n.d. | (8) n.d. (for size) |
| | White | Opaque | Subeq | Subrnd | (9) 100 x 80 |
| Unidentified | Colorless | Transparent | Blocky | Subang | |

Subsamples 283.8 g, 495.5 g, 819.5 g, 1,078.1 g, 535.3 g, 893.3 g, and 1,046.2 g

 $(\Sigma = 5,151.7 \text{ g})$, continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Size (µm) or (XRD ID) |
|------------------|------------------------------|-------------|-----------|----------------------|--------------------------|
| Chrome spinel | Black | Opaque | Subeq | Subrnd | |
| Zircon | Pink | Translucent | Prsmtc | Euhedral/ Angular | 400 x 160 |
| | Pink | Translucent | Irregular | Angular | (10) 240 x 180 |
| | Champagne | Transparent | Blocky | Subang | 160 x 140 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subrnd | 140 x 120 |

XRD ID: (1) D-S 3-9-03 (2) G 7-29-03 (3) D-S 8-7-03 (4) G 2-18-05 (5) G 3-27-03 (6) G 12-16-04 (7) G 12-20-04 (8) G 12-21-04 (9) G 12-22-04 (10) G 7-26-04.

Carawine spherule layer sample 42-1A

Subsamples 216.1 g and 341.4 g ($\Sigma = 557.5$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|----------------------|--|---|---|--|------------------------|
| Anatase (n = 517) | Very light peach- to-peach Very light yellow- peach Light reddish peach Light brown- peach Very light buff-to- buff Amber Pale champagne Light olive green Light olive green Light-to-medium gray Very light brown- gray Uight grayish yellow Clear with light yellow or green tint Very light blue Beige Cream Clear-to-very light gray Clear-to-white White | Mostly Opaque; Translucent- to-Opaque; Translucent Transparent | Mostly Subeq and SIElng; Irregular Blocky Prsmtc Elongate Equant | Mostly Subrnd; Subang-to- Angular; Irregular | Some Waxy |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|---------------------|--------------------------------------|---------------------------|-----------|-----------|------------------------|
| Chrome spinel | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Blocky | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Equant | Wllrnd | |
| | Black | Opaque | Octhdl | Subrnd | |
| | Black | Opaque | Blocky | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| Rutile ± Anatase | Light buff | Opaque | SlElng | Subrnd | |
| | Light buff | Opaque | Irregular | Subrnd | |
| | Light grayish buff | Opaque | Irregular | Subrnd | |
| | Light grayish buff | Opaque | Irregular | Subrnd | |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | SlElng | Subrnd | |
| | Buff | Opaque | Subeq | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Subeq | Subrnd | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | SlElng | Subang | |
| | Buff | Opaque | Irregular | Angular | |
| | Buff | Opaque | Irregular | Angular | |
| | Buff | Opaque | Irregular | Subang | |
| | Light peach | Opaque | Irregular | Subang | |
| | Light yellow- peach | Opaque | Irregular | Angular | |
| | Clear with very light yellow tint | Translucent- to-Opaque | Irregular | Subrnd | |
| | Very light yellow- brown | Opaque | SlElng | Wllrnd | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|--------------------------|--------------------------------------|---------------------------|----------|-----------|------------------------|
| Rutile + Unidentified | White | Opaque | SlElng | Subrnd | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | Blocky | Subrnd | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | SlElng | Subrnd | |
| | White | Opaque | Equant | Subrnd | |
| | White | Opaque | Elongate | Subrnd | |
| | White | Opaque | SlElng | Subrnd | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | Equant | Subrnd | |
| Tourmaline | Olive green | Transparent | Blocky | Subang | |
| Zircon | Pale pink | Transparent | Elongate | Subhedral | 120 x 60 |
| | Pale pink | Translucent | ShPrsm | Subrnd | 80 x 80 |
| | Pink | Transparent | Prsmtc | Subrnd | 240 x 110 |
| | Pink | Transparent | Prsmtc | Subhedral | 120 x 80 |
| | Pink | Transparent | Prsmtc | Subhedral | 160 x 80 |
| | Pink | Transparent | Elongate | Subrnd | 280 x 100 |
| | Clear with light yellow-pink tint | Translucent | Blocky | Subang | 120 x 90 |
| | Champagne | Transparent | SlElng | Subrnd | 140 x 80 |
| | Champagne | Transparent | ShPrsm | Subrnd | 85 x 85 |
| | Champagne | Transparent | Blocky | Subang | 100 x 80 |
| | Champagne | Transparent | Blocky | Subang | 100 x 85 |
| | Light reddish peach | Opaque | Subeq | Subrnd | 140 x 100 |
| | Peach | Opaque | Prsmtc | Subhedral | 240 x 100 |
| | Clear with very light yellow tint | Translucent- to-Opaque | Subeq | Subrnd | 100 x 90 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|----------|-----------------------------------|---------------------------|-----------|-----------|------------------------|
| Zircon | Clear with very light yellow tint | Translucent- to-Opaque | Prsmtc | Subhedral | 140 x 70 |
| | Clear with very light yellow tint | Opaque | ShPrsm | Subhedral | 90 x 80 |
| | Clear with light yellow tint | Translucent | Blocky | Subang | 120 x 120 |
| | Clear with light yellow tint | Transparent | Irregular | Angular | 140 x 80 |
| | Clear with yellow tint | Translucent | ShPrsm | Subang | 100 x 100 |
| | Clear with yellow tint | Transparent | Blocky | Subang | 100 x 80 |
| | Clear with yellow tint | Opaque | Equant | Subang | 100 x 100 |
| | Clear with yellow tint | Translucent- to-Opaque | Subeq | Subrnd | 90 x 60 |
| | Clear with yellow tint | Translucent- to-Opaque | Subeq | Subrnd | 100 x 60 |
| | Clear with yellow tint | Translucent | ShPrsm | Subhedral | 140 x 90 |
| | Clear with yellow tint | Translucent | Prsmtc | Subhedral | 120 x 60 |
| | Clear with yellow tint | Translucent | Blocky | Subrnd | 70 x 60 |
| | Clear with light green tint | Translucent | ShPrsm | Subrnd | 140 x 100 |
| | Light gray-to- white | Opaque | Prsmtc | Subhedral | 140 x 80 |
| | Light gray-to- white | Opaque | Equant | Subrnd | 90 x 70 |

Subsamples 216.1 g and 341.4 g ($\Sigma = 557.5$ g), continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|---------------------|--|-------------|---|-----------------------------|------------------------|
| Anatase (n = 83) | Light peach-to- peach Very light buff- to-light buff Cream | Opaque | Mostly Subeq and SIElng; Irregular | Mostly Subrnd; Subang | Some Waxy |
| Clinopyroxene | Very light yellow-to-olive green | Translucent | Elongate | Angular | |
| Rutile ± Anatase | Very light buff | Opaque | Irregular | Subang | |
| | Very light buff | Opaque | Irregular | Subang | |
| | Very light buff | Opaque | Subeq | Subrnd | |
| | Very light buff | Opaque | Irregular | Angular | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | Irregular | Subang | |
| | Light buff | Opaque | Irregular | Angular | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| Zircon | Pink | Transparent | Subeq | Wllrnd | 260 x 200 |
| | Pink | Transparent | Prsmtc | Subhedral | 230 x 120 |
| | Pink | Transparent | Prsmtc | Subhedral | 220 x 130 |
| | Light amber | Translucent | Equant | Subang | 180 x 160 |
| | Light amber | Translucent | Prsmtc | Subang | 300 x 180 |
| | Amber | Translucent | Prsmtc | Subhedral | 340 x 180 |
| | Red-peach | Opaque | Equant | Wllrnd | 160 x 160 |

Carawine spherule layer sample X38-2

Subsamples 85.0879 g and 144.3 g ($\Sigma \approx 229.4$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|------------------------|--|--|--|--|---|
| Actinolite | Light olive green | Transparent | Prsmtc | Subang | |
| | Light olive green | Transparent | Blocky | Subang | |
| | Light olive green | Transparent | SlElng | Subang | |
| Anatase (n = 1,069) | Very light peach Light peach Clear with light yellow tint Light golden Light gray-to- medium gray Light olive Beige White | Mostly Opaque; a few Translucent-to- Opaque | Mostly Subeq and SIEIng; Blocky Elongate Irregular | Mostly Subrnd; Subang Angular | Some Waxy |
| Anglesite | Light gray | Opaque | Blocky | Subrnd | (1) |
| | Light gray | Translucent | Blocky | Subrnd | (2) |
| | Clear with very light blue tint | Transparent | Equant | Wllrnd | (3) |
| | Clear with light yellow tint | Translucent-to- Opaque | Blocky | Subrnd | (4) |
| Brookite | Light yellow- peach | Opaque | Subeq | Subrnd | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|---------------|----------|-------------|--------|-----------|---|
| Chrome spinel | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | Very little green matrix |
| | Black | Opaque | Subeq | Wllrnd | |
| | Black | Opaque | Subeq | Wllrnd | |
| | Black | Opaque | Subeq | Subang | |
| | Black | Opaque | Subeq | Subang | |
| | Black | Opaque | Subeq | Subang | |
| | Black | Opaque | Subeq | Subang | |
| | Black | Opaque | Subeq | Angular | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Wllrnd | |
| | Black | Opaque | Equant | Wllrnd | |
| | Black | Opaque | Octhdl | Subrnd | |
| | Black | Opaque | Octhdl | Subrnd | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|---------------|-----------------|-------------|-----------|-----------|---|
| Chrome spinel | Black | Opaque | Octhdl | Subrnd | (5) |
| | Black | Opaque | Octhdl | Subrnd | (6) |
| | Black | Opaque | Octhdl | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | SlElng | Subang | |
| | Black | Opaque | Elongate | Subrnd | |
| | Black | Opaque | Irregular | Subang | (7) |
| | Black | Opaque | n.d. | n.d. | |
| | Dark steel gray | Opaque | Subeq | Subrnd | Emerald green matrix |
| | Dark steel gray | Opaque | Subeq | Subrnd | Emerald green matrix |
| | Dark steel gray | Opaque | Subeq | Subrnd | Emerald green matrix |
| | Dark steel gray | Opaque | Subeq | Subrnd | Emerald green matrix |
| | Dark steel gray | Opaque | Subeq | Subrnd | Emerald green matrix |
| | Dark steel gray | Opaque | Subeq | Subrnd | Colorless-to- green matrix |
| | Dark steel gray | Opaque | Subeq | Subrnd | (8) Emerald green matrix |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|---|---|--|---|---|---|
| Chrome spinel | Dark steel gray | Opaque | Equant | Wllrnd | Emerald green matrix |
| | Dark steel gray | Opaque | Equant | Wllrnd | Emerald green matrix |
| | Dark steel gray | Opaque | Blocky | Subang | Emerald green matrix |
| | Dark steel gray | Opaque | SlElng | Subrnd | (9) Emerald green matrix |
| | Dark steel gray | Opaque | n.d. | n.d. | Emerald green matrix |
| | Medium dark gray | Opaque | Equant | Wllrnd | Emerald green matrix |
| Clinozoisite/ Epidote | Clear with light yellow tint | Translucent | Blocky | Subang | (10) |
| Rutile \pm TiO ₂ II \pm Anatase (n = 296) | Mostly very light peach-to- peach and very light buff-to- buff; Reddish peach Light brown-to- brown Light reddish brown Amber Reddish amber Brownish amber Clear with yellow tint | Mostly Opaque; rarely Transparent-to- Translucent | Mostly Subeq-to- SIEIng; Blocky Elongate Equant Irregular Prsmtc | Mostly Subrnd-to- Subang; Wllrnd | Some Waxy |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|-------------------------|-------------------|-------------|--------|-----------|---|
| Tourmaline ± Anatase | Light olive green | Transparent | ShPrsm | Subang | (11) |
| | Light olive green | Transparent | ShPrsm | Subhedral | |
| | Light olive green | Translucent | ShPrsm | Subrnd | |
| | Light olive green | Translucent | ShPrsm | Subang | |
| | Light olive green | Transparent | Blocky | Subang | (12) |
| | Light olive green | Translucent | Blocky | Subang | |
| | Light olive green | Translucent | Blocky | Subang | |
| | Light olive green | Translucent | Subeq | Subrnd | (13) |
| | Light olive green | Opaque | Blocky | Subang | |
| | Light olive green | Opaque | Blocky | Subrnd | |
| | Olive green | Translucent | Subeq | Subrnd | |
| | Olive green | Translucent | Subeq | Subang | |
| | Olive green | Translucent | Subeq | Subang | |
| | Olive green | Translucent | Equant | Subrnd | |
| | Olive green | Translucent | Blocky | Subang | |
| | Olive green | Translucent | Blocky | Subang | |
| | Olive green | Translucent | Blocky | Subang | |
| | Olive green | Translucent | Blocky | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|-------------------------|------------------------|---------------------------|-----------|-----------|---|
| Tourmaline ± Anatase | Olive green | Opaque | Subeq | Subrnd | (14) |
| | Olive green | Opaque | Subeq | Subang | |
| | Olive green | Opaque | ShPrsm | Subrnd | |
| | Olive green | Opaque | Blocky | Subrnd | |
| | Olive green | Opaque | Irregular | Subang | |
| | Light green | Transparent | Blocky | Angular | |
| | Pale green | Translucent | Irregular | Subrnd | Waxy |
| | Light pink-green | Transparent | Elongate | Subang | (15) |
| | Green | Translucent-to- Opaque | Subeq | Subrnd | (16) |
| | Light yellow- green | Translucent | Blocky | Subrnd | |
| | Light yellow | Translucent | n.d. | Subrnd | |
| | Light yellow- olive | Transparent | ShPrsm | Subrnd | |
| | Light yellow- olive | Transparent | ShPrsm | Subhedral | (17) |
| | Light yellow- olive | Transparent | Blocky | Subrnd | |
| | Light yellow- olive | Translucent | Blocky | Subrnd | |
| | Light yellow- olive | Translucent | Blocky | Subang | |
| | Light yellow- olive | Translucent | Blocky | Subang | |
| | Colorless | Translucent | Blocky | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|---------------------------|---------------------------|-----------|-----------|---|
| Zircon | Very light yellow-pink | Translucent | ShPrsm | Subhedral | (18) 70 x 60 |
| | Very light yellow-pink | Translucent-to- Opaque | Blocky | Subang | (19) 90 x 80 |
| | Very light yellow-pink | Opaque | Blocky | Subrnd | (20) 110 x 100 |
| | Very pale pink | Translucent-to- Opaque | Blocky | Angular | (21) 90 x 90 |
| | Pale pink | Transparent | ShPrsm | Subhedral | (22) 80 x 60 |
| | Pale pink | Transparent | ShPrsm | Wllrnd | (23) 100 x 80 |
| | Pale pink | Transparent | Prsmtc | Subhedral | 160 x 65 |
| | Pale pink | Translucent-to- Opaque | Blocky | Subang | (24) 80 x 70 |
| | Pale pink | Opaque | Blocky | Subang | (25) 90 x 60 |
| | Pale pink-to- white | Translucent-to- Opaque | Blocky | Subang | (26) 100 x 100 |
| | Pink | Transparent | Subeq | Subrnd | 100 x 80 |
| | Pink | Transparent | Subeq | Subrnd | 80 x 60 |
| | Pink | Transparent | Subeq | Subrnd | 100 x 70 |
| | Pink | Transparent | Subeq | Subrnd | 100 x 60 |
| | Pink | Transparent | Irregular | Angular | 130 x 80 |
| | Pink | Transparent | Elongate | Subang | 180 x 70 |
| | Pink | Transparent | SlElng | Subang | 100 x 60 |
| | Pink | Transparent | SlElng | Subang | 100 x 60 |
| | Pink | Transparent | SlElng | Subang | 80 x 60 |
| | Pink | Transparent | SlElng | Subang | 100 x 60 |
| | Pink | Transparent | SlElng | Angular | 110 x 60 |
| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|--------------------|---------------------------|--------------------|-----------|---|
| Zircon | Pink | Transparent ShPrsm | | Subrnd | 160 x 100 |
| | Pink | Transparent | ShPrsm | Subrnd | 100 x 80 |
| | Pink | Transparent | ShPrsm | Subhedral | 120 x 80 |
| | Pink | Transparent | ShPrsm | Subhedral | 140 x 70 |
| | Pink | Transparent | ShPrsm | Subhedral | 100 x 50 |
| | Pink | Transparent | Prsmtc | Euhedral | 120 x 45 |
| | Pink | Transparent | Prsmtc | Euhedral | (27) 80 x 60 |
| | Pink | Transparent | Prsmtc | Subhedral | 200 x 80 |
| | Pink | Transparent | Prsmtc | Subhedral | 120 x 60 |
| | Pink | Transparent Prsmtc | | Subhedral | 160 x 50 |
| | Pink | Transparent | Transparent Prsmtc | | 120 x 40 |
| | Pink | Transparent | Transparent Blocky | | 100 x 80 |
| | Pink | Transparent | Blocky | Angular | 80 x 45 |
| | Pink | Translucent-to- Opaque | n.d. | n.d. | (28) n.d. (for size) |
| | Pink | Translucent-to- Opaque | n.d. | n.d. | (29) n.d. (for size) |
| | Pinkish white | n.d. | Equant | Subrnd | (30) 100 x 90 |
| | Light champagne | Transparent | ShPrsm | Subhedral | 120 x 60 |
| | Light champagne | Transparent | ShPrsm | Subang | 120 x 50 |
| | Light champagne | Transparent | Prsmtc | Subhedral | 100 x 60 |
| | Champagne | Transparent | ShPrsm | Subhedral | 90 x 60 |
| | Champagne | Transparent | ShPrsm | Subhedral | 90 x 60 |
| | Champagne | Transparent | ShPrsm | Subhedral | 120 x 60 |
| | Champagne | Transparent | ShPrsm | Subhedral | 80 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|-----------|-------------|----------------------|-----------|---|
| Zircon | Champagne | Transparent | ShPrsm | Subhedral | 80 x 40 |
| | Champagne | Transparent | ShPrsm | Subhedral | 80 x 40 |
| | Champagne | Transparent | ShPrsm | Subhedral | 100 x 60 |
| | Champagne | Transparent | ShPrsm | Subhedral | 100 x 60 |
| | Champagne | Transparent | ShPrsm | Subhedral | 90 x 45 |
| | Champagne | Transparent | ShPrsm | Subhedral | 80 x 45 |
| | Champagne | Transparent | ShPrsm | Subhedral | 80 x 45 |
| | Champagne | Transparent | ShPrsm | Subang | 100 x 80 |
| | Champagne | Transparent | ShPrsm | Subang | 85 x 50 |
| | Champagne | Transparent | ShPrsm | Euhedral | 90 x 45 |
| | Champagne | Transparent | Transparent ShPrsm S | | 100 x 60 |
| | Champagne | Transparent | Prsmtc | Subhedral | 100 x 60 |
| | Champagne | Transparent | Prsmtc | Subhedral | 120 x 45 |
| | Champagne | Transparent | Transparent Prsmtc | | 100 x 45 |
| | Champagne | Transparent | Prsmtc | Euhedral | 100 x 45 |
| | Champagne | Transparent | Blocky | Subang | 80 x 70 |
| | Champagne | Transparent | Blocky | Subang | 80 x 40 |
| | Champagne | Transparent | Subeq | Subrnd | 90 x 60 |
| | Champagne | Transparent | Subeq | Subrnd | 90 x 60 |
| | Champagne | Transparent | Subeq | Subrnd | 65 x 40 |
| | Champagne | Transparent | Subeq | Subang | 70 x 50 |
| | Champagne | Transparent | Equant | Subrnd | 80 x 80 |
| | Champagne | Transparent | Equant | Subang | 70 x 65 |
| | Champagne | Transparent | SlElng | Subang | 85 x 45 |
| | Champagne | Transparent | Irregular | Subang | 100 x 80 |
| | Champagne | Transparent | Irregular | Angular | 120 x 60 |
| | Champagne | Transparent | Irregular | Angular | 100 x 60 |
| | Champagne | Translucent | Subeq | Subrnd | 80 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Diaphaneity Shape R | | Luster or Other or Size (µm) or (XRD ID) |
|----------|------------------------------------|---------------------------|---------------------|-----------|---|
| Zircon | Champagne | Translucent | Subeq | Subrnd | 80 x 50 |
| | Champagne | Translucent | Subeq | Subang | 80 x 60 |
| | Champagne | Translucent | ShPrsm | Subhedral | 80 x 60 |
| | Clear with very light yellow tint | Opaque | ShPrsm | Subhedral | (31) 80 x 70 |
| | Clear with light yellow tint | Transparent | ShPrsm | Subhedral | 70 x 40 |
| | Clear with light yellow tint | Transparent | Prsmtc | Subhedral | 130 x 70 |
| | Clear with light yellow tint | Transparent | SlElng | Subang | 80 x 40 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subhedral | 80 x 45 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subrnd | 100 x 60 |
| | Clear with light yellow tint | Translucent | ShPrsm | Euhedral | 80 x 45 |
| | Clear with light yellow tint | Translucent | ShPrsm | Euhedral | 75 x 40 |
| | Clear with light yellow tint | Translucent | Prsmtc | Subhedral | 110 x 50 |
| | Clear with light yellow tint | Translucent | Prsmtc | Subhedral | 90 x 45 |
| | Clear with light yellow tint Tr | Translucent | Prsmtc | Euhedral | 80 x 40 |
| | Clear with light yellow tint | Translucent-to- Opaque | Blocky | Subrnd | (32) 80 x 40 |
| | Clear with light yellow tint | Translucent-to- Opaque | ShPrsm | Subhedral | (33) 90 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|------------------------------|---------------------------|--------------------|-----------|---|
| Zircon | Clear with light yellow tint | Translucent-to- Opaque | ShPrsm | Subhedral | (34) 80 x 50 |
| | Clear with light yellow tint | Translucent-to- Opaque | Prsmtc | Subhedral | (35) 100 x 70 |
| | Clear with light yellow tint | Translucent-to- Opaque | Prsmtc | Subrnd | (36) 100 x 50 |
| | Clear with light yellow tint | Opaque | Opaque Blocky Subr | | (37) 100 x 60 |
| | Clear with light yellow tint | Opaque | Blocky | Subang | (38) 80 x 60 |
| | Clear with light yellow tint | Opaque | Blocky | Subang | 80 x 45 |
| | Clear with light yellow tint | Opaque | ShPrsm | Subhedral | (39) 100 x 100 |
| | Clear with light yellow tint | Opaque | ShPrsm | Subhedral | (40) 80 x 70 |
| | Clear with light yellow tint | Opaque | ShPrsm | Subhedral | (41) 80 x 50 |
| | Clear with light yellow tint | Opaque | ShPrsm | Subrnd | (42) 80 x 70 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subrnd | (43) 70 x 40 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subang | (44) 90 x 40 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subang | (45) 80 x 60 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subhedral | (46) 120 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|------------------------------|-------------|--------|-----------|---|
| Zircon | Clear with light yellow tint | Opaque | Prsmtc | Subhedral | (47) 80 x 50 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subhedral | (48) 80 x 40 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subhedral | (49) 70 x 40 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subhedral | (50) 90 x 40 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subhedral | (51) 100 x 30 |
| | Clear with light yellow tint | Opaque | Prsmtc | Euhedral | (52) 110 x 50 |
| | Clear with light yellow tint | Opaque | Prsmtc | Euhedral | (53) 80 x 60 |
| | Clear with light yellow tint | Opaque | Prsmtc | Euhedral | (54) 80 x 40 |
| | Clear with light yellow tint | Opaque | Subeq | Subrnd | (55) 100 x 60 |
| | Clear with light yellow tint | Opaque | Subeq | Subrnd | 90 x 45 |
| | Clear with light yellow tint | Opaque | Subeq | Subrnd | (56) 80 x 60 |
| | Clear with light yellow tint | Opaque | Subeq | Subrnd | (57) 70 x 50 |
| | Clear with light yellow tint | Opaque | Equant | Subrnd | (58) 80 x 80 |
| | Clear with light yellow tint | Opaque | Equant | Subrnd | (59) 80 x 80 |
| | Clear with yellow tint | Transparent | Blocky | Subang | 80 x 50 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|------------------------|-------------|--------|-----------|---|
| Zircon | Clear with yellow tint | Transparent | Blocky | Subang | 70 x 60 |
| | Clear with yellow tint | Transparent | Prsmtc | Subhedral | 120 x 40 |
| | Clear with yellow tint | Transparent | Prsmtc | Subhedral | 100 x 45 |
| | Clear with yellow tint | Transparent | Prsmtc | Subhedral | 100 x 60 |
| | Clear with yellow tint | Transparent | Prsmtc | Euhedral | 120 x 50 |
| | Clear with yellow tint | Transparent | SlElng | Subrnd | 80 x 45 |
| | Clear with yellow tint | Transparent | SlElng | Subrnd | 80 x 40 |
| | Clear with yellow tint | Transparent | SlElng | Subang | 100 x 45 |
| | Clear with yellow tint | Transparent | Subeq | Subang | 80 x 60 |
| | Clear with yellow tint | Transparent | Subeq | Subang | 80 x 60 |
| | Clear with yellow tint | Transparent | Equant | Subrnd | 80 x 50 |
| | Clear with yellow tint | Translucent | ShPrsm | Subhedral | 80 x 40 |
| | Clear with yellow tint | Translucent | ShPrsm | Subhedral | 90 x 60 |
| | Clear with yellow tint | Translucent | ShPrsm | Subang | 100 x 50 |
| | Clear with yellow tint | Translucent | ShPrsm | Subrnd | 100 x 80 |

| Phase(s) | Color(s) | Diaphaneity | Diaphaneity Shape F | | Luster or Other or Size (µm) or (XRD ID) |
|----------|--------------------------------|---------------------------|---------------------|-----------|---|
| Zircon | Clear with yellow tint | Translucent | ShPrsm | Subrnd | 100 x 45 |
| | Clear with yellow tint | Translucent | Prsmtc | Subhedral | 100 x 45 |
| | Clear with yellow tint | Translucent | Prsmtc | Subhedral | 70 x 45 |
| | Clear with yellow tint | Translucent | Prsmtc | Subhedral | 90 x 45 |
| | Clear with yellow tint | Translucent | Prsmtc | Subrnd | 110 x 45 |
| | Clear with yellow tint | Translucent | Prsmtc | Euhedral | 80 x 40 |
| | Clear with yellow tint | Translucent | Subeq | Subrnd | 90 x 60 |
| | Clear with yellow tint | Translucent | Subeq | Subrnd | 70 x 45 |
| | Clear with yellow tint | Translucent | Subeq | Subang | 80 x 60 |
| | Clear with yellow tint | Translucent | Equant | Subrnd | 70 x 60 |
| | Clear with yellow tint Trar | Translucent | Equant | Subrnd | 80 x 60 |
| | Clear with yellow tint | Translucent-to- Opaque | ShPrsm | Subhedral | 100 x 80 |
| | Clear with yellow tint | Translucent-to- Opaque | ShPrsm | Subhedral | (60) 80 x 50 |
| | Clear with yellow tint | Translucent-to- Opaque | ShPrsm | Subhedral | (61) 70 x 60 |
| | Clear with yellow tint | Opaque | Blocky | Subrnd | (62) 90 x 60 |

| Phase(s) | Color(s) | Diaphaneity | Diaphaneity Shape R | | Luster or Other or Size (µm) or (XRD ID) |
|----------|--|---------------------------|---------------------|-----------|---|
| Zircon | Clear with yellow tint | Opaque | ShPrsm | Subang | (63) 100 x 50 |
| | Clear with yellow tint | Opaque | Prsmtc | Euhedral | (64) 100 x 60 |
| | Clear with yellow tint | Opaque | Elongate | Subrnd | (65) 120 x 80 |
| | Clear with light yellow-pink tint | Translucent-to- Opaque | Prsmtc | Euhedral | (66) 180 x 80 |
| | Clear with light pinkish yellow tint | Opaque | ShPrsm | Subrnd | (67) 90 x 70 |
| | Clear with light yellow-peach tint | Opaque | Subeq | Subrnd | 100 x 60 |
| | Clear with light yellow-green tint | Transparent | ShPrsm | Subhedral | 80 x 40 |
| | Clear with light yellow-green tint | Transparent | ShPrsm | Subhedral | 70 x 40 |
| | Clear with light yellow-green tint | Transparent | ShPrsm | Subrnd | 100 x 45 |
| | Clear with light yellow-green tint | Transparent | ShPrsm | Subrnd | 85 x 40 |
| | Clear with light yellow-green tint | Transparent | Prsmtc | Subhedral | 100 x 45 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|--|---------------------------|--------------------|-----------|---|
| Zircon | Clear with light yellow-green tint | Transparent | nsparent Irregular | | 70 x 40 |
| | Clear with light yellow-green tint | Translucent | Prsmtc | Subhedral | 100 x 45 |
| | Clear with light yellow-green tint | Translucent | Equant | Subrnd | 80 x 60 |
| | Clear with light green tint | Transparent | Blocky | Subrnd | 90 x 70 |
| | Clear with light green tint | Transparent | Subeq | Subrnd | 80 x 50 |
| | Clear with light green tint | Translucent | ShPrsm | Subang | 80 x 45 |
| | Very light pink- yellow | Translucent-to- Opaque | ShPrsm | Subhedral | (68) 90 x 70 |
| | Light yellow | Opaque | Blocky | Subang | (69) 120 x 80 |
| | Light yellow | Opaque | Subeq | Subrnd | (70) 80 x 70 |
| | Yellow | Opaque | Subeq | Subrnd | (71) 80 x 50 |
| | Tan | Opaque | n.d. | n.d. | (72) n.d. (for size) |
| | White | Translucent-to- Opaque | Prsmtc | Subhedral | (73) 90 x 40 |
| | White | Translucent-to- Opaque | Subeq | Subrnd | (74) 130 x 120 |
| | White | Translucent-to- Opaque | Prsmtc | n.d. | (75) n.d. (for size) |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|----------|---------------------------|--------------------------------|-----------|---|
| Zircon | White | Translucent-to- Opaque | n.d. | n.d. | (76) n.d. (for size) |
| | White | Translucent-to- Opaque | n.d. | n.d. | (77) n.d. (for size) |
| | White | Translucent-to- Opaque | n.d. | n.d. | (78) n.d. (for size) |
| | White | Translucent-to- Opaque | n.d. | n.d. | (79) n.d. (for size) |
| | White | Translucent-to- Opaque | Translucent-to- Opaque n.d. | | (80) n.d. (for size) |
| | White | Translucent-to- Opaque | n.d. | n.d. | (81) n.d. (for size) |
| | White | Translucent-to- Opaque | n.d. | n.d. | (82) n.d. (for size) |
| | White | Translucent-to- Opaque | n.d. | n.d. | (83) n.d. (for size) |
| | White | Translucent-to- Opaque | n.d. | n.d. | (84) n.d. (for size) |
| | White | Opaque | Prsmtc | Subrnd | (85) 120 x 50 |
| | White | Opaque | Blocky | Subrnd | (86) 90 x 70 |
| | White | Opaque | Equant | Subrnd | (87) 100 x 80 |
| | White | Opaque | n.d. | n.d. | (88) n.d. (for size) |
| | White | Opaque | n.d. | n.d. | (89) n.d. (for size) |
| | White | Opaque | n.d. | n.d. | (90) n.d. (for size) |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------|-----------------------------------|---------------------------|----------|-----------|---|
| Zircon | White | Opaque | n.d. | n.d. | (91) n.d. (for size) |
| | White | Opaque | n.d. | n.d. | (92) n.d. (for size) |
| | White | Opaque | n.d. | n.d. | (93) n.d. (for size) |
| | White | Opaque | n.d. | n.d. | (94) n.d. (for size) |
| | White | Opaque | Prsmtc | Subrnd | (95) 100 x 40 |
| | White | Opaque | n.d. | n.d. | (96) n.d. (for size) |
| | White | Opaque | n.d. | n.d. | (97) n.d. (for size) |
| | White with very light yellow tint | Opaque | Elongate | Subang | (98) 100 x 50 |
| | White with light yellow tint | Translucent-to- Opaque | Blocky | Subrnd | (99) 80 x 60 |
| | White with light yellow tint | Opaque | ShPrsm | Subhedral | (100) 80 x 40 |
| | White with light yellow tint | Opaque | Elongate | Subrnd | (101) 150 x 100 |
| | White with light yellow tint | Opaque | Blocky | Subrnd | (102) 120 x 90 |
| | White-to-very light peach | Opaque | Subeq | Wllrnd | (103) 130 x 100 |

XRD ID: (1) G 9-20-04 (2) D-S 10-16-05 (3) G 11-22-04 (4) D-S 10-14-05 (5) G 8-4-04/D-S 10-6-05 (6) G 3-1-05/D-S 10-13-05 (7) G 10-28-04 (8) G 10-27-04 (9) D-S 10-20-05 (10) G 11-28-04 (11) G 10-17-04 (12) G 3-21-05 (13) D-S 11-4-05 (14) D-S 11-7-05 (15) D-S 7-17-04 (16) G 3-18-05 (17) D-S 9-8-05 (18) D-S 9-18-05 (19) D-S 9-19-05 (20) D-S 8-24-04 (21) D-S 7-15-04 (22) D-S 8-11-04 (23) D-S 9-7-05 (24) D-S 7-16-05 (25) D-S 7-20-05 (26) D-S 8-21-04 (27) G 10-15-04 (28) D-S 3-25-05 (29) D-S 4-6-05 (30) D-S 7-14-04 (31) D-S 9-23-05 (32) D-S 3-24-05 (33) D-S 4-7-05 (34) D-S 9-16-05 (35) D-S 7-10-05 (36) D-S 8-20-05 (37) D-S 7-27-05 (38) D-S 7-13-05 (39) D-S 7-21-05 (40) D-S 8-25-05 (41) D-S 4-12-05 (42) D-S 8-22-05 (43) D-S 8-8-05 (44) D-S 8-9-05 (45) D-S 8-5-05 (46) D-S 8-10-05 (47) D-S 4-21-05 (48) G 8-18-05 (49) D-S 7-11-05 (50) D-S 7-12-05 (51) D-S 7-24-05 (52) D-S 7-26-05 (53) D-S 4-15-05 (54) D-S 8-1-05 (55) D-S 7-8-05 (56) D-S 7-22-05 (57) D-S 7-25-05 (58) D-S 8-23-05 (59) D-S 8-24-05 (60) D-S 3-22-05 (61) D-S 3-23-05 (62) D-S 4-13-05 (63) D-S 7-14-05 (64) D-S 8-3-05 (65) D-S 8-9-04 (66) D-S 8-4-04 (67) D-S 7-29-05 (68) D-S 9-20-05 (69) D-S 9-15-05 (70) D-S 3-21-05 (71) D-S 7-15-05 (72) G 12-1-04 (73) D-S 3-19-05 (74) D-S 8-3-04 (75) D-S 8-26-04 (76) G 8-22-04 (77) D-S 3-9-05 (78) G 8-27-04 (79) D-S 3-11-05 (80) D-S 3-18-05 (81) D-S 3-28-05 (82) D-S 3-29-05 (83) D-S 3-31-05 (84) D-S 4-4-05 (85) D-S 8-19-04 (86) D-S 7-6-05 (87) D-S 9-28-05 (88) D-S 8-16-04 (89) D-S 8-18-04 (90) D-S 8-23-04 (91) D-S 3-7-05 (92) G 8-25-04 (93) D-S 3-30-05 (94) D-S 4-1-05 (95) D-S 4-14-05 (96) D-S 7-28-05 (97) G 4-21-05 (98) D-S 8-4-05 (99) D-S 3-20-05 (100) D-S 3-8-05 (101) D-S 8-19-05 (102) G 8-5-05 (103) D-S 8-22-04.

Subsamples 85.0879 g and 144.3 g ($\Sigma \approx 229.4$ g), continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Size (µm) or (XRD ID) |
|---|---|--|---|------------------|--------------------------|
| Anatase (n = 14) | Very light peach Light gray Colorless-to- white | Mostly Opaque; rarely Translucent- to-Opaque | Mostly Subeq-to- SIEIng; Blocky Irregular | Subrnd Subang | |
| Rutile \pm TiO ₂ II \pm Anatase (n = 4) | Peach Buff Light gray | Opaque | Blocky SIElng | Subrnd Subang | |
| Zircon | Pink | Translucent | ShPrsm | Subrnd | (104) 170 x 120 |
| | White | Opaque | Blocky | Subang | (105) 180 x 120 |

XRD ID: (104) G 7-14-04/D-S 8-15-04 (105) G 9-9-04/D-S 3-27-05.

Appendix T

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE CARAWINE CONTEXT SAMPLES

Introductory Note: The following abbreviations are used in Appendix T:

Admntn = Adamantine; n = number of grains; n.d. = no data; Prsmtc = Prismatic;

ShPrsm = Short Prism; SlElng = Slightly Elongate; Subang = Subangular;

Subeq = Subequant; Subrnd = Subrounded; Wllrnd = Well-rounded.

Carawine context sample 104141

Subsample 357.2 g

Size Fraction: 63-125 µm

| | [| | | | |
|---------------------|---|-----------------------|----------------------------|---|-------------------------------------|
| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
| Anatase (n = 43) | Golden light orange Light brownish peach Very light peach- to-peach Light medium gray Olive gray Colorless | Translucent Opaque | Mostly Subeq; Equant | Mostly Subrnd; Subang; a few are Wllrnd | Some are Waxy or Admntn |
| Chrome spinel | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|---------------|----------|-------------|-------|-----------|-------------------------------------|
| Chrome spinel | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Light yellow matrix |
| | Black | Opaque | Subeq | Subrnd | Light yellow matrix |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|---------------|-----------------|-------------|--------|-----------|-------------------------------------|
| Chrome spinel | Black | Opaque | Subeq | Subrnd | Clear-to- green matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- green matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- green matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- green matrix |
| | Black | Opaque | Subeq | Subrnd | Very minor green matrix |
| | Black | Opaque | Subeq | Subang | Light yellow-green matrix |
| | Black | Opaque | Subeq | Subang | Light yellow-green matrix |
| | Black | Opaque | Equant | Subrnd | Clear-to- green matrix |
| | Black | Opaque | Equant | Subrnd | Green matrix |
| | Black | Opaque | Equant | Subrnd | Clear-to- light yellow matrix |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | SlElng | Subrnd | |
| | Black | Opaque | SlElng | Subrnd | Clear-to- green matrix |
| | Black | Opaque | n.d. | Subrnd | |
| | Dark steel gray | Opaque | Subeq | Subrnd | Clear-to- light yellow matrix |
| | Dark steel gray | Opaque | n.d. | Subrnd | Green matrix |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|---------------------|-----------------------------------|---------------------------|--------|-----------|------------------------------------|
| Chrome spinel | Dark reddish brown | Translucent-to- Opaque | n.d. | Subrnd | |
| | Dark red | Translucent-to- Opaque | Equant | Wllrnd | |
| Rutile + Anatase | Light brown-to- cream | Opaque | Blocky | Subrnd | |
| | Very light brown- peach | Opaque | SlElng | Subrnd | |
| Tourmaline | Light yellow-olive | Translucent | Subeq | Subrnd | |
| | Olive green | Translucent | Prsmtc | Subhedral | |
| | Olive green | Translucent | Blocky | Subrnd | |
| Zircon | Light champagne | Transparent | ShPrsm | Subhedral | 120 x 80 |
| | Light champagne | Transparent | ShPrsm | Subhedral | 100 x 90 |
| | Light champagne | Transparent | Blocky | Subang | 90 x 70 |
| | Clear with very light yellow tint | Translucent | Prsmtc | Subhedral | 150 x 80 |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | 100 x 70 |
| | Clear with light yellow tint | Transparent | ShPrsm | Subhedral | 130 x 100 |

Subsample 357.2 g, continued

Size Fraction: 125-250 µm

| Phase | Color | Diaphaneity | Shape | Roundness | Size (µm) |
|---------|------------------|-------------|--------|-----------|-----------|
| Anatase | Light peach | Opaque | SlElng | Subrnd | |
| | Light brown-gray | Opaque | SlElng | Subrnd | |
| Zircon | Light champagne | Translucent | Prsmtc | Subhedral | 160 x 120 |

Carawine context sample 104175

Subsample 235.4 g

Size Fraction: 63-125 µm

| Phase(s) | Color | Diaphaneity | Shape | Roundness |
|--------------|-------------------|---------------------------|-------|-----------|
| Unidentified | Light bluish gray | Opaque | Subeq | Subrnd |
| | White | Translucent-to- Opaque | n.d. | Subrnd |

Carawine context sample X68-1

Subsamples 300.0 g and 304.7 g ($\Sigma = 604.7$ g)

Size Fraction: 63-125 µm

| Phase | Color(s) | Diaphaneity | Shape | Roundness | Luster |
|------------|--|---------------------------|--------|-----------|--------|
| Anatase | Clear with very light yellow tint | Translucent | Blocky | Subang | |
| | Clear with light yellow tint | Opaque | Blocky | Subang | |
| | Clear with yellow tint | Opaque | Blocky | Subang | |
| | Clear with light golden tint | Translucent | Blocky | Subang | |
| | Clear with light yellow- green tint | Translucent- to-Opaque | Blocky | Subang | |
| Rutile | Clear with very light yellow tint | Opaque | Subeq | Subang | Admntn |
| | Yellow | Opaque | Subeq | Subang | |
| | Very light brown | Opaque | SlElng | Subang | Waxy |
| Tourmaline | Light yellow-green | Translucent | n.d. | Subang | |

Appendix U

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE JEERINAH SPHERULE LAYER SAMPLES

Introductory Note: The following abbreviations are used in Appendix U:

Admntn = Adamantine; ID = Identification; n = number of grains; n.d. = no data;

Octhdl = Octahedral; Prsmtc = Prismatic; ShPrsm = Short Prism; SlElng = Slightly

Elongate; Subang = Subangular; Subeq = Subequant; Subrnd = Subrounded;

Wllrnd = Well-rounded; XRD ID = the identification number of a grain that was analyzed by XRD.

Jeerinah spherule layer sample W94-1Q

Subsamples 10.3210 g, 13.0639 g, and 15.3415 g ($\Sigma \approx 38.73$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|--------------------------------------|---|---|--|--|------------------------------------|
| Anatase (n = 551) | Very light peach-to-light peach Very light yellow-green Light gray- brown Very light gray Beige | Mostly Opaque; Translucent- to-Opaque (minor) | Mostly Subeq, Blocky, and SIElng; Irregular Wllrnd | Mostly Subrnd; Subang | Several Admntn |
| Anatase + K-feldspar (n = 183) | Clear with very light yellow tint Beige White | Opaque; Translucent- to-Opaque | Blocky Elongate SIElng Subeq Irregular | Mostly Subang-to- Angular; Subrnd | |
| Chrome spinel | Black | Opaque | Irregular | Wllrnd | |
| | Dark gray with red tint | Opaque | Equant | Subrnd | |
| Ilmenite | Black | Opaque | Irregular | Subrnd | |
| Rutile ± Anatase | Light buff | Opaque | Blocky | Subrnd | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | SlElng | Subrnd | |
| | Light buff | Opaque | Irregular | Subang | |
| | Light buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | SlElng | Subrnd | |
| | Buff | Opaque | SlElng | Subrnd | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|-------------------------|-----------------------------------|---------------------------|-----------|-----------|------------------------------------|
| Rutile ± Anatase | Buff | Opaque | SlElng | Subang | |
| | Buff | Opaque | Elongate | Subrnd | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Light golden amber | Opaque | Subeq | Subang | |
| | Light golden amber | Opaque | Blocky | Subang | |
| | Amber | Translucent | Subeq | Subang | |
| | Amber | Translucent | Irregular | Angular | |
| | Amber | Translucent- to-Opaque | Elongate | Angular | |
| | Amber | Opaque | Blocky | Subang | |
| Tourmaline ± Anatase | Very light yellow-green | Opaque | Subeq | Subang | |
| | Very light yellow-green | Opaque | Blocky | Subang | |
| | Very light yellow-green | Opaque | Irregular | Wllrnd | |
| | Light yellow- green | Opaque | Blocky | Subang | |
| | Light yellow- olive | Opaque | Blocky | Subrnd | White matrix |
| | Golden | Translucent | Blocky | Subang | |
| Zircon | Pale pink | Translucent | Blocky | Subrnd | 120 x 100 |
| | Pink | n.d. | n.d. | n.d. | n.d. (for size) |
| | Clear with very light yellow tint | Translucent | ShPrsm | Subhedral | 80 x 50 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|----------|--|-------------|--------|-----------|------------------------------------|
| Zircon | Clear with very light yellow tint | Translucent | Prsmtc | Euhedral | 110 x 40 |
| | Clear with very light yellow- green tint | Transparent | SlElng | Subang | 100 x 60 |
| | Clear with very light yellow- pink tint | Transparent | Blocky | Subrnd | 100 x 70 |

Subsamples 10.3210 g, 13.0639 g, and 15.3415 g ($\Sigma \approx 38.73$ g), continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|-------------------------------------|---|--|---|-----------------------------|---|
| Anatase (n = 98) | Very light peach-to-light peach Clear with very light yellow tint (minor) Light gray Beige | Mostly Opaque; Translucent- to-Opaque | Blocky Irregular SIEIng Subeq | Mostly Subrnd; Subang | |
| Anatase + K-feldspar (n = 23) | Clear with very light yellow tint Beige White | Translucent- to-Opaque | Typically Blocky; SIElng Irregular | Mostly Subang; Subrnd | |
| Rutile + Anatase | Light buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | Blocky | Subang | |
| | Brownish peach | Opaque | Blocky | Subang | Light greenish- gray matrix |
| Tourmaline | Light apple green | Opaque | Subeq | Subrnd | (1) Waxy |
| Zircon | Pink | Transparent | Prsmtc | Subhedral | 310 x 120 |

XRD ID: (1) G 10-5-05.

Jeerinah spherule layer sample X21-1

Subsamples 7.5830 g, 15.1772 g, 15.6521 g, 21.7690 g, 22.3758 g, 22.6439 g, 29.9445 g, 30.7247 g, 32.5125 g, 32.9150 g, and 34.2206 g ($\Sigma \approx 265.52$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|--------------------------------------|---|---|--|-----------------------------|---|
| Actinolite | Very light green | Transparent | Blocky | Subang | |
| Anatase (n = 3,041) | Very light peach-to-peach Light gray Light medium gray Clear with yellow tint Light yellow- green Amber Beige | Opaque; Translucent- to-Opaque (minor) | Subeq SIElng Blocky Equant Irregular | Mostly Subrnd; Subang | Commonly Admntn |
| Anatase + K-feldspar (n = 283) | Clear with light yellow tint Beige White | Opaque; Translucent- to-Opaque | Blocky SlElng Irregular Subeq | Subang Angular | |
| Anglesite | Light brownish gray | Opaque | Blocky | Subrnd | |
| | Colorless | Transparent | Subeq | Angular | |
| Barite | Clear with light yellow- green tint | Translucent- to-Opaque | Blocky | Subrnd | |
| | Clear with very light green tint | Translucent | Subeq | Subrnd | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------------------------|------------------------|---------------------------|--------|-----------|---|
| Barite | Colorless | Transparent | Blocky | Subrnd | |
| | Colorless | Transparent | SlElng | Subang | |
| | White | Opaque | Blocky | Subrnd | |
| | White | Opaque | SlElng | Subrnd | |
| | White | Opaque | SlElng | Subrnd | |
| | White | Opaque | SlElng | Subrnd | |
| Brookite | Light golden orange | Translucent- to-Opaque | Blocky | Subang | |
| Chrome spinel ± Anatase | Black | Opaque | Subeq | Subrnd | (1) |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subrnd | |
| | Black | Opaque | Subeq | Subang | |
| | Black | Opaque | Subeq | Subang | White anatase matrix |
| | Black | Opaque | Equant | Subrnd | (2) |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Subrnd | |
| | Black | Opaque | Equant | Wllrnd | |
| | Black | Opaque | Equant | Wllrnd | |
| | Black | Opaque | Equant | Wllrnd | |
| | Black | Opaque | Equant | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|----------------------------|--|--------------------------------|--------|-----------|---|
| Chrome spinel ± Anatase | Black | Opaque | Equant | Subang | |
| | Black | Opaque | Blocky | Subang | |
| | Black | Opaque | Blocky | Angular | |
| | Black | Opaque | Blocky | Angular | |
| | Black | Opaque | SlElng | Subrnd | |
| | Black | Opaque | SlElng | Subang | |
| | Black | Opaque | SlElng | Subang | |
| | Black | Opaque | Octhdl | Subang | |
| | Black | Opaque | n.d. | Subrnd | |
| | Dark steel gray-to-black | Opaque | SlElng | Subrnd | Anatase matrix |
| | Dark steel gray with slight red tint | Opaque | Equant | Wllrnd | |
| Clinopyroxene | Light yellow- green | Transparent | Blocky | Subang | |
| | Light yellow- green | Transparent | SlElng | Subrnd | |
| | Light yellow- green | Transparent- to-Translucent | Subeq | Subang | |
| Hematite | Black | Opaque | Blocky | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|--|--|---------------------------|--|--|---|
| Rutile \pm TiO ₂ II \pm Anatase (n = 196) | Light buff-to- buff Gray-buff Light peach- to-peach Light brown- peach Amber Light red- amber Clear with light yellow tint | Opaque | Blocky SIEIng Irregular Subeq Elongate | Mostly Subang and Subrnd; Angular | |
| Tourmaline | Very light olive green | Opaque | Blocky | Subang | |
| | Light olive green | Translucent- to-Opaque | Blocky | Subrnd | |
| | Light olive green | Opaque | SlElng | Subrnd | |
| | Olive green | Translucent- to-Opaque | Blocky | Subang | |
| | Olive green | Opaque | Irregular | Subrnd | |
| | Light yellow- green-to-apple green | Opaque | Blocky | Subrnd | |
| Zircon ± Anatase | Pale pink | Transparent | Blocky | Angular | 120 x 80 |
| | Pale pink | Transparent | ShPrsm | Subhedral | 120 x 60 |
| | Pale pink | Transparent | Prsmtc | Subhedral | 240 x 80 |
| | Pale pink | Translucent | ShPrsm | Subhedral | 120 x 80 |
| | Pale pink | Translucent | ShPrsm | Subhedral | 90 x 50 |
| | Pale pink | Translucent- to-Opaque | Blocky | Angular | 100 x 100 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|------------------|----------|--------------------------------|--------|-----------|---|
| Zircon ± Anatase | Pink | Transparent | Subeq | Subrnd | 80 x 60 |
| | Pink | Transparent | Subeq | Wllrnd | 90 x 80 |
| | Pink | Transparent | Subeq | Subang | 125 x 120 |
| | Pink | Transparent | Subeq | Subang | 80 x 80 |
| | Pink | Transparent | Blocky | Subrnd | 130 x 90 |
| | Pink | Transparent | Blocky | Subrnd | 100 x 80 |
| | Pink | Transparent | Blocky | Subang | 120 x 100 |
| | Pink | Transparent | Blocky | Subang | (3) 110 x 80 |
| | Pink | Transparent | Blocky | Subang | 100 x 100 |
| | Pink | Transparent | Blocky | Subang | 100 x 100 |
| | Pink | Transparent | Blocky | Subang | 100 x 80 |
| | Pink | Transparent | Blocky | Subang | 80 x 60 |
| | Pink | Transparent | Blocky | Angular | 120 x 100 |
| | Pink | Transparent | ShPrsm | Subhedral | 120 x 80 |
| | Pink | Transparent | ShPrsm | Subhedral | 110 x 100 |
| | Pink | Transparent | ShPrsm | Subhedral | 110 x 100 |
| | Pink | Transparent | Prsmtc | Subhedral | 200 x 100 |
| | Pink | Transparent | Prsmtc | Subhedral | 150 x 100 |
| | Pink | Transparent | Prsmtc | Subhedral | 140 x 50 |
| | Pink | Transparent | Prsmtc | Subhedral | 120 x 100 |
| | Pink | Transparent | Prsmtc | Subhedral | 120 x 70 |
| | Pink | Transparent | Prsmtc | Euhedral | 160 x 80 |
| | Pink | Transparent | Prsmtc | Subrnd | 140 x 80 |
| | Pink | Transparent | Prsmtc | Subang | 140 x 80 |
| | Pink | Transparent- to-Translucent | Blocky | Subang | 100 x 100 |
| | Pink | Translucent | Blocky | Subang | 120 x 80 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|------------------|---|---------------------------|--------|-----------|---|
| Zircon ± Anatase | Light champagne | Transparent | Blocky | Subang | 120 x 110 |
| | Light champagne | Translucent | Blocky | Angular | 80 x 80 |
| | Champagne | Transparent | Subeq | Subang | 80 x 80 |
| | Clear with very light yellow tint | Transparent | Blocky | Angular | 100 x 80 |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | 100 x 100 |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | 80 x 60 |
| | Clear with very light yellow tint | Translucent | ShPrsm | Subhedral | 140 x 80 |
| | Clear with very light yellow tint | Translucent- to-Opaque | Blocky | Subang | 140 x 80 |
| | Clear with very light yellow tint | Translucent- to-Opaque | Prsmtc | Subhedral | 170 x 80 |
| | Clear with very light yellow tint | Translucent- to-Opaque | Prsmtc | Subhedral | 160 x 80 |
| | Clear with very light yellow tint | Translucent- to-Opaque | Prsmtc | Subhedral | 140 x 70 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|------------------|---|---------------------------|-----------|-----------|---|
| Zircon ± Anatase | Clear with very light yellow tint | Translucent- to-Opaque | Prsmtc | Euhedral | 200 x 100 |
| | Clear with light yellow tint | Translucent | Blocky | Subang | 100 x 80 |
| | Clear with light yellow tint | Translucent | Blocky | Subang | 100 x 60 |
| | Clear with light yellow tint | Translucent | Blocky | Angular | 110 x 90 |
| | Clear with light yellow tint | Translucent | SlElng | Subang | 70 x 60 |
| | Clear with light yellow tint | Translucent | Irregular | Subang | 110 x 80 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subhedral | 140 x 80 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subhedral | 130 x 80 |
| | Clear with light yellow tint-to-white | Translucent- to-Opaque | Prsmtc | Subhedral | 220 x 80 |
| | Clear with light yellow- pink tint | Transparent | ShPrsm | Subhedral | 80 x 40 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|------------------|--|---------------------------|-----------|-----------|--|
| Zircon ± Anatase | Clear with light yellow- pink tint | Transparent | Prsmtc | Subhedral | 90 x 80 |
| | Clear with light yellow- pink tint | Translucent | Equant | Subrnd | 80 x 80 |
| | Clear with light yellow- pink tint | Translucent | Blocky | Subang | 80 x 80 |
| | Clear with light yellow- pink tint | Translucent | Prsmtc | Subhedral | 180 x 80 |
| | Clear with light yellow- pink tint | Translucent- to-Opaque | Blocky | Subang | 110 x 80 |
| | Clear with very light yellow-green tint | Translucent | ShPrsm | Subhedral | 100 x 80 |
| | Clear-to-white | Translucent | Prsmtc | Euhedral | 180 x 80 |
| Unidentified | Colorless | Transparent | Irregular | Angular | Very small peak at 1051 cm ⁻¹ on Raman spectrum |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) or (XRD ID) |
|--------------|---|---------------------------|----------|-----------|--|
| Unidentified | Colorless | Transparent | Blocky | Subang | A moderate peak at 520 cm ⁻¹ , and small peaks at 1051 and 1130 cm ⁻¹ on Raman spectrum |
| | Clear with very light yellow tint | Transparent | SIEIng | Subang | Small peaks at 1050 and 1130 cm ⁻¹ on Raman spectrum |
| | Clear with light yellow- green tint | Opaque | Blocky | Subang | A very small peak at 1051 cm ⁻¹ on Raman spectrum |
| | Light amber | Translucent- to-Opaque | Subeq | Subrnd | Small peaks at 856 and 1002 cm ⁻¹ on Raman spectrum |
| | Beige | Opaque | Elongate | Subrnd | Small peak at 223 cm ⁻¹ on Raman spectrum |

XRD ID: (1) G 10-19-05 (2) G 10-14-05 (3) G 10-16-05.

Appendix V

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE BEE GORGE (WITTENOOM) SAMPLES

Introductory Note: The following abbreviations are used in Appendix V:

Admntn = Adamantine; n = number of grains; n.d. = no data; Prsmtc = Prismatic;

ShPrsm = Short Prism; SlElng = Slightly Elongate; Subang = Subangular;

Subeq = Subequant; Subrnd = Subrounded; Wllrnd = Well-rounded.

Notes for sample BB: Sample BB consists of a spherule layer sandwiched between two context layers. There is no stratigraphic "up" arrow on the sample, so the relative age of the three layers is unknown. The spherule layer (sl) is referred to as "BB (sl)". One of the context layers is named "context layer #1" and it is referred to as "BB (#1)". The other context layer is named "context layer #2" and it is referred to as "BB (#2)".

Notes for samples 96714A and 96714B: The samples are from the same rock, and they are mirror images of one another. Each sample consists of a basal carbonate lutite (Bcl) context layer that is directly overlain by a spherule layer. The spherule layer consists of three subdivisions that were processed separately. In ascending stratigraphic order, the three subdivisions are as follows: 1) Lowermost spherule-rich sublayer (Lspsl) 2) Spherule-bearing lutite sublayer (Splsl) 3) Upper spherule/lutite sublayers (Usplsl).

Bee Gorge sample BB

Spherule layer (BB (sl))

Subsamples 9.8364 g, 10.6019 g, and 10.7999 g ($\Sigma \approx 31.24$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|------------|--|-------------|-----------|-----------|------------------------|
| Actinolite | Clear with very light green-yellow tint | Transparent | Prsmtc | Subhedral | |
| | Clear with very light green tint | Transparent | SlElng | Subang | |
| Anatase | Very light peach | Opaque | SlElng | Subrnd | |
| | Light peach | Opaque | Subeq | Subrnd | |
| | Light peach | Opaque | Subeq | Subrnd | |
| | Very light yellow-green | Opaque | Subeq | Subang | |
| | Very light buff | Opaque | Irregular | Subang | |
| | Medium gray | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subang | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
Spherule layer (BB (sl)), continued

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|-------------------------|------------------------------------|---------------------------|-----------|-----------|------------------------|
| Anatase | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | SlElng | Subrnd | |
| | Beige | Opaque | SlElng | Subrnd | |
| | Beige | Opaque | SlElng | Subrnd | |
| | Beige | Opaque | Irregular | Subang | |
| | Beige | Opaque | Irregular | Subang | |
| | Clear-to- white | Translucent- to-Opaque | Blocky | Subang | |
| | Clear-to- white | Translucent- to-Opaque | Blocky | Subang | |
| Anatase + K-feldspar | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Angular | |
| | Clear with light yellow tint | Translucent- to-Opaque | SlElng | Angular | |
| | Clear with yellow tint | Opaque | Blocky | Subang | |
| | Light gray | Opaque | Blocky | Subrnd | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | Subeq | Subang | |
| | White | Opaque | Blocky | Subang | |
| | White | Opaque | Blocky | Subang | |
| | White | Opaque | Blocky | Subang | |
| | White | Opaque | Irregular | Angular | |
| Chrome spinel | Dark brownish black | Opaque | Subeq | Subang | |

Spherule layer (BB (sl)), continued

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|------------------|------------------------------------|-------------|--------|-----------|------------------------|
| Clinozoisite | Clear with light yellow tint | Transparent | Blocky | Subrnd | |
| Monazite | Clear with light golden tint | Transparent | Equant | Subrnd | |
| | Clear with yellow tint | Transparent | Blocky | Subang | |
| Rutile ± Anatase | Light peach | Opaque | Subeq | Subrnd | |
| | Peach | Opaque | Equant | Subrnd | Waxy |
| | Peach | Opaque | Blocky | Subrnd | Waxy |
| | Light orange- peach | Opaque | SIEIng | Subrnd | Waxy |
| | Light brownish peach | Opaque | Subeq | Subrnd | |
| | Light brownish peach | Opaque | Subeq | Subrnd | Waxy |
| | Yellow- peach | Opaque | Subeq | Subrnd | Waxy |
| | Light reddish brown | Opaque | SlElng | Subrnd | |
| | Light buff | Opaque | Subeq | Subrnd | |
| | Buff | Opaque | Subeq | Subrnd | Waxy |
| | Buff | Opaque | Subeq | Subrnd | Waxy |
| | Buff | Opaque | Subeq | Subrnd | Waxy |
| | Buff | Opaque | Subeq | Subrnd | Waxy |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | SlElng | Subrnd | Waxy |

Spherule layer (BB (sl)), continued

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|-------------------------|---|-------------|--------|-----------|------------------------|
| Rutile ± Anatase | Light brownish buff | Opaque | Blocky | Subrnd | |
| | Light brownish buff | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subang | |
| | White | Opaque | Blocky | Subrnd | |
| Tourmaline ± Anatase | Light brownish green | Translucent | Prsmtc | Subhedral | |
| | Olive green | Translucent | ShPrsm | Subhedral | |
| | Olive green | Translucent | ShPrsm | Subhedral | |
| Zircon | Clear with yellow tint | Transparent | Blocky | Subang | 85 x 65 |
| | Clear with light yellow- green tint | Transparent | Prsmtc | Subrnd | 100 x 60 |
| | Clear with light yellow- green tint | Transparent | SlElng | Subrnd | 90 x 60 |

Spherule layer (BB (sl)), continued

Subsamples 9.8364 g, 10.6019 g, and 10.7999 g ($\Sigma \approx 31.24$ g), continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|-------------------------|------------------------------------|---------------------------|-----------|-----------|
| Actinolite | Clear with light yellow-green tint | Translucent | Elongate | Subang |
| Anatase | Beige | Opaque | Subeq | Subrnd |
| | Beige | Opaque | Irregular | Subrnd |
| Anatase + K-feldspar | Clear with very light yellow tint | Translucent | Blocky | Subang |
| | Beige | Opaque | Blocky | Subrnd |
| | Beige | Opaque | Blocky | Subrnd |
| | Beige | Opaque | Blocky | Subang |
| | Beige | Opaque | Blocky | Subang |
| | Beige | Opaque | Blocky | Subang |
| | Beige | Opaque | SlElng | Subrnd |
| | Clear-to-white | Translucent- to-Opaque | Blocky | Subang |
| | White | Opaque | Blocky | Subang |
| Clinozoisite | Clear with very light yellow tint | Transparent | Elongate | Subang |

Context layer #1 (BB (#1))

Subsample 5.4035 g

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Size (µm) |
|---------------------------|---|-------------|--------|-----------|--------------|
| Anatase | White | Opaque | Subeq | Subrnd | |
| Clinozoisite + Anatase | Clear with very light green-yellow tint | Translucent | SlElng | Subang | |
| Rutile ± Anatase | Peach | Opaque | Blocky | Subrnd | |
| | Peach | Opaque | SlElng | Subrnd | |
| | Buff | Opaque | SlElng | Subrnd | |
| Tourmaline ± Anatase | Olive green | Translucent | Blocky | Subang | |
| | Olive green | Translucent | Blocky | Subang | |
| | Dark olive green | Transparent | SlElng | Subang | |
| Zircon | Clear with light green-yellow tint | Translucent | Prsmtc | Subhedral | 120 x 50 |

Context layer #2 (BB (#2))

Subsample 14.89 g

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|---------------------|--------------------------------------|-------------|--------|-----------|------------------------|
| Anatase | Light peach | Opaque | Blocky | Subrnd | |
| | Light peach | Opaque | SlElng | Subang | |
| | Clear with very light yellow tint | Opaque | Blocky | Subang | |
| | Clear with very light yellow tint | Opaque | Blocky | Subang | |
| Anglesite | Clear with very light yellow tint | Translucent | Blocky | Subrnd | |
| Chrome spinel | Dark brownish black | Opaque | Blocky | Subang | |
| Clinozoisite | Clear with light yellow tint | Translucent | Blocky | Subrnd | |
| Rutile ± Anatase | Light peach | Opaque | Blocky | Subrnd | Waxy |
| | Light peach | Opaque | Blocky | Subrnd | |
| | Peach | Opaque | Blocky | Subrnd | |
| | Peach | Opaque | Blocky | Subrnd | |
| | Peach | Opaque | Blocky | Subrnd | Waxy |
| | Orange-peach | Opaque | Blocky | Subrnd | Waxy |
| | Light golden peach | Opaque | SlElng | Subrnd | |
| | Amber | Translucent | Blocky | Subrnd | |
| | Golden amber | Transparent | Blocky | Subrnd | |
| | Light buff | Opaque | Blocky | Subrnd | Waxy |
| | Light buff | Opaque | Blocky | Subrnd | |
| | Light buff | Opaque | Blocky | Subrnd | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | Blocky | Subrnd | |

Context layer #2 (BB (#2)), continued

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Size (µm) |
|------------|---|-------------|-----------|-----------|------------------------|
| Tourmaline | Olive green | Transparent | Irregular | Subrnd | |
| | Olive green | Translucent | Blocky | Subang | |
| | Light yellow-green | Transparent | Blocky | Subang | |
| | Light greenish golden | Translucent | Prsmtc | Subhedral | |
| Zircon | Amber | Translucent | ShPrsm | Subhedral | 100 x 50 |
| | Clear with very light yellow tint | Translucent | ShPrsm | Subrnd | 100 x 60 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subhedral | 100 x 60 |
| | Clear with yellow tint | Translucent | Subeq | Subang | 110 x 100 |
| | Clear with very light yellow-green tint | Transparent | Prsmtc | Subhedral | 110 x 60 |
| | Clear with light green tint | Transparent | Prsmtc | Subhedral | 100 x 60 |

Bee Gorge sample 96714A

Basal carbonate lutite (Bcl) context layer

Subsamples 6.8001 g, 9.5376 g, 10.0687 g, 10.5610 g, 10.9594 g, 11.1877 g, 11.4911 g,

and 11.6547 g ($\Sigma \approx 82.26$ g)

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|-------------------------------------|--|---|--|--|--------------|
| Anatase | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subang | |
| | Beige | Opaque | SlElng | Subang | |
| | Beige | Opaque | Irregular | Subang | |
| | Beige | Opaque | Irregular | Angular | |
| | Clear-to-beige | Opaque | Blocky | Subang | |
| Anatase + K-feldspar (n = 31) | Mostly Beige Clear with light yellow tint Clear-to-white White | Mostly Opaque; Translucent Translucent- to-Opaque | Mostly Blocky and Subeq; SIEIng Elongate | Mostly Subang; Subrnd Angular | |
| Rutile ± Anatase | Beige | Opaque | Subeq | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Irregular | Subang | |
| | Black | Opaque | Blocky | Subang | (+ Hematite) |

Lowermost spherule-rich sublayer (Lspsl)

Subsamples 7.3433 g and 8.5769 g ($\Sigma \approx 15.92$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Texture |
|----------------------------------|--|-------------|---|--|----------------------|
| Almandine | Clear with light green tint | Transparent | Subeq | Subang | Glassy |
| Anatase | Beige | Opaque | Blocky | Subang | |
| Anatase + K-feldspar | Clear with very light yellow tint | Translucent | Blocky | Subang | |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | |
| Rutile ± Anatase (n = 515) | Grayish yellow Medium dark gray and yellow | Opaque | Mostly Irregular; Blocky SIElng Subeq | Angular Subang Subrnd (minor) | Appears grainy |

Spherule-bearing lutite sublayer (Splsl)

Subsample 10.3574 g

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|-------------------------|------------------------------|-------------|-----------|-----------|
| Anatase + K-feldspar | Clear with light yellow tint | Translucent | Blocky | Angular |
| | Beige | Opaque | Subeq | Subrnd |
| | Beige | Opaque | Blocky | Subang |
| Anglesite | Clear with light yellow tint | Translucent | Irregular | Angular |

Upper spherule/lutite sublayers subdivision (Usplsl)

Subsamples 8.4057 g and 8.7879 g ($\Sigma \approx 17.19$ g)

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|-------------------------|---|-------------|-----------|-----------|-----------------------|
| Anatase | Clear with yellow tint | Opaque | Subeq | Subang | |
| | Very light buff | Opaque | Subeq | Subrnd | |
| | Very light buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | SlElng | Subrnd | |
| | Very light gray | Opaque | Blocky | Subang | |
| | Beige | Opaque | Subeq | Subrnd | |
| Anatase + K-feldspar | Clear with very light yellow tint | Translucent | Blocky | Subang | |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | |
| | Clear with very light yellow tint | Opaque | Blocky | Subang | |
| Anglesite | Clear with very light green tint | Transparent | Subeq | Subrnd | |
| | Clear with very light green- yellow tint | Transparent | Blocky | Subang | |
| Rutile ± Anatase | Very light peach | Opaque | Subeq | Subang | |
| | Very light peach | Opaque | Blocky | Subrnd | |
| | Very light peach | Opaque | n.d. | Subrnd | |
| | Peach | Opaque | Subeq | Subrnd | |
| | Peach | Opaque | SlElng | Subrnd | |
| | Very light buff | Opaque | Blocky | Subrnd | + TiO ₂ II |
| | Very light buff | Opaque | Blocky | Subrnd | + TiO ₂ II |
| | Light buff | Opaque | Subeq | Subrnd | |
| | Light buff | Opaque | Subeq | Subrnd | |
| | Light buff | Opaque | Subeq | Subrnd | |

| Opper spherule/lutile sublayers suburvision (Ospisi), contin |
|--|
|--|

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|---------------------|------------|-------------|--------|-----------|-----------------------|
| Rutile ± Anatase | Light buff | Opaque | Subeq | Subrnd | |
| | Light buff | Opaque | Subeq | Subrnd | |
| | Light buff | Opaque | Subeq | Subang | |
| | Light buff | Opaque | Subeq | Subang | |
| | Light buff | Opaque | Subeq | Subang | |
| | Light buff | Opaque | Subeq | Subang | |
| | Light buff | Opaque | Subeq | Subang | |
| | Light buff | Opaque | Subeq | Subang | |
| | Light buff | Opaque | Blocky | Subrnd | |
| | Light buff | Opaque | Blocky | Subrnd | |
| | Light buff | Opaque | Blocky | Subang | + TiO ₂ II |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | Subeq | Subrnd | |
| | Buff | Opaque | Subeq | Subrnd | |
| | Buff | Opaque | Subeq | Subang | |
| | Buff | Opaque | Subeq | Subang | |
| | Buff | Opaque | Subeq | Subang | |
| | Buff | Opaque | Subeq | Angular | |
| | Buff | Opaque | Equant | Subrnd | |
| | Buff | Opaque | Equant | Subang | |
| | Buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | Blocky | Subang | |

| opper spherale, facte sucha, ets such iston (ospisi), continue | Upp | er spherule/ | lutite sublayers | s subdivision | (Usplsl), | continued |
|--|-----|--------------|------------------|---------------|-----------|-----------|
|--|-----|--------------|------------------|---------------|-----------|-----------|

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|---------------------|-------------------|-------------|-----------|-----------|-------|
| Rutile ± Anatase | Buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | SlElng | Subrnd | |
| | Buff | Opaque | SlElng | Subang | |
| | Buff | Opaque | SlElng | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | n.d. | Wllrnd | |
| | Light olive gray | Opaque | Equant | Subrnd | |
| | Light olive gray | Opaque | Equant | Subrnd | |
| | Light olive gray | Opaque | n.d. | Subrnd | |
| | Light yellow gray | Opaque | Subeq | Subrnd | |
| | Light yellow gray | Opaque | Subeq | Subrnd | |
| | Light yellow gray | Opaque | Blocky | Subrnd | |
| | Light yellow gray | Opaque | Blocky | Subang | |
| | Light yellow gray | Opaque | Blocky | Subang | |
| | Light yellow gray | Opaque | Irregular | Subang | |
| | Light yellow gray | Opaque | Irregular | Subang | |
| | Light medium gray | Opaque | Subeq | Subrnd | |
| | Light medium gray | Opaque | Subeq | Subrnd | |
| | Light medium gray | Opaque | Subeq | Subrnd | |
| | Light medium gray | Opaque | Subeq | Subrnd | |
| | Light medium gray | Opaque | Blocky | Subang | |
| | Light medium gray | Opaque | SlElng | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |

Bee Gorge sample 96714B

Basal carbonate lutite (Bcl) context layer

Subsamples 9.5155 g, 10.3847 g, 10.7160 g, 11.0042 g, and 11.1367 g ($\Sigma \approx 52.76$ g)

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|-------------------------|-----------------------------------|---------------------------|----------|-----------|
| Anatase | Clear with very light yellow tint | Translucent-to- Opaque | Blocky | Subrnd |
| | Clear with light yellow tint | Opaque | SlElng | Subang |
| | Clear-to-light gray | Opaque | Subeq | Subrnd |
| | Clear-to-light gray | Opaque | Subeq | Subang |
| | Clear-to-light gray | Opaque | Subeq | Subang |
| | Clear-to-light gray | Opaque | Blocky | Subang |
| | Clear-to-light gray | Opaque | Blocky | Subang |
| | Clear-to-light gray | Opaque | Blocky | Subang |
| | Clear-to-light gray | Opaque | Blocky | Subang |
| | Beige | Opaque | Subeq | Subang |
| | White | Opaque | Elongate | Subang |
| Anatase + K-feldspar | Clear-to-light gray | Translucent-to- Opaque | Subeq | Subang |
| Sillimanite | Clear with very light golden tint | Transparent | Blocky | Subang |

Lowermost spherule-rich sublayer (Lspsl)

Subsample 13.8178 g

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Texture |
|----------------------------------|---|-------------|---|--|----------------------|
| Anatase | Clear with very light yellow tint | Opaque | Blocky | Subang | |
| | Light gray | Opaque | Subeq | Subrnd | |
| | Light gray | Opaque | Subeq | Subrnd | |
| Anatase + K-feldspar | Light gray | Opaque | Blocky | Subang | |
| Monazite | Light gray | Opaque | Subeq | Subang | Admntn |
| Rutile ± Anatase (n = 434) | Grayish yellow Medium dark gray and yellow Light gray (one grain) | Opaque | Mostly Irregular; Blocky SIElng Subeq | Angular Subang Subrnd (minor) | Appears grainy |

Spherule-bearing lutite sublayer (Splsl)

Subsamples 6.5066 g and 12.0772 g ($\Sigma \approx 18.58$ g)

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Texture |
|-------------------------|--------------------------------------|---------------------------|-----------|-----------|---------|
| Actinolite | Light green | Transparent | Prsmtc | Subhedral | |
| | Light green | Transparent | Blocky | Angular | |
| Anatase | Very light peach | Opaque | Subeq | Subrnd | |
| | Light grayish brown | Opaque | Prsmtc | Subang | |
| | Light gray | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subang | |
| | Beige | Opaque | SlElng | Subang | |
| | White | Opaque | Blocky | Subang | |
| Anatase + K-feldspar | Clear with very light yellow tint | Transparent | Blocky | Subang | |
| | Clear with very light yellow tint | Translucent- to-Opaque | Blocky | Subang | |
| | Clear with very light yellow tint | Translucent- to-Opaque | Blocky | Angular | |
| | Clear with very light yellow tint | Translucent- to-Opaque | Blocky | Angular | |
| | Clear with light yellow tint | Opaque | Blocky | Angular | |
| Rutile ± Anatase | Grayish yellow | Opaque | Subeq | Subrnd | Grainy |
| | Grayish yellow | Opaque | SlElng | Subang | Grainy |
| | Grayish yellow | Opaque | SlElng | Subang | Grainy |
| | Grayish yellow | Opaque | Irregular | Subang | Grainy |
| | Grayish yellow | Opaque | Irregular | Subang | Grainy |
| | Grayish yellow | Opaque | Irregular | Subang | Grainy |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Texture |
|---------------------|--------------------------------|-------------|-----------|-----------|---------|
| Rutile ± Anatase | Medium dark gray-to- yellow | Opaque | Irregular | Subang | Grainy |
| | Medium dark gray-to- yellow | Opaque | Irregular | Angular | Grainy |
| | Medium dark gray | Opaque | Subeq | Subrnd | |
| | White | Opaque | Blocky | Subang | |

Spherule-bearing lutite sublayer (Splsl), continued

Upper spherule/lutite sublayers subdivision (Usplsl)

Subsample 14.2225 g

Size Fraction: $63-125 \ \mu m$

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|-------------------------|--|-------------------------------|-----------|-----------|-------|
| Anatase | Light gray | Opaque | Irregular | Subrnd | |
| Anatase + Xenotime | Clear with light yellow tint | Opaque | Irregular | Subang | |
| | Clear with light yellow tint | Opaque | Irregular | Subang | |
| | Clear with light yellow tint | with light yellow tint Opaque | | Subang | |
| | Clear with light yellow tint | Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Opaque | Subeq | Subang | |
| Anatase + K-feldspar | se + Clear with very light yellow Transl | | Blocky | Subang | |
| | Clear with light yellow tint | Translucent | Blocky | Angular | |
| Monazite | Light gray | Opaque | Subeq | Subrnd | |
| Rutile ± Anatase | Very light buff Opaque | | Blocky | Subang | |
| | Light buff | Opaque | Subeq | Subrnd | |
| | Light buff | Opaque | Subeq | Subrnd | |

| Upper spherule/lutite sublayers subdivision (Uspisi), contin |
|--|
|--|

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|---------------------|--------------------------|-------------|-----------|-----------|-----------------------|
| Rutile ± Anatase | Light buff | Opaque | Subeq | Subrnd | |
| | Light buff | Opaque | Blocky | Subrnd | |
| | Light buff | Opaque | Blocky | Subrnd | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | SlElng | Subrnd | |
| | Light buff | Opaque | Elongate | Subang | |
| | Light buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | Blocky | Subang | |
| | Buff | Opaque | SlElng | Subrnd | |
| | Buff | Opaque | SlElng | Subrnd | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Very light brownish buff | Opaque | Subeq | Subrnd | |
| | Light grayish buff | Opaque | Subeq | Subrnd | + TiO ₂ II |
| | Light grayish buff | Opaque | Irregular | Subang | + TiO ₂ II |
| | Light gray-to-light buff | Opaque | Subeq | Subrnd | |
| | Light gray-to-light buff | Opaque | Blocky | Subang | |
| | Light grayish yellow | Opaque | Subeq | Subang | |
| | Light grayish yellow | Opaque | Blocky | Subang | |
| | Light gray | Opaque | Subeq | Subang | |
| | Light medium gray | Opaque | Blocky | Subang | |
| | Medium gray | Opaque | Subeq | Subang | |
| | Medium gray | Opaque | Blocky | Subrnd | |
| | Medium gray | Opaque | SlElng | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|----------|------------------------------|-------------|--------|-----------|-------|
| Xenotime | Clear with light yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Transparent | Blocky | Subang | |
| | Clear with yellow tint | Transparent | Blocky | Subang | |
| | Clear with yellow tint | Transparent | Blocky | Angular | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Angular | |
| | Clear with yellow tint | Translucent | Blocky | Angular | |

Upper spherule/lutite sublayers subdivision (Usplsl), continued

Bee Gorge context sample 92058

Heavy mineral grains from subsample 236.3 g

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|---|--------------------------------|-----------|-----------|---|
| Anatase | Clear with light yellow tint | Translucent | Blocky | Subang | |
| | Clear-to-light gray | Opaque | Irregular | Angular | |
| | Clear-to-medium- gray | Opaque | Subeq | Subrnd | |
| | Light medium gray | Opaque | Blocky | Subrnd | |
| | Medium gray | Opaque | Subeq | Subrnd | |
| | Light gray-to-beige | Opaque | Blocky | Subrnd | |
| Monazite ± Anatase | Clear with very light yellow tint | Translucent- to-Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Transparent | Subeq | Subrnd | |
| | Clear with light yellow tint | Transparent | Blocky | Subang | |
| | Clear with light yellow tint | Transparent- to-Translucent | Irregular | Subang | |
| | Clear with light yellow tint | Translucent | Blocky | Angular | |
| | Clear with light yellow tint | Translucent | Irregular | Angular | Occurs as matrix on dark gray quartz (chert?) grains |
| | Clear with light yellow tint | Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Opaque | Irregular | Subang | |
| | Clear with light yellow tint-to-light olive | Opaque | Irregular | Angular | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|-----------------------------|---------------------------|-----------|-----------|--|
| Monazite ± Anatase | Clear with yellow tint | Transparent | Blocky | Subang | |
| | Clear with yellow tint | Transparent | Irregular | Subang | |
| | Clear with yellow tint | Translucent | Blocky | Subang | |
| | Light brownish gray | Opaque | Subeq | Subang | |
| | Very light olive | Opaque | Subeq | Subang | |
| | Light olive gray | Opaque | Subeq | Subrnd | |
| | Light olive gray | Opaque | SlElng | Subrnd | |
| | Medium dark gray | Opaque | Blocky | Subrnd | |
| | Medium dark gray | Opaque | n.d. | Subrnd | |
| | Clear-to-light gray | Opaque | Subeq | Subang | |
| | Clear-to-light gray | Opaque | Irregular | Subang | |
| | Light gray-to-white | Opaque | Blocky | Subrnd | |
| | Clear-to-beige | Translucent- to-Opaque | Blocky | Subrnd | |
| | Colorless | Opaque | Blocky | Subang | |
| | Light yellow-green | Translucent | Irregular | Angular | Occurs as matrix on a dark gray quartz (chert?) grain |
| Rutile + Monazite | Very light brownish gray | Opaque | Subeq | Subrnd | |
| Rutile ± Xenotime | Dark gray | Opaque | Subeq | Subrnd | |
| | Light gray-to-white | Translucent- to-Opaque | Subeq | Subrnd | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|--------------------------------------|-------------|-----------|-----------|---|
| Xenotime ± Anatase | Clear with very light yellow tint | Transparent | Blocky | Subang | |
| | Clear with very light yellow tint | Translucent | Blocky | Subang | |
| | Clear with very light yellow tint | Translucent | Irregular | Angular | Occurs as matrix on a medium gray, opaque grain |
| | Clear with very light yellow tint | Translucent | Irregular | Angular | Occurs as matrix on a medium dark gray, opaque grain |
| | Clear with very light yellow tint | Opaque | Subeq | Subrnd | |
| | Clear with very light yellow tint | Opaque | Blocky | Subang | Attached to a medium dark gray, opaque quartz (chert?) grain |
| | Clear with light yellow tint | Translucent | Irregular | Subang | |
| | Clear with light yellow tint | Translucent | Irregular | Angular | |
| | Clear with light yellow tint | Translucent | Irregular | Angular | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|---------------------------------------|---------------------------|-----------|-----------|---|
| Xenotime ± Anatase | Clear with light yellow tint | Translucent | Irregular | Angular | Occurs as matrix on a medium dark gray quartz (chert?) grain |
| | Clear with light yellow tint | Translucent- to-Opaque | Subeq | Subang | |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Translucent- to-Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Translucent- to-Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Translucent- to-Opaque | Irregular | Angular | Occurs as matrix on a dark gray, opaque quartz (chert?) grain |
| | Clear with light yellow-green tint | Translucent | Subeq | Subrnd | |
| | Clear with light yellow-olive tint | Translucent | Irregular | Angular | Occurs as matrix on a medium dark gray, opaque grain |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|-------------------------------------|-------------|-----------|-----------|--|
| Xenotime ± Anatase | Clear with very light olive tint | Opaque | Irregular | Subang | Occurs as matrix on a medium dark gray, opaque grain |
| | Very light olive-to- medium gray | Opaque | Blocky | Subrnd | |
| | Very light olive gray | Translucent | Irregular | Angular | Occurs as matrix on a dark steel gray, opaque grain |
| | Light olive | Opaque | Blocky | Subang | |
| | Light olive gray | Translucent | Irregular | Angular | Occurs as matrix on a medium dark gray, opaque grain |
| | Light olive gray | Translucent | Irregular | Angular | Occurs as matrix on a medium dark gray, opaque quartz (chert?) grain |
| | Light olive gray | Translucent | Irregular | Angular | Occurs as matrix on a medium dark gray, opaque quartz (chert?) grain |
| | Light olive gray | Opaque | Subeq | Subrnd | |
| | Light olive gray | Opaque | Equant | Subrnd | |
| | Light olive gray | Opaque | Irregular | Subang | |
| | Light gray | Opaque | Blocky | Subang | |
| | Medium dark gray | Opaque | Subeq | Subang | |
| | Medium dark gray | Opaque | Blocky | Subrnd | |
| | Medium dark gray | Opaque | Blocky | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|---------------------|-------------|-----------|-----------|--------------------|
| Xenotime ± Anatase | Medium dark gray | Opaque | Blocky | Subang | |
| | Medium dark gray | Opaque | Irregular | Subang | |
| | Dark gray | Opaque | Equant | Subrnd | |
| | Dark gray | Opaque | Equant | Wllrnd | |
| | Light gray-to-beige | Opaque | Subeq | Subang | |
| | Light gray-to-beige | Opaque | Blocky | Subrnd | |
| | Light gray-to-beige | Opaque | Blocky | Subang | |
| | Clear-to-light gray | Opaque | Subeq | Subang | |
| | Clear-to-light gray | Opaque | Blocky | Subang | |
| | Clear-to-light gray | Opaque | Irregular | Subang | |
| | Clear-to-beige | Opaque | Subeq | Subrnd | Admntn |
| | Clear-to-beige | Opaque | Blocky | Subang | |
| | Clear-to-beige | Opaque | Blocky | Subang | Admntn |
| | Beige | Opaque | Blocky | Subrnd | Admntn |
| | Beige | Opaque | Blocky | Subang | |
| | White | Opaque | Subeq | Subrnd | |

Heavy mineral grains from subsample 236.3 g, continued

Size Fraction: 125-250 μm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|-----------------------|--------------------------------------|---------------------------|-----------|-----------|--|
| Actinolite | Dark olive green | Translucent- to-Opaque | SlElng | Subang | |
| Anatase | Beige | Opaque | SlElng | Subrnd | |
| Monazite | Clear with light yellow tint | Translucent- to-Opaque | SlElng | Subrnd | |
| | Clear with yellow tint | Transparent | Blocky | Subang | |
| Xenotime ± Anatase | Clear with very light yellow tint | Translucent | Irregular | Angular | Occurs as matrix on a light olive, opaque quartz (chert?) grain |
| | Clear with very light yellow tint | Opaque | Irregular | Angular | Occurs as matrix on a beige anatase grain |
| | Very light olive gray | Opaque | Blocky | Subrnd | |
| | Light gray | Translucent | Irregular | Angular | Occurs as matrix on a dark medium gray, opaque quartz (chert?) grain |
| | Light gray-to-beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Irregular | Subang | |

Appendix W

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE MONTEVILLE SPHERULE LAYER SAMPLES

Introductory Note: The following abbreviations are used in Appendix W:

Admntn = Adamantine; n = number of grains; n.d. = no data; Prsmtc = Prismatic;

ShPrsm = Short Prism; SlElng = Slightly Elongate; Subang = Subangular;

Subeq = Subequant; Subrnd = Subrounded; Wllrnd = Well-rounded.

Monteville spherule layer sample U63-1

Subsamples 278.0 g and 315.2 g ($\Sigma = 593.2$ g)

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster |
|------------------------------------|--|--------------------------------------|---|-----------------------------|----------------|
| Anatase (n = 974) | Very light peach- to-light peach (minor) Light-to-medium gray Clear with light yellow tint Cream Beige | Opaque | Mostly Blocky, Subeq, and SIEIng; Irregular Elongate Equant | Subrnd Subang | |
| Chlorite | Clear with light yellow-green tint | Translucent | Irregular | Subang | |
| Monazite ± Anatase (n = 209) | Clear with very light-to-light yellow tint | Translucent- to-Opaque; Opaque | Irregular Blocky Subeq SlElng | Subang Angular Subrnd | Some Admntn |
| Rutile ± Anatase | Very light buff | Opaque | Subeq | Subrnd | |
| | Very light buff | Opaque | Subeq | Subrnd | |
| | Very light buff | Opaque | Subeq | Subang | |
| | Very light buff | Opaque | Irregular | Subang | |
| | Very light buff | Opaque | Irregular | Subang | |
| | Light buff | Opaque | Blocky | Subang | |
| | Light buff | Opaque | Irregular | Subang | |
| | Light buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Subeq | Subrnd | |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | Blocky | Subrnd | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |
| | Buff | Opaque | Irregular | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster |
|--------------------------|-----------------------------------|-------------|-----------|-----------|--------|
| Rutile ± Anatase | Beige | Opaque | Blocky | Subrnd | |
| | Beige with very light yellow tint | Opaque | Irregular | Subrnd | |
| | Light brownish amber | Opaque | Irregular | Subang | |
| Rutile + Unidentified | White | Opaque | Irregular | Subang | |
| Tourmaline ± Anatase | Clear with golden tint | Translucent | Prsmtc | Subang | |
| | Clear with light olive tint | Translucent | Acicular | Angular | |
| | Clear with light olive tint | Translucent | Acicular | Angular | |

Subsamples 278.0 g and 315.2 g ($\Sigma = 593.2$ g), continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|-------------------------|--------------------------------------|---------------------------|--|------------------|------------------------------------|
| Anatase (n = 82) | Light gray Beige | Opaque | Blocky Subeq SIEIng Irregular | Subrnd Subang | |
| Anatase + K-feldspar | Very light peach | Opaque | Subeq | Subrnd | |
| | Very light peach | Opaque | Irregular | Subang | |
| | Clear with light yellow tint | Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Opaque | Irregular | Subang | |
| | White | Opaque | Irregular | Angular | Anatase matrix on K-feldspar |
| Monazite | Clear with very light yellow tint | Translucent- to-Opaque | Blocky | Subang | |
| | Clear with very light yellow tint | Translucent- to-Opaque | Blocky | Angular | |
| | Clear with very light yellow tint | Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Opaque | Subeq | Subang | |
| | Clear with light yellow tint | Opaque | Subeq | Subang | |
| | Clear with light yellow tint | Opaque | Blocky | Subrnd | |
| | Clear with light yellow tint | Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Opaque | SlElng | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|---------------------|------------------------------|-------------|-----------|-----------|-------|
| Monazite | Clear with light yellow tint | Opaque | SlElng | Subang | |
| | Clear with light yellow tint | Opaque | SlElng | Subang | |
| | Clear with light yellow tint | Opaque | Irregular | Angular | |
| Rutile + Anatase | Very light buff | Opaque | Blocky | Subrnd | |
| | Very light buff | Opaque | Blocky | Subrnd | |
| | Very light buff | Opaque | Blocky | Subang | |
| | Very light buff | Opaque | SlElng | Subang | |
| | Light buff | Opaque | Irregular | Subang | |

Size Fraction: 125-250 µm, continued

Monteville spherule layer sample V111

Subsample 219.9 g

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|--|---|--|---|--|------------------------------------|
| Actinolite | Light green | Transparent | Bladed | Subang | |
| | Green | Transparent | Elongate | Subhedral | |
| | Dark green | Transparent | Elongate | Subang | |
| Anatase ± K-feldspar (n = 1,566) | Mostly Beige and light gray; Light medium gray Clear with light yellow tint Beige-to-white Very light buff Very light peach | Mostly Opaque; Translucent- to-Opaque | Mostly Blocky and Subeq; SIEIng Irregular Equant | Mostly Subrnd and Subang; Angular Wllrnd | |
| Anglesite | Clear with very light yellow tint | Opaque | Equant | Subang | Admntn |
| Chlorite ± Anatase | Clear with light yellow- green tint | Translucent | Blocky | Subang | |
| | Very light olive green | Translucent | Blocky | Subang | Has a matrix |
| Chrome spinel ± Anatase | Dark gray | Opaque | Subeq | Subang | Clear-to- light green matrix |
| | Dark gray | Opaque | Subeq | Subang | Clear-to- light green matrix |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|--|---|---|--|--|------------------------------------|
| Chrome spinel ± Anatase | Dark steel gray | Opaque | Subeq | n.d. | Clear-to- light green matrix |
| | Dark steel gray | Opaque | SlElng | Subrnd | Clear-to- light green matrix |
| | Black | Opaque | Subeq | Subrnd | Clear-to- light green matrix |
| Clinopyroxene | Very light olive green | Transparent | Bladed | Subrnd | |
| | Light yellow- green | Transparent | Blocky | Subang | |
| Monazite ± Anatase (n = 785) | Clear with very light yellow-to-light yellow tint | Translucent- to-Opaque; Opaque | Mostly Irregular and Blocky; SIElng Subeq | Mostly Subang; Angular Subrnd | Some Admntn |
| Rutile \pm TiO ₂ II \pm Anatase (n = 347) | Very light buff-to-buff Grayish buff Very light peach-to-peach Light brownish amber Light golden- to-golden amber Amber Light brown Very light-to- light brownish gray | Mostly Opaque; the various shades of amber can be Transparent- to-Translucent | Blocky Subeq Irregular SIElng; the various shades of amber can be Elongate | Mostly Subrnd and Subang | Some are Waxy or Admntn |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|-------------------------|------------------------|---------------------------|-----------|-----------|------------------------------------|
| Tourmaline ± Anatase | Very light olive green | Translucent | Subeq | Subang | |
| | Very light olive green | Translucent | Irregular | Angular | |
| | Light olive green | Transparent | Blocky | Subang | |
| | Light olive green | Transparent | Blocky | Subang | |
| | Light olive green | Transparent | ShPrsm | Subang | |
| | Light olive green | Translucent | Blocky | Subrnd | |
| | Light olive green | Translucent | Blocky | Subrnd | |
| | Light olive green | Translucent | Blocky | Subrnd | |
| | Light olive green | Translucent | Blocky | Subrnd | |
| | Light olive green | Translucent | Blocky | Subang | |
| | Light olive green | Translucent | Blocky | Subang | |
| | Light olive green | Translucent- to-Opaque | Subeq | Subang | |
| | Light olive green | Translucent- to-Opaque | Subeq | Subang | |
| | Light olive green | Translucent- to-Opaque | Blocky | Subang | |
| | Light olive green | Translucent- to-Opaque | Blocky | Subang | |
| | Light olive green | Translucent- to-Opaque | SlElng | Subang | |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|-------------------------|------------------------|---------------------------|----------|-----------|------------------------------------|
| Tourmaline ± Anatase | Light olive green | Opaque | Subeq | Subang | |
| | Light olive green | Opaque | Blocky | Subang | |
| | Light olive green | Opaque | Blocky | Subang | |
| | Light olive green | Opaque | Blocky | Subang | |
| | Light olive green | Opaque | Elongate | Angular | |
| | Olive green | Translucent- to-Opaque | Subeq | Subang | |
| | Dark olive green | Opaque | Subeq | Subrnd | |
| | Dark olive green | Opaque | Blocky | Subrnd | |
| | Clear with yellow tint | Translucent | Blocky | Subrnd | |
| | Clear with golden tint | Transparent | Blocky | Subang | |
| Zircon ± Anatase | Very pale pink | Transparent | ShPrsm | Subhedral | 120 x 65 |
| | Pale pink | Translucent | ShPrsm | Subhedral | 100 x 80 |
| | Pale pink | Translucent | Prsmtc | Subhedral | 80 x 20 |
| | Pale pink | Translucent | Prsmtc | Subhedral | 140 x 70 |
| | Champagne | Transparent | Subeq | Subang | 80 x 80 |
| | Champagne | Transparent | Blocky | Subang | 70 x 60 |
| | Champagne | Transparent | Blocky | Subang | 70 x 50 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|---------------------|------------------------------------|-------------|--------|-----------|------------------------------------|
| Zircon ± Anatase | Clear with light yellow tint | Transparent | ShPrsm | Subhedral | 100 x 60 |
| | Clear with light yellow tint | Translucent | Subeq | Subrnd | 100 x 80 |
| | Clear with light yellow tint | Translucent | Subeq | Subang | 90 x 70 |
| | Clear with light yellow tint | Translucent | Blocky | Subang | 100 x 80 |
| | Clear with light yellow tint | Translucent | Blocky | Subang | 90 x 60 |
| | Clear with light yellow tint | Translucent | Blocky | Subang | 80 x 65 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subhedral | 100 x 60 |
| | Clear with light yellow tint | Translucent | ShPrsm | Subhedral | 85 x 40 |
| | Clear with light yellow tint | Translucent | Prsmtc | Subhedral | 100 x 50 |
| | Clear with light yellow tint | Translucent | Prsmtc | Euhedral | 140 x 50 |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|---------------------|------------------------------------|---------------------------|--------|-----------|------------------------------------|
| Zircon ± Anatase | Clear with light yellow tint | Translucent- to-Opaque | Subeq | Subang | 90 x 90 |
| | Clear with light yellow tint | Translucent- to-Opaque | Subeq | Subang | 80 x 60 |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subrnd | n.d. (for size) |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | 140 x 100 |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | 120 x 80 |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | 80 x 70 |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | 80 x 70 |
| | Clear with light yellow tint | Translucent- to-Opaque | Blocky | Subang | 80 x 60 |
| | Clear with light yellow tint | Translucent- to-Opaque | ShPrsm | Subhedral | 120 x 65 |
| | Clear with light yellow tint | Opaque | Prsmtc | Subhedral | 190 x 100 |
| | Clear with yellow tint | Translucent | Subeq | Subrnd | 80 x 70 |
| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other or Size (µm) |
|---------------------|--|-------------|----------|-----------|---|
| Zircon ± Anatase | Clear with yellow tint | Translucent | Subeq | Subang | 85 x 80 |
| | Clear with yellow tint | Translucent | Blocky | Subang | 80 x 80 |
| | Clear with yellow tint | Translucent | ShPrsm | Subhedral | 90 x 60 |
| | Clear with yellow tint | Translucent | Elongate | Subrnd | 120 x 60 |
| | Clear with very light yellow-green tint | Transparent | Prsmtc | Subhedral | 140 x 60 |
| Unidentified | Colorless | Transparent | SlElng | Angular | |
| | Clear with light yellow- green tint | Transparent | Blocky | Angular | Glassy |
| | Colorless | Transparent | Blocky | Angular | A strong peak at 521 cm ⁻¹ on Raman spectrum |

Subsample 219.9 g, continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|------------|----------------------|-------------|-----------|-----------|--------------------|
| Actinolite | Dark green | Transparent | Subeq | Subang | |
| Anatase | Light gray | Opaque | Blocky | Subrnd | |
| | Light gray | Opaque | Blocky | Subrnd | |
| | Light gray | Opaque | Blocky | Subang | |
| | Light medium gray | Opaque | Subeq | Subrnd | |
| | Light medium gray | Opaque | Blocky | Subang | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Subeq | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | Beige | Opaque | SlElng | Subrnd | |
| | Beige | Opaque | SlElng | Subrnd | |
| | Beige | Opaque | Irregular | Subang | |
| | Beige | Opaque | Irregular | Subang | |
| | Beige | Opaque | Irregular | Angular | |
| | White | Opaque | Blocky | Subrnd | |
| | White | Opaque | Blocky | Subang | |

Size Fraction: 125-250 µm, continued

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|--|---------------------------|-----------|-----------|------------------------------------|
| Chrome spinel | Dark steel gray | Opaque | Subeq | Subang | Clear-to- light green matrix |
| Monazite ± Anatase | Clear with very light yellow tint | Opaque | Irregular | Subang | |
| | Clear with very light yellow tint | Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Translucent- to-Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Translucent- to-Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Opaque | Blocky | Subang | |
| | Clear with light yellow tint | Opaque | Irregular | Subang | |
| | Clear with light yellow tint | Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Opaque | Irregular | Angular | |
| | Clear with light yellow tint | Opaque | Irregular | Angular | |
| | Clear with light yellow tint-to- white | Opaque | Irregular | Angular | |
| | Light gray-to- white | Translucent- to-Opaque | Blocky | Subang | |

| Size Fraction: | 125-250 | μm, continued |
|----------------|---------|---------------|
|----------------|---------|---------------|

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|--------------------------------------|-------------|-----------|-----------|---|
| Monazite ± Anatase | Light gray-to- white | Opaque | Subeq | Subang | |
| | Light gray-to- white | Opaque | Irregular | Angular | |
| | Light gray-to- white | Opaque | Irregular | Angular | |
| | Beige | Opaque | Blocky | Subang | |
| | White | Opaque | Subeq | Subrnd | |
| Rutile ± Anatase | Very light peach | Opaque | Subeq | Subrnd | |
| | Very light peach | Opaque | Blocky | Subrnd | |
| | Very light peach | Opaque | Blocky | Subang | |
| | Very light buff | Opaque | Subeq | Subrnd | |
| | Very light buff | Opaque | Blocky | Subrnd | |
| | Very light buff | Opaque | Blocky | Subang | + TiO ₂ II |
| | Very light buff | Opaque | Blocky | Subang | |
| | Very light buff | Opaque | Blocky | Subang | |
| | Very light buff | Opaque | Blocky | Subang | |
| | Very light buff | Opaque | Blocky | Subang | |
| | Very light buff | Opaque | Blocky | Subang | |
| | Very light buff | Opaque | SlElng | Subrnd | |
| | Very light buff | Opaque | Irregular | Subang | |
| | Very light buff | Opaque | Irregular | Subang | |
| | Beige | Opaque | Subeq | Subang | |
| Unidentified | Clear with very light yellow tint | Transparent | Subeq | Subang | Glassy; peak at 520 cm ⁻¹ on Raman spectrum |

Appendix X

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE MONTEVILLE CONTEXT SAMPLES

Introductory Note: The following abbreviations are used in Appendix X:

Admntn = Adamantine; n = number of grains; n.d. = no data; SlElng = Slightly Elongate;

Subang = Subangular; Subeq = Subequant; Subrnd = Subrounded.

Monteville context sample T149-1

Subsamples 105.1 g and 109.2 g ($\Sigma = 214.3$ g)

Size Fraction: 63-125 μ m

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster |
|-----------------------|--|--|--|--|----------------|
| Anatase | Very light greenish gray | Translucent- to-Opaque | Blocky | Subrnd | |
| | Clear with light yellow tint | Translucent- to-Opaque | Irregular | Subang | |
| | Beige | Translucent- to-Opaque | Irregular | Subang | |
| | Beige | Opaque | Irregular | Subang | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | Subeq | Subang | |
| | White | Opaque | SlElng | Subrnd | |
| Chlorite (n = 36) | Clear with very light yellow-to- yellow tint Clear with very light yellow- green-to-yellow- green tint | Mostly Transparent and Translucent; Opaque | Mostly Blocky and Irregular; SIEIng Subeq | Mostly Subang; Angular Subrnd | |
| Monazite (n = 117) | Clear with very light yellow-to- light yellow tint Clear-to-very light peach Beige White | Translucent- to-Opaque; Opaque | Mostly Irregular and Blocky; SIEIng Subeq | Mostly Subang; Angular Subrnd | Some Admntn |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster |
|-----------------------|-----------------------------------|---------------------------|-----------|-----------|--------|
| Monazite + Anatase | Very pale peach | Opaque | Irregular | Subang | |
| | Very light peach | Translucent- to-Opaque | Blocky | Subang | |
| | Clear with very light yellow tint | Opaque | Irregular | Subang | |
| | Clear with light yellow tint | Opaque | Irregular | Subang | |
| | Beige | Translucent- to-Opaque | Irregular | Subang | |
| | Beige | Opaque | Blocky | Subang | |
| | White | Opaque | Subeq | Subrnd | |
| | White | Opaque | Blocky | Subrnd | |

Monteville context sample T149-1, continued

Monteville context sample II67-1B

Subsamples 286.9 g and 329.8 g ($\Sigma = 616.7$ g)

Size Fraction: 63-125 µm

| Phase | Color(s) | Diaphaneity | Shape | Roundness | Other |
|---------|---|-------------|-----------|-----------|-------|
| Anatase | Light buff | Opaque | Subeq | Subang | |
| | Clear with very light yellow tint | Opaque | Blocky | Subang | |
| | Clear with very light yellow tint | Opaque | Blocky | Subang | |
| | Clear with very light yellow tint | Opaque | Irregular | Subang | |
| | Clear with very light yellow-green tint | Translucent | Blocky | Subang | |
| | Clear with very light yellow-green tint | Translucent | Blocky | Subang | |
| | Clear with very light yellow-green tint | Translucent | Irregular | Subang | |
| | Clear with light yellow-green tint | Translucent | Blocky | Subang | |
| | Clear with very light green tint | Translucent | Subeq | Subang | |
| | Clear with light green tint | Transparent | Blocky | Subang | |
| | Very light olive green | Opaque | Blocky | Subang | |
| | Very light olive green | Opaque | Irregular | Subang | |
| | Very light olive green | Opaque | Irregular | Subang | |

| Phase | Color(s) | Diaphaneity | Shape | Roundness | Other |
|---------------|------------------------|---------------------------|-----------|-----------|----------------------------|
| Anatase | Light gray | Opaque | Irregular | Subrnd | |
| | Light gray | Translucent- to-Opaque | Blocky | Subrnd | |
| | Light gray | Translucent- to-Opaque | Blocky | Subrnd | |
| | Light gray | Translucent- to-Opaque | Blocky | Subrnd | |
| | Beige | Opaque | Blocky | Subrnd | |
| Chrome spinel | Medium dark gray | Opaque | Subeq | Subrnd | Emerald green matrix |
| | Medium dark gray | Opaque | Subeq | Subrnd | Emerald green matrix |
| | Medium dark gray | Opaque | n.d. | Subrnd | Light green matrix |
| Rutile | Light orange- amber | Translucent | SlElng | Subrnd | |

Monteville context sample II67-1B, continued

Appendix Y

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE GRÆNSESØ SPHERULE LAYER SAMPLES

Introductory Note: The following abbreviations are used in Appendix Y: n = number of grains; Prsmtc = Prismatic; ShPrsm = Short Prism; SlElng = Slightly Elongate; Subang = Subangular; Subeq = Subequant; Subrnd = Subrounded;

Wllrnd = Well-rounded.

Grænsesø spherule layer sample GL8904-1

Subsample 349.3 g

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|---------------------------|---|---|--|------------------|--|
| Anatase (n = 47) | Very light peach Very light-to-light gray Clear with very light-to-light yellow tint Beige White | Mostly Opaque; Translucent-to- Opaque | Subeq Blocky Irregular SIEIng Equant | Subrnd Subang | |
| Anglesite/ Barite | Clear with very light yellow tint | Transparent | Blocky | Angular | Glassy |
| | Clear with light yellow tint | Transparent | Subeq | Subrnd | |
| | Clear with light yellow tint | Transparent | Subeq | Subang | |
| | Clear with light yellow tint | Transparent | Equant | Subrnd | |
| | Clear with light yellow tint | Transparent | Blocky | Subang | |
| | Clear with light yellow tint | Transparent | Irregular | Angular | Glassy |
| | Clear with very light green tint | Transparent | Blocky | Subang | Glassy |
| | Clear with light green tint | Transparent | Subeq | Subang | |
| Chrome spinel (n = 48) | Dark steel gray-to- black | Opaque | Subeq Blocky SIElng Equant | Subrnd Subang | Light green, light yellow- green, or light emerald green matrix |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-------------------------------------|---|---|--|---|--------------------|
| Magnetite | Black | Opaque | Blocky | Subang | |
| Rutile ± Anatase (n = 12,551) | Light-to-very dark gray Light yellowish gray Light brown Light grayish brown Light buff-to-buff Light grayish buff Light grayish buff Light grayish yellow Very light peach- to-peach Amber Reddish amber Light brownish amber Golden amber Orange-amber | Mostly Opaque; the various shades of amber can be Translucent-to- Opaque | Mostly Subeq, Blocky, and SIElng; Equant Irregular | Mostly Subrnd-to- Wllrnd; Subang | |
| Tourmaline (n = 2,340) | Mostly light-to- dark olive green; Light golden-to- golden amber Clear with light green tint Clear with light blue or blue-green tint | Mostly Transparent and Translucent; Opaque | Blocky ShPrsm Subeq Prsmtc SlElng | Mostly Subrnd; Subang Wllrnd | |

Grænsesø spherule layer sample GL8904-1, continued

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Luster or Other |
|-----------------------|--|---|---|---------------------------------------|--------------------|
| Zircon (n = 2,551) | Very pale pink-to- pink Light champagne- to-champagne Clear with very light yellow-to- light yellow tint Light grayish yellow Very light-to-light yellow-pink Clear with very light green tint Light pinkish gray Light pinkish beige Light pinkish white | Mostly Transparent, and Transparent-to- Translucent; Translucent-to- Opaque; Opaque | Subeq ShPrsm Prsmtc Blocky SIElng Equant | Mostly Subrnd; Subang Wllrnd | |
| Unidentified | Dark amber | Translucent-to- Opaque | Subeq | Subrnd | |
| | Pinkish gray | Opaque | Blocky | Subrnd | |
| | Clear with very light yellow tint | Translucent | Blocky | Subrnd | |

Grænsesø spherule layer sample GL8904-1, continued

Grænsesø spherule layer sample GL8904-1, continued

Subsample 349.3 g, continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|----------------------------------|---|---|---|-----------------------------|
| Anatase (n = 7) | Light gray Light gray Clear with very light = 7) yellow tint Clear-to-white | | Subeq Blocky SIElng | Subrnd |
| Rutile ± Anatase (n = 127) | Mostly medium dark gray-to-dark gray Light gray Yellowish gray Buff | Opaque | Subeq Blocky SIElng Irregular | Mostly Subrnd; Subang |
| Tourmaline (n = 88) | Mostly olive-to-dark olive green Light green Light golden amber | Mostly Transparent; Translucent Opaque | Mostly Subeq, Blocky, and ShPrsm; Prsmtc Equant | Mostly Subrnd; Wllrnd |
| Zircon | Pale pink | Transparent | Prsmtc | Subrnd |
| | Pink | Translucent | SlElng | Subrnd |

Grænsesø spherule layer sample GL8904-3

Subsample 487.8 g

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|---|--|--|---|---|
| Anatase \pm K-feldspar (n = 13) | Anatase ± K-feldspar (n = 13)Clear with very light yellow tint Clear-to-white Beige | | Mostly Blocky; Subeq | Subang |
| Anglesite (n = 8) | Clear with very light yellow-green tint | Transparent | Blocky SlElng | Subang |
| Barite (n = 5) | Clear with very light yellow-green tint | Transparent | Equant Subeq Blocky SIElng | Wllrnd Subrnd |
| Chrome spinel | Chrome spinel Black | | Subeq | Subang |
| | Black | Opaque | Equant | Subrnd |
| Rutile (n = 2,062) | Mostly medium-to-dark gray; Light gray Very light brown Light pale brown Cream Light grayish brown Cream Light brownish buff Buff-to-light peach Amber Reddish amber Brownish amber Light golden amber Very light-to-light yellow amber | Mostly Opaque; some shades of amber can be Translucent | Mostly Subeq, SIEIng, and Blocky; Irregular Equant Prsmtc | Mostly Subrnd and Wllrnd; Subang |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|-------------------------|--|--|---|---------------------------------------|
| Tourmaline (n = 369) | Light-to-dark olive green Amber Light golden amber Light bluish green | Mostly Transparent; Translucent Opaque | Blocky ShPrsm Subeq Prsmtc | Mostly Subrnd; Wllrnd Subang |
| Zircon (n = 486) | Mostly pale pink-to-pink, champagne, and clear with light yellow tint; Pink-to-pinkish white Yellowish pink White | Mostly Transparent; Transparent- to-Translucent Opaque | ShPrsm Prsmtc SIEIng Subeq Blocky Equant | Mostly Subrnd; Wllrnd Subang |

Grænsesø spherule layer sample GL8904-3, continued

Grænsesø spherule layer sample GL8904-3, continued

Subsample 487.8 g, continued

Size Fraction: 125-250 µm

| Phase | Color(s) | Diaphaneity | Shape | Roundness | Other |
|--------------------------|--|---|--|-----------------------------|---|
| Barite | Clear with very light green tint | Transparent | Blocky | Subrnd | |
| Chrome spinel (n = 3) | Dark steel gray | Opaque | Subeq Blocky | Subrnd Subang | Light emerald green, translucent matrices |
| Rutile (n = 77) | Mostly medium dark-to-dark gray Light gray Light yellowish brown Amber | Opaque | Subeq Blocky SIElng Irregular | Mostly Subrnd; Subang | |
| Tourmaline (n = 25) | Mostly light golden amber- to-amber Light-to-dark olive green | Mostly Transparent; Translucent Opaque | Subeq ShPrsm SIElng Blocky | Mostly Subrnd; Wllrnd | |
| Zircon | Clear with light yellow tint | Translucent- to-Opaque | Prsmtc | Wllrnd | |
| | Light peach | Translucent- to-Opaque | Prsmtc | Subrnd | |
| | Very light grayish pink | Opaque | Prsmtc | Subrnd | |

Grænsesø spherule layer sample GL8904-4

Subsamples 187.9 g and 294.1 g ($\Sigma = 482.0$ g)

Size Fraction: 63-125 µm

| Phase(s) | Color(s) Diaphaneity | | Shape | Roundness |
|-------------------------------------|--|--|--|------------------|
| Anatase ± K-feldspar (n = 38) | Light-to-dark gray Clear with light yellow tint Beige White | Translucent- to-Opaque; Opaque | Subeq Blocky SIEIng Irregular | Subrnd Subang |
| Anglesite (n = 24) | Clear with very light yellow-to-yellow tint Clear with light yellow- green tint | vith very light to-yellow tint th light yellow- reen tint | | Subrnd Subang |
| Barite | Clear with very light green tint | Translucent | Subeq | Wllrnd |
| | Clear with very light yellow-green tint | Transparent | Subeq | Wllrnd |
| | Clear with light yellow- green tint | Transparent | Blocky | Subrnd |
| Chrome spinel | Black | Opaque | Equant | Wllrnd |
| | Black | Opaque | SlElng | Wllrnd |
| | Black | Opaque | Blocky | Subrnd |
| | Black | Opaque | Blocky | Subrnd |

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|---|---|---|--|---------------------------------------|
| Rutile \pm Anatase (n = 1,335) | Light-to-dark gray Light yellowish gray Very light brownish gray Very light brown-to-light brown Light yellowish brown Very light-to-light grayish brown Light olive brown Very light-to-dark olive Amber Light brownish-to- brownish amber Orange-amber Light golden amber | Mostly Opaque; shades of amber can be Translucent- to-Opaque | Mostly Subeq, Blocky, and SIEIng; Irregular Elongate Equant | Mostly Subrnd; Wllrnd Subang |
| Tourmaline (n = 266)Light-to-dark olive green Amber Light bluish green Green | | Mostly Transparent; Translucent Opaque | ShPrsm Blocky Prsmtc SIElng | Mostly Subrnd; Wllrnd Subang |
| Zircon (n = 219) Very pale pink-to-pink Champagne Clear with very light yellow-to-yellow tint Light grayish yellow Light yellowish gray Light yellowish beige | | Mostly Transparent; Transparent- to-Translucent; Opaque | Prsmtc ShPrsm Subeq Blocky SIEIng Equant | Mostly Subrnd; Wllrnd Subang |

Grænsesø spherule layer sample GL8904-4, continued

Grænsesø spherule layer sample GL8904-4, continued

Subsamples 187.9 g and 294.1 g ($\Sigma = 482.0$ g), continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|-------------------------------------|--|--------------------------------------|--|---------------------------------------|
| Anatase ± K-feldspar (n = 14) | Clear with very light yellow tint Beige White | Translucent- to-Opaque; Opaque | Mostly Blocky; Irregular | Subang Subrnd |
| Anglesite | Clear with light yellow tint | Transparent | Blocky | Subrnd |
| | Clear with light yellow-green tint | Transparent | Blocky | Subang |
| Barite | Clear with very light yellow-green tint | Transparent | Equant | Wllrnd |
| | Clear with light yellow-green tint | Transparent | Blocky | Subrnd |
| Rutile ± Anatase (n = 53) | Light-to-dark gray | Opaque | Mostly Subeq, Blocky, and SlElng; Irregular | Mostly Subrnd; Wllrnd Subang |
| Tourmaline (n = 23) | Light-to-dark olive green Amber | Mostly Translucent; Opaque | ShPrsm Subeq Blocky SIEIng | Mostly Subrnd; Subang Wllrnd |
| Zircon | Very pale pink | Transparent | ShPrsm | Wllrnd |
| | Pink | Transparent | Equant | Wllrnd |

Appendix Z

TABLES FOR DESCRIPTIONS OF HEAVY MINERAL GRAINS IN THE GRÆNSESØ CONTEXT SAMPLES

Introductory Note: The following abbreviations are used in Appendix Z:

ID = Identification; n = number of grains; Prsmtc = Prismatic; ShPrsm = Short Prism;

SlElng = Slightly Elongate; Subang = Subangular; Subeq = Subequant;

Subrnd = Subrounded; XRD ID = the identification number of a grain that was analyzed by XRD.

Grænsesø context sample SP3

Subsample 155.0 g

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness | Other |
|-------------------------------------|---|-------------|--|-----------------------------|------------------------|
| Anglesite | Clear with very light green tint | Transparent | Blocky | Subrnd | |
| Magnetite | Black | Opaque | Subeq | Subang | Grain has facets |
| Rutile | Dark gray | Opaque | Blocky | Subrnd | |
| | Medium yellowish gray | Opaque | Subeq | Subrnd | |
| Rutile + Tourmaline (n = 225) | Very light-to-light olive gray Very light olive gray- to-beige Light brown Medium dark gray White | Opaque | Subeq SlElng Blocky Elongate Irregular | Mostly Subrnd; Subang | |
| Tourmaline | Light olive green | Translucent | Prsmtc | Subang | |
| | Light olive green | Translucent | Prsmtc | Subang | |
| | Olive green | Translucent | Blocky | Subang | |
| | Olive green | Translucent | SlElng | Subang | |
| | Olive green | Translucent | SlElng | Subrnd | |
| Zircon | Very pale pink | Transparent | Blocky | Subrnd | |
| | Pale pink | Transparent | ShPrsm | Subrnd | |

Grænsesø context sample SP3, continued

Subsample 155.0 g, continued

Size Fraction: 125-250 µm

| Phase(s) | Color(s) | Diaphaneity | Shape | Roundness |
|------------------------------------|--|-------------|--|--------------------------|
| Rutile + Tourmaline (n = 42) | Very light-to-light olive gray Very light olive gray- to-beige Medium gray | Opaque | Blocky SlElng Subeq Irregular | Mostly Subrnd; Subang |
| Unidentified | Black | Opaque | Subeq | Subrnd |

Grænsesø context sample GL8904-6

Subsample 321.1 g

Size Fraction: 63-125 µm

| Phase(s) | Color(s) | Diaphaneity | Diaphaneity Shape | | Other or (XRD ID) |
|---------------------------------|--|---------------------------|--|-----------------------------|--|
| Anatase | Beige | Translucent- to-Opaque | Blocky | Subang | |
| Anatase + K-feldspar | Beige | Translucent- to-Opaque | SlElng | Subrnd | |
| Chrome spinel | Medium dark gray | Opaque | Subeq | Subrnd | Colorless-to- light green matrix |
| | Medium dark gray | Opaque | Subeq | Subrnd | Colorless-to- light green matrix |
| | Medium dark gray | Opaque | Subeq | Subrnd | Colorless-to- light green matrix |
| Rutile ± Anatase (n = 40) | Light-to-dark gray Light buff-to- buff Light brownish gray Light grayish yellow | Opaque | Mostly Subeq, Blocky, and SIEIng; Elongate Irregular | Mostly Subrnd; Subang | |
| Tourmaline | Olive green | Translucent | Blocky | Subrnd | (1) |
| | Olive green | Translucent | Blocky | Subrnd | |
| | Olive green | Translucent | Blocky | Subrnd | |
| | Dark olive green | Translucent | Blocky | Subrnd | |
| | Dark olive green | Opaque | Subeq | Subrnd | |
| Zircon | Pink | Transparent | Blocky | Subrnd | (2) |
| | Pink | Transparent | Blocky | Subang | (3) |

XRD ID: (1) G 1-3 9-4-06 (2) D-S 1-2 9-3-06 (3) D-S 2-3 9-3-06.

Appendix AA

RAMAN SPECTRA FOR CARAWINE SPHERULE LAYER SAMPLE X38-2



Figure 300: Unnormalized Raman spectrum of rutile (R) + TiO₂ II + anatase (A) + quartz (Q) grain #11 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). The bands at wavenumbers 175, 279, 316, 356, and 532 cm⁻¹, and the shoulders at wavenumbers 429 and 580 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). Raman spectra for anatase and quartz standards are shown in Figures 21 and 41, respectively.



Figure 301: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #12 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). The bands at wavenumbers 150, 173, 284, 313, 339, 355, 430, and 534 cm⁻¹, and the shoulder at wavenumber 579 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.



Figure 302: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #19 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). The bands at wavenumbers 174, 315, 339, 358, and 534 cm⁻¹, and the shoulders at wavenumbers 149, 285, and 427 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001).



Figure 303: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #9 (Table 40) from Carawine spherule layer sample X38-2 (cf., Fig. 90). The bands at wavenumbers 149, 172, 280, 313, 339, 356, 428, and 533 cm⁻¹, and the shoulder at wavenumber 576 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.



Figure 304: Unnormalized Raman spectrum of rutile (R) + TiO₂ II + quartz (Q) grain #3 (Table 40) from the 125-250 μ m size fraction of Carawine spherule layer sample X38-2 (cf., Fig. 90). The bands at wavenumbers 174, 284, 315, 339, 357, and 532 cm⁻¹, and the shoulders at wavenumbers 149, 427, and 568 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). A Raman spectrum for a quartz standard is shown in Figure 41. There is an unindexed (U) band at wavenumber 525 cm⁻¹.

Appendix BB

RAMAN SPECTRA FOR BEE GORGE (WITTENOOM) SAMPLES



Figure 305: Raman spectra of a possible actinolite grain from the Bee Gorge spherule layer in sample BB, and an actinolite standard from the RRUFF Raman spectral database.



Figure 306: Raman spectra of a rutile grain from the Bee Gorge spherule layer in sample BB, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 307: Raman spectra of a hematite grain from Bee Gorge context layer #1 in sample BB, and a hematite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 308: Raman spectra of an anatase grain from Bee Gorge context layer #1 in sample BB, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 309: Raman spectra of a rutile grain from Bee Gorge context layer #1 in sample BB, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 310: Raman spectra of an anatase grain from Bee Gorge context layer #2 in sample BB, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 311: Raman spectra of a clinozoisite grain from Bee Gorge context layer #2 in sample BB, and a clinozoisite standard from the RRUFF Raman spectral database.


Figure 312: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Bee Gorge context layer #2 in sample BB (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum.



Figure 313: Raman spectra of an anatase grain from the lowermost spherule-rich sublayer (Lspsl) in Bee Gorge sample 96714A, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 314: Unnormalized Raman spectrum of a granular rutile (R) + anatase (A) grain from the lowermost spherule-rich sublayer (Lspsl) in Bee Gorge sample 96714A (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum.



Figure 315: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from the spherule-bearing lutite sublayer (Splsl) in Bee Gorge sample 96714A (cf., Figs. 42, 43, and 53).



Figure 316: Raman spectra of an anatase grain from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714A, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 317: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714A (cf., Figs. 42, 43, and 53).



Figure 318: Raman spectra of a rutile grain from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714A, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 319: Unnormalized Raman spectrum of an anatase (A) + quartz (Q) grain from the basal carbonate lutite (Bcl) context layer that is stratigraphically below the spherule layer in Bee Gorge sample 96714B (cf., Figs. 39 and 40).



Figure 320: Raman spectra of an anatase grain from the lowermost spherule-rich sublayer (Lspsl) in Bee Gorge sample 96714B, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 321: Unnormalized Raman spectrum of a granular rutile grain from the lowermost spherule-rich sublayer (Lspsl) in Bee Gorge sample 96714B (cf., Fig. 173). No baseline correction was made for the sample spectrum.



Figure 322: Raman spectra of a rutile grain from the upper spherule/lutite sublayers (Usplsl) subdivision in Bee Gorge sample 96714B, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.

Appendix CC

RAMAN SPECTRA FOR MONTEVILLE SPHERULE LAYER SAMPLES



Figure 323: Raman spectra of a monazite grain from Monteville spherule layer sample U63-1, and a monazite standard from the RRUFF Raman spectral database.



Figure 324: Raman spectra of a rutile grain from Monteville spherule layer sample U63-1, and a rutile standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 325: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Monteville spherule layer sample U63-1 (cf., Figs. 27 and 28).



Figure 326: Raman spectra of a white opaque rutile grain with unindexed (U) bands ("rutile + unidentified") from Monteville spherule layer sample U63-1, and a rutile standard from the RRUFF Raman spectral database (cf., Figs. 29 and 77).



Figure 327: Unnormalized Raman spectrum of a quartz (Q) + anatase (A) grain from Monteville spherule layer sample V111 (cf., Figs. 39, 40, and 41).



Figure 328: Unnormalized Raman spectrum of an anatase (A) + K-feldspar (K) grain from Monteville spherule layer sample V111 (cf., Figs. 42 and 43).



Figure 329: Raman spectra of a monazite grain from Monteville spherule layer sample V111, and a monazite standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum.



Figure 330: Unnormalized Raman spectrum of a monazite (MON) + anatase (A) grain from Monteville spherule layer sample V111. The bands at wavenumbers 247, 319, 367, and 707 cm⁻¹ are unindexed (U). Raman spectra of anatase and monazite standards are shown in Figures 21 and 329, respectively.



Figure 331: Unnormalized Raman spectrum of a monazite (MON) + anatase (A) + quartz (Q) grain from Monteville spherule layer sample V111. Raman spectra of monazite, anatase, and quartz standards are given in Figures 329, 21, and 41, respectively.



Figure 332: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Monteville spherule layer sample V111 (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum.



Figure 333: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #16 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 175, 319, 339, and 358 cm⁻¹, and the shoulder at wavenumber 284 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.



Figure 334: Unnormalized Raman spectrum of rutile (R) + TiO₂ II + quartz (Q) grain #1 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 174, 315, 341, 358, and 534 cm⁻¹, and the shoulder at wavenumber 284 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). There are five bands that match those of a quartz standard (see Fig. 41), but the band of strongest intensity for quartz at wavenumber ~464 cm⁻¹ is not evident.



Figure 335: Unnormalized Raman spectrum of rutile (R) + TiO₂ II + anatase (A) grain #5 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 173, 280, 318, 340, and 359 cm⁻¹, and the shoulder at wavenumber 429 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). A Raman spectrum of an anatase standard is shown in Figure 21. No baseline correction was made for the sample spectrum.



Figure 336: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #6 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 175, 318, 339, and 357 cm⁻¹, and the shoulder at wavenumber 284 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.



Figure 337: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #13 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 149, 174, 284, 315, 339, 357, 430, and 532 cm⁻¹, and the shoulder at wavenumber 573 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001).



Figure 338: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #14 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 149, 173, 283, 314, 339, 356, and 531 cm⁻¹, and the shoulders at wavenumbers 428 and 571 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.



Figure 339: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #44 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 149, 174, 282, 314, 339, 357, and 532 cm⁻¹, and the shoulder at wavenumber 429 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.



Figure 340: Unnormalized Raman spectrum of rutile (R) + TiO₂ II + anatase (A) grain #23 (Table 52) from Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 175, 285, 315, 339, 358, and 529 cm⁻¹, and the shoulders at wavenumbers 428 and 570 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). A Raman spectrum of an anatase standard is shown in Figure 21. There are unindexed (U) bands at wavenumbers 262 and 786 cm⁻¹.



Figure 341: Unnormalized Raman spectrum of rutile (R) + TiO₂ II grain #15 (Table 52) from the 125-250 μ m size fraction of Monteville spherule layer sample V111 (cf., Fig. 90). The bands at wavenumbers 149, 173, 285, 314, 339, 356, 428, and 531 cm⁻¹, and the shoulder at wavenumber 569 cm⁻¹ are attributed to TiO₂ II (see Mammone et al., 1980; El Goresy et al., 2001). No baseline correction was made for the sample spectrum.

Appendix DD

RAMAN SPECTRA FOR MONTEVILLE CONTEXT SAMPLES



Figure 342: Raman spectra of a monazite grain from Monteville context sample T149-1, and a monazite standard from the RRUFF Raman spectral database. The sample was collected ~1 m stratigraphically below the Monteville spherule layer.



Figure 343: Unnormalized Raman spectrum of a monazite (MON) + K-feldspar (K) grain from Monteville context sample T149-1. Raman spectra of monazite and K-feldspar standards are shown in Figures 342 and 43, respectively. The band at wavenumber 700 cm⁻¹ is unindexed (U). The sample was collected ~1 m stratigraphically below the Monteville spherule layer.



Figure 344: Unnormalized Raman spectrum of a monazite (MON) + anatase (A) grain from Monteville context sample T149-1. Raman spectra of monazite and anatase standards are shown in Figures 342 and 21, respectively. The sample was collected ~1 m stratigraphically below the Monteville spherule layer.



Figure 345: Raman spectra of a goethite grain from Monteville context sample II67-1B, and a goethite standard from the RRUFF Raman spectral database. The sample was collected ~20 cm stratigraphically above the Monteville spherule layer.

Appendix EE

RAMAN SPECTRA FOR GRÆNSESØ SPHERULE LAYER SAMPLE GL8904-1



Figure 346: Raman spectra of an anatase grain from Grænsesø spherule layer sample GL8904-1, and an anatase standard from the RRUFF Raman spectral database. No baseline correction was made for the sample spectrum. The Raman spectrum for the anatase standard was acquired using a 514-nm laser.



Figure 347: Unnormalized Raman spectrum of a rutile (R) + anatase (A) grain from Grænsesø spherule layer sample GL8904-1 (cf., Figs. 27 and 28). No baseline correction was made for the sample spectrum.


Figure 348: Raman spectra of quartz matrix material on the surface of a rutile grain from Grænsesø spherule layer sample GL8904-1, and a quartz standard from the RRUFF Raman spectral database.

Appendix FF

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Dear Frank,

What a pleasant surprise. I knew there was a good reason for me keeping my lpl email address (I am now based in Perth, Australia).

Firstly, yes, you are welcome to use the photograph and credit me. I would estimate the length of the sledge hammer to be \sim 70 cm. This is consistent with comments regarding layer thickness in my 2006 report to you.

Thank you very much for the update on your work, with the Greenland and other samples. [Continued].

Best regards and yes, please do keep my updated, Mark