STATE OF DELAWARE

UNIVERSITY OF DELAWARE

DELAWARE GEOLOGICAL SURVEY

ROBERT R. JORDAN, STATE GEOLOGIST

BULLETIN NO. 18

CLAY AND CLAY-SIZE MINERAL COMPOSITION OF THE CRETACEOUS-TERTIARY SECTION, TEST WELL Je32-04, CENTRAL DELAWARE

BY

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ABSTRACT

This study complements Delaware Geological Survey
Bulletin No. 17 and deals exclusively with clays and clay-size
minerals. The cored section at the location of Je32-04 has
been subdivided into 25 clay zones on the basis of major
changes in trends and degree of crystallinity of clay
minerals. The composition of clay minerals varies from zone
to zone. These clay minerals have been identified: kaolinite,
berthierine, chlorite, illite, smectite, chlorite/smectite,
illite/smectite, glauconite/smectite, and glauconite pellets.
Other minerals present in the section include: zeolites
(clinoptilolite-heulandite), gypsum, and elemental sulfur.

Correlation of clay mineral assemblages with the
paleowater-depth curve suggests an improvement of clay mineral
crystallinity with depth of deposition. Crystallinity also
tends to improve immediately below and above major
unconformities with one notable exception, the Danian-
Thanetian unconformity.

In general there is a relationship of clay minerals to
other lithologic elements, although there are some major
exceptions that are explained by subtle changes in
depositional environments.

There is also a reasonably good correlation between the
clay zones and time-stratigraphic units at the stage level.

All these relationships suggest that the clay mineral
zonation was established in its present form during or shortly
after deposition. Most of the alterations of clay minerals
have since been either minor or are taking place at a very
slow rate.

The presence of zeolites (clinoptilolite-heulandite), and possibly sulfur, testifies to the influence of extensive volcanic activity particularly during Paleocene and early to early middle Eocene times. Sporadic volcanic activity also took place at other times but was less extensive and discontinuous. Volcanic activity is supported by the presence of at least five unconformities in the section.

A detailed study of clays and clay-size minerals in one well is useful for gaining a better understanding of geologic changes through time; its application to the regional geology of the Atlantic Coastal Plain, however, is limited.

INTRODUCTION

This study is an extension of Delaware Geological Survey Bulletin No. 17 (Benson, Jordan, and Spoljaric, 1985). It deals exclusively with clays and clay-size minerals, some of which were mentioned only briefly in the Bulletin.

In general, clays (clay minerals) can provide invaluable information on pre-, syn-, and post-depositional changes in sedimentary rocks. They can indirectly assist in the understanding of drainage characteristics in source areas, provide clues about geochemical conditions in depositional environments, and are useful in interpreting depositional environments.

Clay minerals are, to a degree, indicators of general paleoclimatic conditions in the environment of their formation, but in older rocks this importance is generally diminished due to postdepositional alteration.

Clay-size sediment particles usually contain other minerals that may provide additional information about the geology of the area. For example, zeolites may indicate past volcanic activity not evident from other characteristics of the rocks.

Purpose

The present study was initiated to complement the results already published in Bulletin No. 17, and also to contribute to a better understanding of geologic events that took place in the Cretaceous-Tertiary time interval in the Coastal Plain of Delaware and surrounding areas. It should be emphasized, however, that information obtained from one deep well is not sufficient to expand the geologic interpretation on a regional scale; nevertheless, it does provide important insight into geologic events that occurred during that time interval.

Acknowledgments

I wish to extend my thanks to members of the Delaware Geological Survey for discussions of various aspects of the study: R. R. Jordan, J. H. Talley, and A. S. Andres. Special

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METHODS

One hundred and forty core samples taken from well Je32-04 (Figure 1) were used in the study. Clay slides prepared for X-ray analyses (Spoljaric, 1971) were analyzed untreated, glycolated, and heated to 400° and 550°C. Clay minerals were identified employing standard methods of identification (Brindley and Brown, 1980; Starkey et al., 1984),

In determining percentages of expandable clays in illite/smectite minerals, the modified peak-height method of Schultz (1978) was employed. During the course of the study it became apparent that the usefulness of the peak-migration method was quite limited due to either weak intensity of reflectors, interference by other mineral peaks, or both.

No quantitative analyses of clay mineral assemblages were carried out due to a number of variables and problems inherent in these types of studies. These include, but are not limited to, selective absorption of X-rays by chemical components in clay minerals, the degree of crystallinity, size of clay particles, orientation of clay particles on slides, and true representation of mineral composition in the thin layer on the slide exposed to X-rays. For these and other reasons it was decided to present clay mineral composition only qualitatively. There is no doubt that this decision resulted in omissions in the study, but inaccuracies and misleading quantitative results would most likely result in misinterpretation of the clay mineral assemblages and their significance. However, the individual diffractograms (Plate 1) should be comparable as the conditions of slide preparation and X-ray diffraction analyses were maintained constant throughout.

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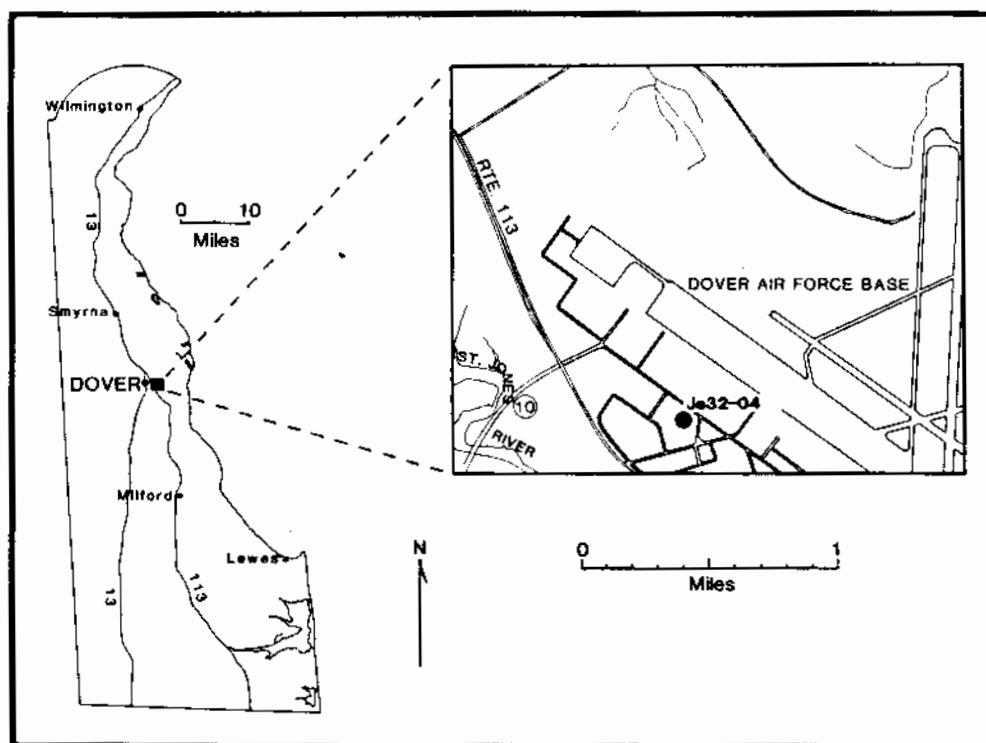
Figure 1.   Location of test well Je32-04.

RESULTS

To simplify both the presentation and interpretation of
the results, clay minerals in the section are grouped into
"clay zones."   The criteria for subdivision into zones are
quite arbitrary and are based primarily on the variability and
apparent degree of crystallinity of the clay minerals.   The
zone boundaries generally indicate a change in those
characteristics or a shift in the apparent trend of clay
mineral changes within a particular zone.

X-ray diffractograms (untreated clay slides) of clay
zones are shown in Plate 1. Clay mineral composition, other
clay-size minerals, and crystallinity trends are shown in
Plate 2.

Description of Clay Zones

Zone I (20711-20709)

Sample 20711 is represented by kaolinite and 14$\overset{o}{A}$ chlorite
(trace). In the upper part of the zone clay mineral
assemblage becomes a little more complex and the minerals
identified are illite/smectite, kaolinite, and traces of
gypsum and possibly illite. There appears to be a
proportionate decrease in kaolinite upward through the zone.

Any reference to relative amounts of specific clay
minerals in the following descriptions is based solely on peak
sizes.

Zone II (20708-20706)

Definite trends are recognizable through the zone.
Kaolinite is well crystallized and shows little, if any,
change. Illite shows a distinct decrease through the zone.
Illite/smectite is developed at the base of the zone only.
Traces of chlorite are revealed, after treatment, in the upper
two samples. Trace amounts of gypsum are identified in
samples 20708 and 20707.

Zone III (20705-20703)

The base of this zone is an unconformity separating the
underlying Potomac Formation from the Magothy Formation above.
The zone is entirely in the lower part of the Magothy
Formation. Distinct mineral trends are recognized: illite,
illite-smectite, and chlorite show improvements toward the
upper part of the zone. Kaolinite is again well crystallized
and shows a slight increase toward the base of the zone. A
trace of gypsum occurs in sample 20703.

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Zone IV (20702-20698)

The first appearance of clinoptilolite-heulandite zeolites is recorded in this zone. Traces of degraded kaolinite were detected in the two lower samples (20702 and 20701). Berthierine (7Å chlorite) is present throughout the zone and has a distinct tendency to increase in crystallinity from the base toward the top of the zone. Possible chlorite/smectite is present in samples 20699 and 20698. Illite/smectite is developed in the lower half of the zone (20702, 20701, 20700); gypsum is present throughout.

Zone V (20697-20689)

Minerals in the lowermost sample (20697) appear to be very poorly crystallized. The presence of glauconite/smectite (illite?), kaolinite(?), and chlorite(?) is indicated. Rather symmetrical 10Å peaks developed in all the other samples suggests well developed glauconite/smectite with the smectite component comprising only about 10% of the mineral. Double peaks at 7Å and 3.5Å indicate the presence of both kaolinite and chlorite. Small amounts of gypsum are detected in all samples.

In addition to chlorite, the uppermost sample (20689) also contains illite/smectite. A trace of clinoptilolite-heulandite is noted in sample 20696.

Zone VI (20688-20676)

A rather symmetrical 10Å peak throughout the zone, with the exception of samples nos. 20684, 20679, 20678, and possibly the topmost two samples (20676 and 20677), indicates the presence of glauconite/smectite. In the other samples illite appears to be the dominant 10Å clay. Kaolinite-chlorite double peaks at 7Å and 3.5Å are well developed and show a general tendency toward improvement in crystallinity toward the base of the zone. Illite/smectite is sporadic in occurrence, samples 20688, 20685, and 20684. Other samples, with the exception of 20679, contain chlorite/smectite. Traces of gypsum were observed in samples 20688, 20687, 20684, 20683, 20682, 20681, 20680, 20679, 20678, and 20677. In general, crystalline phases appear to be better developed in the basal than in the uppermost part of the zone.

Zone VII (20675-20669)

Illite/smectite is developed throughout the zone. Traces of what appears to be glauconite/smectite are indicated in all the samples; 7Å chlorite (berthierine) seems to show an improvement in crystallinity up through the section. Gypsum is present in the basal sample (20675) only; elemental sulfur is developed throughout the zone with the exception of sample 20669.

Zone VIII (20668-20667)

The zone is characterized by the presence of illite/smectite in trace amounts, glauconite/smectite, 7Å chlorite (berthierine), and gypsum. The upper boundary of the zone is the Cretaceous-Tertiary unconformity.

Zone IX (20666-20663)

This zone is bounded by the Cretaceous-Tertiary unconformity at the base and the Danian-Thanetian unconformity at the top. Illite/smectite is developed throughout the zone and so is glauconite/smectite. The crystallinity of glauconite/smectite decreases both upward and downward from the central part of the zone. Traces of chlorite and gypsum were detected in all the samples except 20666.

Zeolites (clinoptilolite-heulandite) are the best crystallized phase of the zone.

Zone X (20662-20659)

Illite/smectite, glauconite/smectite, and zeolites (clinoptilolite-heulandite) are present in all samples. Traces of 7Å chlorite (berthierine) and gypsum are also indicated throughout the zone. There seems to be a slight tendency for minerals to improve in crystallinity from the top toward the base of the zone.

Zone XI (20658-20652)

Glauconite/smectite is developed throughout the zone. A degraded 7Å peak suggests the presence of kaolinite. Chlorite/smectite is present in all the samples except 20658 and illite/smectite is developed in the basal part of the zone. Zeolites (clinoptilolite-heulandite) are consistently well represented in all the samples; gypsum is present in trace amounts only.

Zone XII (20651-20649)

Glauconite/smectite and illite/smectite are present throughout the zone. The latter shows a decrease in crystallinity upward. A generally degraded 7Å peak suggests the presence of kaolinite. Zeolites are well developed except at the top of the zone where they appear to be degraded to a considerable degree. Gypsum is present in trace amounts throughout the zone.

Zone XIII (20648-20641)

Illite/smectite is present throughout and seems to be progressively better developed in the basal part of the zone. Zeolites show just the opposite trend possibly indicating alteration to illite/smectite. Degraded kaolinite is present in the lower half of the zone, mostly in trace amounts, and the degree of degradation increases upwards. Glauconite/smectite and traces of gypsum were recognized in all samples. Sample 20648 contains a trace of sulfur.

Zone XIV (20640-20638)

The predominant mineral is illite/smectite. Traces of poorly crystallized glauconite/smectite and zeolites (clinoptilolite-heulandite) were detected in all samples. Samples 20639 and 20638 appear to contain trace amounts of elemental sulfur as well.

Zone XV (20637-20628)

Zeolites are by far the predominant minerals of this zone. Glauconite/smectite is developed throughout and shows a distinct tendency to increase in crystallinity upward through the zone. Illite/smectite is developed in the upper part of the zone and traces of elemental sulfur are recognized in the lower half. Gypsum, also in trace amounts, appears to be present in samples 20630, 20631, and 20633.

Zone XVI (20627-20626)

The mineral assemblage is comprised of illite/smectite, glauconite/smectite, and traces of degraded kaolinite. There is a slight tendency for crystallinity of illite/smectite and glauconite/smectite to improve toward the base.

Zone XVII (20625-20604)

Glauconite/smectite is by far the most important mineral in the zone. The upper boundary of the zone is the Eocene-Oligocene unconformity. The uppermost two samples, 20605 and 20604, display very poorly crystallized glauconite/smectite. Well crystalized gypsum is present in samples 20622, 20612, and 20611. Degraded kaolinite was identified in samples 20607 and 20606, and traces of clinoptilolite-heulandite in samples 20625, 20608, and 20607.

Zone XVIII (20603-20602)

The mineral assemblage consists of 7$\mathring{A}$ chlorite (berthierine), illite, and chlorite/smectite (sample 20602). Sample 20603 also contains traces of zeolites (clinoptilolite-heulandite) and gypsum.

Zone XIX (20601-20600)

The crystallinity greatly improves upward through the zone. The major minerals are 7$\mathring{A}$ chlorite (berthierine) and illite/smectite. Glauconite/smectite appears to be present only in trace amounts and is poorly crystallized. Traces of gypsum are recognized only in sample 20600.

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Zone XX (20599-20597)

The mineral assemblages display a well defined trend of increasing crystallinity from the base toward the top of the zone. The identified minerals are illite/smectite, poorly crystallized glauconite/smectite, 7Å chlorite (berthierine), and traces of clinoptilolite-heulandite.

Zone XXI (20596-20591)

The degree of crystallinity of minerals decreases both up and down from the central part of the zone. The major mineral is chlorite with some illite/smectite. The latter is absent from the lowermost two samples, 20596 and 20595, which contain chlorite/smectite instead. Traces of gypsum were observed in all the samples except 20596. Clinoptilolite-heulandite are also present in trace amounts in sample 20591. Trace amounts of glauconite/smectite were recognized in all but sample 20591.

Zone XXII (20590-20587)

The lower two samples contain fully expendable smectite. Illite/smectite is present higher in the zone but is absent from the uppermost sample, 20587. Traces of degraded kaolinite and possibly illite were observed in all but sample 20588 where kaolinite is absent. Gypsum and traces of clinoptilolite-heulandite are present throughout.

Zone XXIII (20586-20577)

The dominant mineral is chlorite/smectite showing progressive increase in the degree of crystallinity from the top toward the base of the zone. Traces of degraded kaolinite are present throughout. Poorly crystallized trace amounts of what appears to be illite, are observed in the lower half of the zone. Samples 20586, 20585, 20584, 20583, and 20582 may also contain some small amounts of gypsum.

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Zone XXIV (20576-20575)

The basal part of the zone is dominated by chlorite/smectite. Because of a very poor quality of the X-ray diffractogram of sample 20575, probably due to a low degree of crystallinity, it was not possible to identify the 14Å peak mineral. Degraded kaolinite is present in both samples. Gypsum is present only in sample 20576.

Zone XXV (20574-20571)

Illite/smectite appears to be present in all except the topmost sample (20571), which is just below the Tertiary - Quaternary unconformity separating marine sediments below from the fluvial Columbia Formation above. Traces of degraded kaolinite were recognized in samples 20572 and 20571. Sample 20574 contains fully expendable smectite.

DISCUSSION

Lithostratigraphy and Clays

Potomac Formation

The clay assemblage of the sandy part of the Potomac Formation consists of traces of chlorite, illite, kaolinite, and illite/smectite, and corresponds to zone I (Plate 2). The sediment is a fluvial sand and all the clay minerals were produced by weathering processes on land. Evidence for some minor post-depositional alteration is provided by traces of gypsum.

In the upper, clayey, portion of the Potomac section, clay minerals are represented by chlorite, illite, and kaolinite. The contact with the overlying Magothy Formation is an unconformity. It is possible that the uppermost part of the Potomac was exposed before the Magothy deposition and thus subjected to weathering. This seems to be reflected in a definite trend in both degree of crystallinity and relative amounts of clay minerals (zone II). Kaolinite appears to have been little affected by the changes.

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Magothy Formation

Clay zones III, IV, and the lower part of zone V are
represented in the Magothy Formation (Plate 2). The clay
minerals present are: chlorite, illite, berthierine,
kaolinite, illite/smectite and chlorite/smectite. Kaolinite
is present in the lower part of the Magothy Formation, is
absent from most of the central part, and present again in the
upper part. Zeolites (clinoptilolite-heulandite) and
glauconite/smectite were also identified in the upper half of
the formation. This is, in fact, the first appearance of
zeolites in the section. Gypsum is developed throughout
except in the lower two samples (20705 and 20704).

Merchantville Formation

There is a distinct difference in the clay mineral
assemblages between the lower and upper parts of the formation
(Plate 2). In the lower part the assemblage is represented by
glauconite/smectite, chlorite, and degraded kaolinite.
Glauconite pellets compose up to about 70% of the sand
fraction. The clay mineral suite in the upper part consists
of chlorite/smectite, illite, and degraded kaolinite. The
transitional middle part also contains some illite/smectite.
Gypsum is present in most of the samples; glauconite pellet
content in the upper part is considerably less than in the
lower part.

"Englishtown" Formation

The clay assemblage is made up primarily of
glauconite/smectite, chlorite/smectite, chlorite, and degraded
kaolinite (Plate 2). The basal and the topmost parts of the
formation lack glauconite/smectite but contain illite instead.
The lowermost two samples (20685 and 20684) also contain
illite/smectite, whereas chlorite/smectite is absent here as
well as in sample 20679. Gypsum is lacking in the lowermost
sample (20685) only; zeolites are identified in the uppermost
two samples (20680 and 20679). Glauconite pellets are present
throughout but not abundant.

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"Marshallton" Formation

There is a distinct difference in clay composition between the sandy lower part and the silty upper part (Plate 2). The clay composition of the lower part includes chlorite/smectite, chlorite, illite, and degraded kaolinite. The upper part is represented by glauconite/smectite, 7Å chlorite (berthierine), and illite/smectite. Glauconite pellets are more abundant in the lower part and account for up to about 70% of the sand fraction. The first appearance of elemental sulfur is recorded in the upper part. Gypsum is absent except in sample 20675.

Pamunkey(?) Formation

This formation encompasses at least nine clay zones (Plate 2). Glauconite/smectite is the only clay mineral consistently present throughout the formation. Up to the Maastrichtian-Danian (Cretaceous-Tertiary) unconformity, it is accompanied by 7Å chlorite (berthierine) and illite/smectite.

The section of the formation from the top of Danian to the depth to about 900 feet contains a clay suite composed of glauconite/smectite, 7Å chlorite (berthierine), and illite/smectite. Zeolites and gypsum are present continuously through zones IX and X. Glauconite pellets are well developed although they generally make up less than 20% of the sand fraction. A trace amount of elemental sulfur was detected in sample 20663. Gypsum is common.

The section above the Ypresian-Lutetian unconformity contains primarily glauconite/smectite and zeolites. Zeolites are absent in the uppermost part; degraded kaolinite is present. The central part also contains elemental sulfur; above and below illite/smectite is present. Glauconite pellets are developed in various amounts throughout the section. Gypsum is rare.

Piney Point Formation

The formation, below the Eocene-Oligocene unconformity, is composed predominantly of glauconite/smectite (Plate 2). Zeolites, degraded kaolinite, and traces of gypsum are rare and sporadic in occurrence. Glauconite pellets are abundant and present throughout the formation.

The clay assemblage above the unconformity is considerably different. It consists of 7Å chlorite (berthierine), illite, traces of zeolite just above the unconformity, and chlorite/smectite. Glauconite pellets are absent.

Calvert Formation

The Chattian part of the formation contains the clay suite glauconite/smectite, 7Å chlorite (berthierine), and illite/smectite (Plate 2). Trace amounts of gypsum were recognized at the base, while rare glauconite pellets are present throughout. Zeolites were also identified.

The silty section up to about 240 feet contains chlorite/smectite at the base and chlorite and illite/smectite in the remaining part. Gypsum is present throughout.

The sandy section that follows upward (240 feet to about 200 feet) consists of fully expendable smectite in the lower part, illite/smectite, illite, and kaolinite in the lower part. Gypsum is present in most of the sand section. Zeolites are present throughout.

Above the sandy section and up to the Miocene-Pleistocene unconformity, the most common minerals are degraded kaolinite, chlorite/smectite, and illite. Illite, however, is only present in the lower part of this section and chlorite/smectite extends from the base up to a depth of about 90 feet. Illite/smectite is present in the upper part of the formation.

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Paleoenvironments and Clays

The basal part of the section, the Potomac Formation, is made up of fluvial deposits (Plate 2). The clay minerals appear to have been formed primarily by weathering processes on land although there is evidence for post-depositional changes. This is particularly evident in zone II where the gradational alterations are well illustrated by the examples of both illite and 14Å clays.

Zone III corresponds to the initial marginal marine sediments of the Magothy Formation (Plate 2). Distinct trends in the degree of crystallinity of clay minerals are recognized (Plate 1). The possible influence of marine water brought about development of illite from the upgrading of either illite/smectite or detrital micas or both.

Gradual and intermittent deepening of water corresponding to zone IV resulted in the formation of 7Å chlorite (berthierine), breakdown of kaolinite, and improvement of illite crystal structure. The presence of authigenic zeolites suggests volcanic activity along the nearby continental margin. Some illite/smectite may have been formed by alteration of zeolites. As transgression progressed, water deepened, and both chlorite and glauconite/smectite were developed (zone V). Kaolinite is present but its structure has been degraded due to its instability in a marine environment. This section encompasses the upper part of the Magothy and most of the Merchantville. Glauconite is also developed in sand-size pellets in the Merchantville and dominates the sand fraction.

The first regression began in middle Campanian resulting in shallowing of the sea (Plate 2), and the clay minerals composition changed accordingly. This is illustrated in zone VI where the degree of crystallinity decreases upward through the zone. This trend seems to have not been affected by changes in lithology. The presence of more zeolites in the upper part of zone VI (upper part of the Englishtown Formation) suggests possible sporadic volcanic activity at that time.

The next transgressive phase began in late Campanian and continued through part of middle Maastrichtian resulting in rather rapid deepening of the sea (Plate 2). As a result the trend displayed by clay minerals is opposite to that observed

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in zone VII above; here, the crystallinity improves upward
through the section. Kaolinite is absent. Berthierine shows
gradual improvement upward, while glauconite/smectite is
poorly developed, although glauconite pellets are well
developed but generally not abundant. Elemental sulfur is
characteristic for this zone.

Just below the Cretaceous-Tertiary boundary, evidence
suggests a sudden shallowing of the sea from upper bathyal to
middle neritic (Plate 2). The clay assemblage (zone VIII) is
composed primarily of glauconite/smectite and 7Å chlorite
(berthierine). A faint improvement in crystallinity downward
is indicated. Glauconite pellets are well developed and
abundant. This section, together with most of zone VII below,
makes up the lower part of the Pamunkey Formation.

The Danian section (zone IX) of the Pamunkey Formation is
bounded by unconformities (Plate 2). Water depth is
considerably deeper than that indicated for zone VIII below.
Glauconite/smectite is developed throughout. Zeolites are
well developed also, but some may have been partially altered
to illite/smectite. A slight improvement in crystallinity up
through the section is indicated. Glauconite pellets are
abundant in the basal part only.

The Thanetian part of the Pamunkey Formation roughly
corresponds to zone X. The sediments of the lower half of
this part were deposited in the deepest water of all the
sediments in the Je32-04 well. The clays are represented
primarily by glauconite/smectite and 7Å chlorite
(berthierine). Zeolites are abundant. Illite/smectites are
also well represented and in part may have been formed by the
alterations of zeolites. Glauconite pellets are present in
small amounts.

The clay assemblage of zone XI occupies an interval of
the Pamunkey Formation of uncertain age, and was probably
deposited in a slowly regressing sea. Glauconite/smectite and
degraded kaolinite are developed throughout the zone.
Chlorite/smectite and illite/smectite have also been
identified. Zeolites are well developed, as are glauconite
pellets.

The sediments of the upper middle part of the Pamunkey
Formation, bounded at the top by the Ypresian-Lutetian
unconformity, correspond to zone XII and zone XIII. The

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sediments of zone XII were deposited in slightly deeper water than those of zone XIII. Unstable degraded kaolinite, glauconite/smectite, and illite/smectite are developed throughout zone XII. A slight increase in crystallinity downward is indicated. Although no definite relationship between zeolites and illite/smectite is discernable, it is possible that some of the illite/smectite are the alteration products of the zeolites. Glauconite pellets are present in small amounts only.

The deposition of zone XIII sediments appears to have taken place in slightly shallower water than those of zone XII (Plate 2). Zeolites show distinct negative correlation with illite/smectite indicating the genetic relationship of the two. The percent of smectite in the mixed-layer clays also progressively increases downward. Glauconite/smectite is present throughout; unstable kaolinite disappears about half way up the zone. Glauconite pellets are rare.

The silty section at the base of the Lutetian and just above the Lutetian-Ypresian unconformity roughly corresponds to zone XIV (Plate 2). Glauconite/smectite and illite/smectite are present throughout this section. Glauconite/smectite is poorly crystallized. Traces of zeolites and elemental sulfur were also recognized. The deposition of the sediments of this section, as well as those of zone XV above, took place at upper bathyal depths. Zone XV corresponds to all except the topmost part of the remaining Pamunkey Formation. The clay assemblage is composed of glauconite/smectite and illite/smectite (in the upper part only). Again, the genetic relationship of illite/smectite to zeolites is evident. Elemental sulfur is present in the lower part only. Crystallinity improves upward through the section.

The sediments of the uppermost part of the Pamunkey Formation correspond to zone XVI and were deposited in progressively shallow water. Glauconite/smectite, illite/smectite, and traces of degraded kaolinite make-up the clay mineral suite. Zeolites are absent possibly indicating the end of the Paleocene-early and early middle Eocene volcanic activity along the continental margin. The increasing crystallinity trend of clays in zone XVI is toward the base. Glauconite pellets are abundant.

The clay mineral composition of the Piney Point Formation is rather simple and persistent up to the Eocene-Oligocene unconformity and made up almost exclusively of glauconite/smectite (Plate 2). The water depth was within the outer and middle neritic range reflecting a generally slow regression. Zeolites are present only sporadically. Rare degraded kaolinite was identified only close to and below the Eocene-Oligocene unconformity. Glauconite pellets are abundant and by far the predominant component of the sand fraction. Degree of glauconite/smectite crystallinity is consistent throughout the section, with the exception of the uppermost part, where it improves downward.

The part of the Piney Point Formation above the Eocene-Oligocene unconformity and below the Calvert Formation lacks glauconite. The clay assemblage is primarily composed of 7Å chlorite (berthierine), illite, and a trace of chlorite/smectite in the upper part. This suite possibly reflects both reworking processes and sudden deepening of the sea which occurred in early Chattian. The crystallinity improves up through the section (zone XVIII). A trace of possible zeolites may be present in the basal part.

The deposition of the sediments of the basal part of the Calvert Formation occurred during a relatively short transgressive phase followed by an even shorter regressive phase (Plate 2). These phases correspond to clay zones XIX and XX respectively. The clay assemblage of the transgressive phase consists of glauconite/smectite, 7Å chlorite (berthierine), and illite/smectite. Rare glauconite pellets were also identified. The regressive phase deposits have a similar clay mineral suite. Traces of zeolites were noted throughout suggesting volcanic activity in the nearby region at the end of the Oligocene. There is a definite upward improvement in crystallinity indicated in clay assemblages of both transgressive and regressive sections.

Throughout the Miocene time the water depth was generally shallow marginal marine to inner neritic. The basal part has a clay suite similar to that of the underlying Oligocene suite: glauconite/smectite, chlorite, illite/smectite, and some chlorite/smectite. Glauconite pellets are absent. Zeolites are present in trace amounts only at the top of this sequence (zone XXI). The best crystallized minerals are in the central part of this zone.

In the upper part of the lower Miocene section the sediments are sands deposited in shallow water in a delta-front environment. The clay assemblage is dominated by smectite and illite/smectite although they are both absent in the uppermost part of the section. Degraded kaolinite and traces of illite were also identified. Presence of zeolites testifies to renewed volcanic activity along the continental margin at that time. This sequence corresponds to clay zone XXII.

The remaining part of the Miocene extends to the erosional unconformity that marks the boundary with the overlying Pleistocene fluvial sediments. This part of the Miocene corresponds to the three clay zones: XXIII, XXIV, and XXV. Degraded kaolinite is present in most of the section. Illite is primarily developed in the lower part, whereas chlorite/smectite in the lower and middle parts. Smectite and illite/smectite are rare and restricted to the upper part. The depositional environment was exposed to a very slow and gradual regression eventually resulting in the emergence and erosion of the sediments. The continuation of volcanic activity from the early Miocene into the earliest middle Miocene is suggested by traces of zeolites.

INTERPRETATION OF RESULTS AND CONCLUSIONS

Changes in the degree of crystallinity within the clay zones suggest the following:

(1) The processes that brought about the trends displayed within each clay zone have either greatly slowed down or possibly ceased completely. Otherwise, clay zones, as defined in this study, would not be clearly defined and most likely gradational changes would mask the zone boundaries.

(2) If the above assertion is correct, the changes within the zones most likely took place during or shortly after the deposition.

Although kaolinite is greatly degraded, even in the oldest marine formations of the section studied, its presence seems to support the above suggestions. Kaolinite develops on land by weathering processes in environments where effective

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leaching (good drainage) removes easily soluble components.
In a marine environment, it signifies the influx of
terrestrial material. Most likely, preservation of kaolinite
in a marine environment occurred in shallow depths and close
to both the land where it developed and the mouth of rivers
through which it was transported into the sea. Comparing the
occurrences of kaolinite with the paleoenvironmental depth
curve (Plate 2) suggests that for the most part that was
indeed the case in the section studied. The exceptions are
parts of the Maastrichtian and Ypresian sections where
kaolinite seems to have been deposited in outer neritic-upper
bathyal depths.

The distribution of illite/smectite, irrespective of
lithology, suggests that at least some of this mineral may
also be detrital in origin derived from mica or other clays.
Once in a marine environment, it was probably upgraded to
illite by fixation of potassium from sea water (Velde and
Bystrom-Bruzewitz, 1972). Other illite/smectite may have
developed by alteration of zeolites (clinoptilolite-
heulandite).

Illite is commonly formed in a marine environment,
favoring carbonate facies, but is also present, and not
uncommonly dominant, in clay facies of ancient rocks (Weaver,
1957; Grim, 1968). In the marine environment it develops most
likely by upgrading of random mixed-layered clays or detrital
micas. Authigenic or upgraded illites found in the present
study appear to be characterized by a high degree of
crystallinity. They are rather sporadic in occurrence in the
section except in the part comprising zones I to VI, where
they are almost continuous. However, they are also developed
as a mixed-layered clay illite/smectite. The typical detrital
and terrestrial illites are present at the base of the
section, in the Potomac Formation.

Chlorites are present in sedimentary rocks of all ages
(Weaver, 1959). In the present study chlorites occur in both
the terrestrial and marine parts of the section.

Chlorites (14Å) identified in the Potomac Formation were
formed by weathering processes on land. The same origin may
be ascribed the 14Å chlorites in the basal, transitional non-
marine-marine part of the overlying Magothy Formation (zone
(III). Higher up in the Magothy 7Å chlorite is present,
commonly as a pelletal chlorite similar to glauconite and

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known as berthierine; it is present only in the basal part of
zone IV. It is generally found near river mouths (Odin and
Matter, 1981). Other occurrences in the present study are in
the Maastrichtian, Paleocene, and Oligocene parts of the
section.

Chlorite (14Å) and chlorite/smectite are present
sporadically in the lower and upper parts of the section,
appear to be primarily of marine origin, and are absent from
the middle part encompassing the rocks of Eocene age. They
appear to be primarily of marine origin. In a marine
environment, with increasing salinity, chlorites progressively
develop from mixed-layered clays (Powers, 1967). Presence of
magnesium in sea water also favors development of chlorite.

At shallower water depths, where magnesium is
considerably more abundant than potassium, magnesium will be
taken-up by mixed-layer clays replacing calcium and sodium
resulting in the formation of chlorites (Hauff and McKee,
1982). Their association with glauconite in the section
supports marine origin for chlorites. Chlorite/smectite
present at several intervals in the section may represent a
transitional phase from illite/smectite into chlorite (Van
Moort, 1971).

Glauconite is abundant and quite persistent throughout
most of the marine part of the section in pelletal form, as
part of some clays, and as a matrix in coarser sediments.

The mineral identified in Je32-04 as glauconite is
actually glauconite/smectite with glauconite making up
generally about 90% of the mineral (Thompson and Hower, 1975;
Brindley and Brown, 1980). Much has been written about
glauconite pellets and hypotheses about their origin abound
(Kemper, 1982; Odin and Matter, 1981). Discussion of these is
not relevant to the present study but several problems which
arose during the course of this study are discussed below. It
is well known that glauconites, once formed to maturity or
close to it, as indicated by the amount of potassium in their
composition, will not change much during most diagenetic
conditions of burial (Velde, 1983). The persistence of this
mineral in the Je32-04 section from early Upper Cretaceous to
Oligocene seems to support this. It is primarily associated
with 7Å chlorite and illite/smectite or illite,
chlorite/smectite, and illite/smectite. All of these minerals
in these associations appear to be diagenetic and formed or

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upgraded in marine environments. The exception to this is the
section corresponding to the Piney Point Formation; here,
glauconite is generally the only clay mineral in the
sediments. It is particularly interesting, and possibly
significant, that zeolites are extremely rare in the same
section.

The major discovery in the course of this study was the
presence and selective abundance of zeolites (clinoptilolite-
heulandite). They are diagenetic minerals and almost always
display sharp peaks on X-ray diffractograms suggesting a high
degree of crystallinity. There is a general consensus that
clinoptilolite results from alteration of acidic volcanic
glass, volcanic ash, and volcanic debris in general (Mason and
Sand, 1960; Utada, 1970; Gottardi and Obradovic, 1978). In
the Je32-04 section, Jordan and Adams (1962) were the first to
discover evidence for early Tertiary volcanic activity.

Transformation of volcanic glass into clinoptilolite is
an extremely slow process; consequently, glass is generally
present in rocks younger than Eocene, whereas clinoptilolite
is abundant in sediments of Cretaceous to Eocene ages. The
results of the present study generally confirm this; zeolites
are most abundant and persistent from the Cretaceous-Tertiary
boundary to lower middle Eocene (Plate 1). This suggests
rather extensive and continuous volcanic activity along the
nearby continental margin during that time interval. Tectonic
instability in the same time period is also indicated by at
least three unconformities: Cretaceous-Paleocene, Danian-
Thanetian, and Ypresian-Lutetian. The continuous occurrence
and the greatest abundance of zeolites also generally coincide
with the existence of the deepest water in the
paleoenvironments of Je32-04 section; upper bathyal to outer
neritic-upper bathyal (Plate 2). Alteration of clinoptilolite
commonly results in the development of illite/smectite or
heulandite (Mason and Sand, 1960). In the present study the
alteration of clinoptilolite into illite/smectite is
particularly well evident in clay zone XIII.

Gypsum and elemental sulfur are developed in trace
amounts only. Gypsum is present in most of the section below
the Ypresian-Lutetian unconformity and in parts of the lower
and middle Miocene sections. With a few minor exceptions, it
is absent in the section corresponding to the Piney Point

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Formation. Elemental sulfur was detected only in parts of the Maastrichtian and Lutetian sections and possibly in the basal part of the Thanetian and basal and topmost parts of Ypresian.

The original source of sulfur is unknown although it is possible that it was volcanic gases. This assumption is based primarily on the volcanic activity revealed by this study. Gypsum appears to have been formed by breakdown of calcite and pyrite with calcium and sulfur combining into gypsum. The presence of gypsum suggests at least locally well-aerated water.

Elemental sulfur found in the present study may have formed by reduction of gypsum, possibly by organic activity.

There is a general relationship of the clay zones to lithology, although in some parts of the section this relationship appears to be lacking. The most notable example is the part of the section bounded by the Danian-Thanetian and Ypresian-Lutetian unconformities. Although the section displays a rather uniform lithology on both gamma-ray and electric logs, four distinct clay zones are recognized. This probably reflects deposition in four different environments, as indicated by the paleowater-depth curve (Plate 2).

It is interesting to note that, for the most part, the degree of crystallinity coincides with increasing paleowater depth; the crystallinity of clays improves with water depth.

The degree of crystallinity at all but one unconformity persistently increases away from the unconformity, both above and below it. The only exception is the Danian-Thanetian unconformity where the trends are opposite.

There also appears to be a reasonably good correlation between clay zones and time-stratigraphic units at the stage level. Excellent correlations are noted for Danian, Thanetian, Thanetian(?)-Ypresian(?), Lutetian-Bartonian(?), and Langhian where a separate, single clay zone correlates with each of the above stages. In other cases several clay zones correspond to a specific stage, for example, Maastrichtian (two zones), Lutetian (two zones), Chattian (three zones), Langhian-Serravallian (two zones).

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All of these not only seem to support the validity of the original arbitrary subdivision of the section into clay zones, but also strongly suggests that the present clay assemblages within each zone were established during or shortly after the deposition of the sediments. The only exceptions are the clays composing the zones in the continental deposits which appear to have been formed primarily by weathering processes on land.

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