

CLAY MINERAL STUDIES OF SOME RECENT MARINE SEDIMENTS OFF THE NORTH CAROLINA COAST

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ABSTRACT

Studies of Recent marine sediments from the North Atlantic Ocean were made in order to understand better the effects of diagenesis on the clay minerals. Samples from the continental shelf, the continental slope and the floor of the northwestern basin, north of Bermuda, were made available through the courtesy of the Lamont Geological Observatory of Columbia University.

Most of the argillaceous material in these sediments is a poorly crystalline, complex mixture of chlorite and illite. The samples contain a small amount of kaolinite and montmorillonite. Some of the problems involved in the identification of these complex mixtures are discussed. Studies of the clay minerals reveal that a slight diagenetic change takes place, as indicated by the increasing crystallinity of chlorite and illite, with increasing depth below the clay-water interface and with increasing water depth. Some of the cores contain zones of red clay and the clay minerals contained therein are relatively well crystallized materials in contrast to the clay minerals in the greenish-gray clays. An hypothesis based on the oxidation state of the iron is advanced to explain the differences between the crystallinity of the three layer clay minerals in the red and greenish-gray clays.

INTRODUCTION

All geologists are familiar with the axiom that the present is the key to the past. Before we can completely understand the significance of the clay minerals in the ancient sedimentary rocks, we should try to understand the geologic implications of clay minerals in Recent sediments. As a small part of this attempt, this paper presents results of a study of the clay mineral composition of a series of core samples from the bottom sediments of the Atlantic Ocean off the coast of North Carolina.

Grim (1953, p. 348) has pointed out that Recent sediments are frequently composed of mixtures of poorly crystallized minerals which make identifications very difficult. Refined techniques have to be employed in order to identify many of the clay mineral components. In recent years, many significant contributions have been made to our knowledge of Recent sediments. The American Petroleum Institute has been, and is, actively supporting research programs which cover many aspects of Recent sediments including mineralogy, biology, zoology, chemistry, etc.

This study had several objectives which can be enumerated as follows:

1. To identify the clay minerals present in these particular Recent marine sediments.

2. To determine if there is a relationship between distance from shore and type of clay minerals present.
3. To see if depth of water has any effect on clay mineralogy.
4. To study the clay minerals from top to bottom of the cores at closely spaced intervals and see if there are any variations in clay mineralogy.
5. To observe if there are any changes in the clay minerals which could be related to color change, because some of the cores contained red colored sediments in addition to the more typical greenish-gray sediment.

Actually, all five of these phases relate to diagenesis which is defined as post-depositional changes in a sediment which lead to lithification (Pettijohn, 1949, p. 477). We must understand these changes before we can relate the true history of a sedimentary rock and make deductions concerning its environment of deposition, origin, etc.

ACKNOWLEDGMENTS

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LOCATION AND DESCRIPTION OF THE CORES

The cores used in this study were collected during the years 1949 to 1951 and are stored at Lamont Geological Observatory of Columbia University under the filing code of C8-1, C8-3, C8-4, A156-4, A167-5, A167-9 and A167-10. The cores studied were from the continental shelf, the continental slope, and the deep basin northwest of Bermuda. The geographic location of the cores is shown on Figure 1. Tolstoy (1951, p. 443) characterizes the broad abyssal basins in this area as having smooth floors or plains covering an area of more than 200,000 square miles. Ericson *et al.* (1952, p. 498) have indicated that some coarse sediments on the deep abyssal plains are indicative of turbidity currents.

The following table shows some of the pertinent data for each core:

Core No.	Length in cm.	Water depth in meters	Latitude N.	Longitude W.
C8-1	388	165	34°38½'	75°39½'
C8-3	406	860	34°40'	75°29½'
C8-4	494	1025	34°50¼'	75°18'
A156-4	540	3100	34°49'	74°41'
A167-5	964	5118	34°09'	70°51'
A167-9	320	4645	33°14½'	73°41'
A167-10	517	5030	31°47'	73°24'

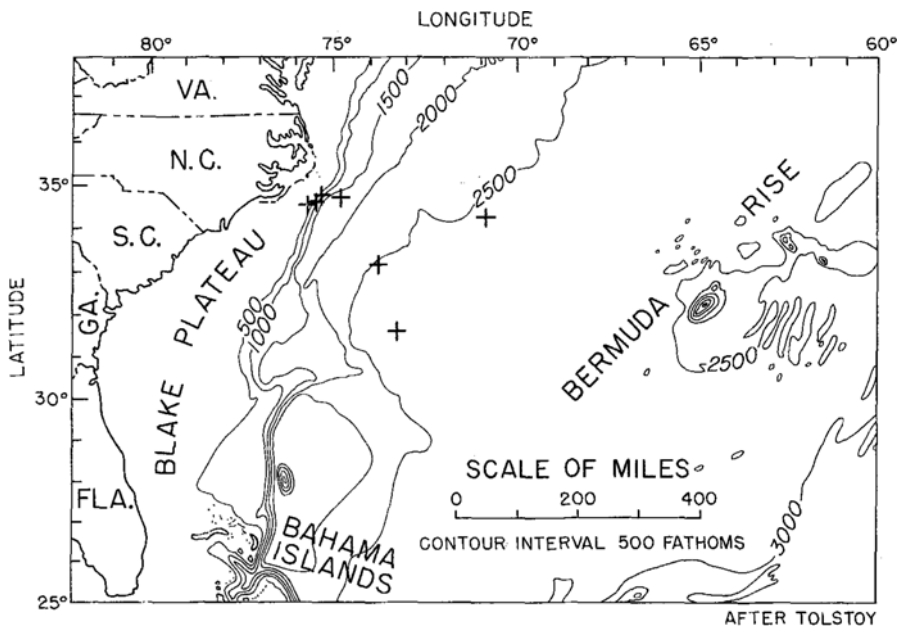


FIGURE 1. — Locations of core samples.

The length of the cores varies from 320 to 964 cm. and the water depth varies from 165 to 5,118 meters. The water depth and distance from shore where the core was taken are shown diagrammatically on Figure 2.

In general the cores were similar lithologically but there were some significant variations. The shallowest core C8-1 is a gray-green sandy-silty clay. Cores C8-3 and C8-4 are composed predominantly of gray-green silty clay. C8-4 contained one rose colored zone at a depth of 480 cm. The A156-4, A167-5, A167-9, and A167-10 cores are composed predominantly of gray-green clays with one or two red clay zones and a few interspersed silty zones. The lithologies of some of these cores have been described by Ericson *et al.* (1952, pp. 501-511).

The Foraminifera from all cores except A167-5 and A167-10 have been described by Sayyab (1954, pp. 15-27) and all the forms range in age from Pleistocene to Recent so that the exact age of the sediments was not determined. A statistical study of species might indicate whether the sediment at the bottom of the core is Pleistocene or Recent but no attempt has been made to do so in these cores.

ANALYTICAL PROCEDURE

The cores, stored at Lamont Geological Observatory in plastic covered troughs, had air dried completely when the samples were taken for this study. The procedure used in preparation and storage of the cores has

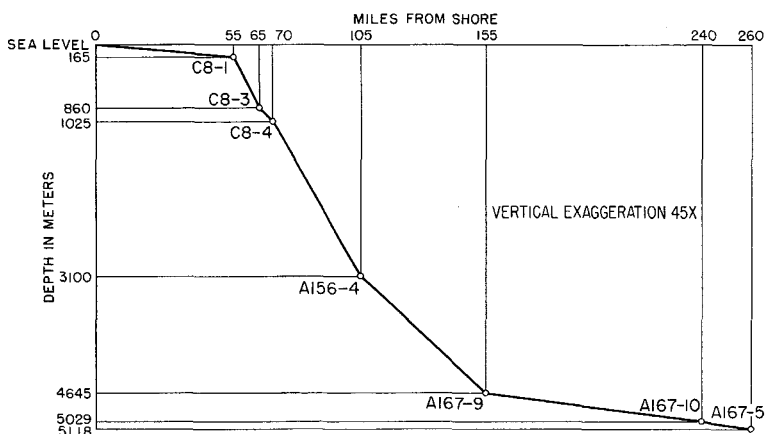


FIGURE 2. — Approximate profiles showing water depth and distance from shore of core samples.

been described by Ericson (1953, p. 6). The core samples, approximately 5 cm. in diameter, had been split in half parallel to the axis of the core. Continuous strips of one-quarter of cores of C8-1, C8-3, and C8-4 were taken. Chips approximately 3 cm. long were taken every 10 cms. along the core length of A156-4 and A167-9. Only selected samples of red clay zones were taken from cores A167-5 and A167-10.

Each individual sample was placed in distilled water and disaggregated with a mechanical mixer. The suspension was then passed through a 300-mesh ASTM sieve and the material retained on the sieve was dried and saved for microscopic study. The clay fraction ($<2 \mu$) was separated by a sedimentation procedure. Sodium hexametaphosphate was used as the dispersing agent when needed. A General Electric XRD-3D spectrogoniometer using nickel-filtered copper radiation was used in the X-ray identifications. The clay material was settled on glass slides (Bradley, Grim, and Clark, 1937, p. 216) for X-ray study, which orients the basal planes of the clay minerals. Some of the clays were treated with glycerol and some were heated to 200° C for one-half hour to determine the presence or absence of montmorillonite.

CLAY MINERAL INVESTIGATIONS

Relatively few detailed investigations have been made of the clay mineral composition of Recent marine sediments. Correns (1937, pp. 137-190) found that the fine-clay fraction of Recent marine sediments is substantially all crystalline, and that mica, kaolinite, montmorillonite, and halloysite were present in samples collected from the middle and south Atlantic ocean.

Dietz (1941) found that illite was the predominant clay mineral in the majority of Recent sediments studied by him, especially those most distant

from shore. He found kaolinite and a minor amount of montmorillonite, especially in near shore samples. Dietz felt that illite develops by alteration of montmorillonite after deposition in the sea.

Grim, Dietz, and Bradley (1949, pp. 1806-1807) found illite, montmorillonite, kaolinite and some chlorite in the Recent sediments off the coast of California. According to their findings, illite is the most abundant clay mineral present and kaolinite the least abundant. The clay minerals in these samples were poorly crystalline, complex mixtures of intimately intergrown and discrete mineral types. They believed that kaolinite is slowly converted to chlorite and illite by diagenetic changes.

Grim and Johns (1954, pp. 81-103) from a study of some Recent sediments in the Gulf of Mexico, reported that montmorillonite is carried by the Guadalupe River into the Gulf in the Rockport, Texas, area, but that illite and chlorite predominate in the marine environment.

Powers (1954, pp. 68-80) reported on a study of Recent sediments in Chesapeake Bay and found that degraded illite is being converted to chlorite in estuaries of the bay.

RESULTS OF THIS INVESTIGATION

A total of 266 X-ray spectrograms were run on the core samples in this study. Each core was analyzed individually and X-ray spectrograms of each 10 cm. were compared; comparisons were then made of X-ray spectrograms from each core. A few of the more significant and representative X-ray spectrograms will be discussed in detail in order to show reasons for the conclusions that were reached in this study.

The core sample nearest the shore and shallowest in depth is C8-1. The clay minerals at the top and bottom of this core are shown on Figure 3. At the top the clay minerals are very poorly crystalline.* The X-ray reflections of this top sample indicate that there is a predominance of mixed-layer illite (10 Å) and chlorite-montmorillonite (14.2 Å). Some montmorillonite is present because, on treatment with glycerol, there is a slight expansion of some reflections to a broad subdued peak between 17-18 Å. It is very difficult to detect this expandable clay because of intimate three component intergrowths of illite, chlorite, and montmorillonite. The intensity of the X-ray reflections increases toward 14.2 Å from 10 Å indicating a predominance of larger spacings in the intergrown clay material. The amount of intergrowth material is approximately twice that of discrete chlorite and illite, as determined by adding the total intensity of the intergrowths and comparing this total with the total intensity of illite (10 Å) and chlorite

* The expression poorly crystalline is used to describe the clay unit layers which are either disordered, and/or in which the layers are stacked in a disorderly fashion. This poor crystallinity is indicated on X-ray diagrams because the reflections are less intense, broad, and diffuse in contrast to the sharp, intense reflections of good crystalline materials. Extremely small crystallites also cause less intense, broad, and diffuse reflections.

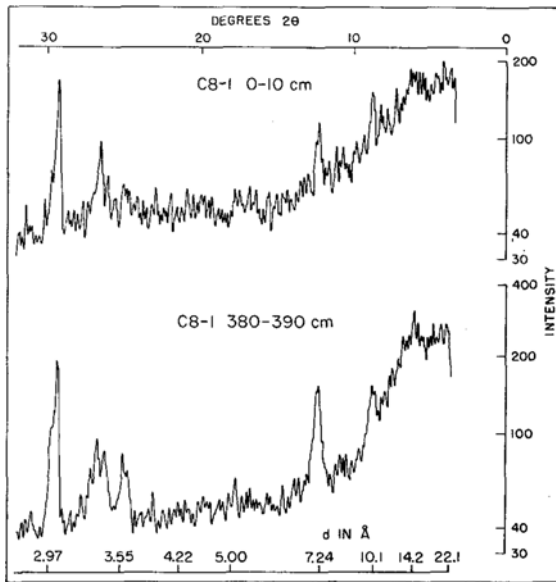


FIGURE 3.—X-ray spectrograms of two clay fractions in Core C8-1.

(14.2 Å) reflections. The intensity of intergrowth material can be measured by dividing the distance between 10 Å and 14.2 Å into equal parts, each part being equal to the width of a discrete illite or chlorite reflection, then adding the intensity of each part, and subtracting the background. Quartz (3.35 Å) and calcite (3.05 Å) reflections appear in this sample and in all other core samples. At the bottom of this core at a depth of 380-390 cm. (Fig. 3) the clay mineral reflections are better defined indicating better crystallinity. Again there is a predominance of intergrown illite and chlorite-montmorillonite but there is also discrete illite (10 Å), chlorite (14.2 Å), and probably some kaolinite (7.2 Å). The heating test sometimes used (Brindley, 1951, p. 49) to distinguish between chlorite and kaolinite does not differentiate the two minerals in this case because the basal reflections are destroyed by 525°-550° C.

Core sample C8-3 is from the continental slope at a depth of 860 meters, 65 miles from shore. The clay minerals in the top 10 cm. (Fig. 4) are relatively poorly crystalline compared to the clay minerals which were examined from greater depths in this core. Again, the mixed-layer material is most abundant and in addition discrete chlorite, illite and a small amount of montmorillonite are present. The clay minerals in the interval from 10-20 cms. from the top of the core (Fig. 4) are better crystalline and mixed-layer intergrowths, illite, chlorite and a slight amount of montmorillonite are also present. The clay minerals at the bottom of this core (Fig. 4) at a depth of 400-406 cm. are relatively well crystallized. The intergrowth of illite and chlorite-montmorillonite is still present but in a smaller amount.

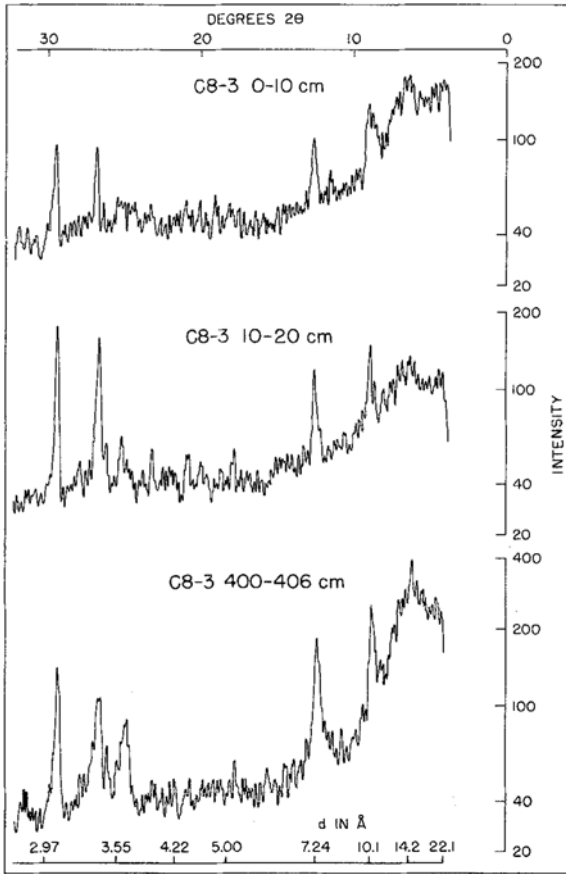


FIGURE 4. — X-ray spectrograms of three clay fractions in Core C8-3.

Illite, chlorite, a small amount of montmorillonite, and kaolinite are the clay mineral components.

Core C8-4 was taken at a water depth of 1,025 meters 70 miles from shore. The clay minerals in the top 10 cm. (Fig. 5) are relatively poorly crystalline in comparison with those at lower depths in this core but relatively better crystalline than those at the tops of the two preceding cores (Figs. 3 and 4). The clay mineralogy is unchanged with intergrowths, illite, chlorite, some montmorillonite, and kaolinite present. At a depth of 470-480 cm. (Fig. 5) the clay minerals become better crystalline with relatively less amount of intergrowths of illite and chlorite-montmorillonite. At a depth of 490 cm. in this core, the color of the sediment changes from greenish-gray to red. In the red clay, there is a marked change in the crystallinity of the clay minerals (Fig. 5). The red clay is composed of illite, chlorite, a small amount of montmorillonite, and a relatively small

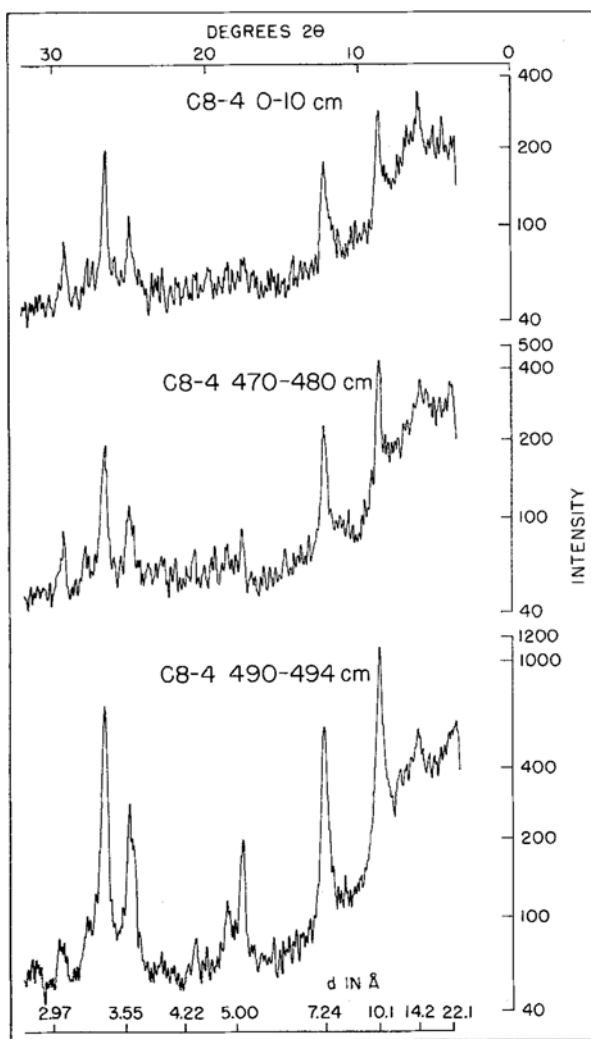


FIGURE 5. — X-ray spectrograms of three clay fractions in Core C8-4.

amount of intergrowths of illite and chlorite-montmorillonite as compared to the greenish-gray clays. The illite in the red clay is a very good crystalline material with a muscovite crystallinity. If the (001) reflections of illite are compared, we can conclude, on the basis of the work of Brown (1951, p. 162) that the illite is dioctahedral, with significant occupation of the octahedral positions with ferric iron.

Core sample A156-4 was taken at a water depth of 3,100 meters and 105 miles from shore. The top of the core (Fig. 6) contains relatively poorly

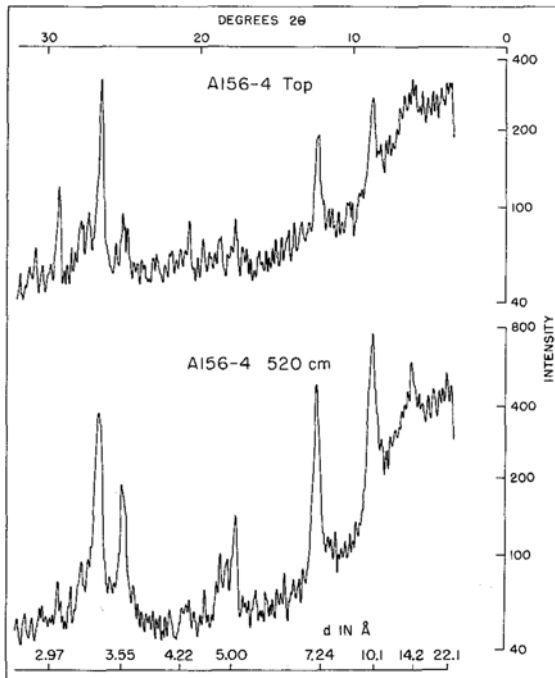


FIGURE 6.—X-ray spectrograms of two clay fractions in Core A156-4.

crystalline illite, chlorite, kaolinite and intergrowths of illite and chlorite-montmorillonite clays, and a small amount of discrete montmorillonite. At a depth of 520 cm. in this core, the clay minerals are better crystallized as is evidenced by the sharper, better defined X-ray reflections (Fig. 6).

Core sample A167-9 was taken at a water depth of 4,645 meters 155 miles from shore. The clay minerals at the top of this core (Fig. 7) are relatively poorly crystalline in comparison with those in the rest of the core, but better crystalline than those in the tops of the preceding cores. At a depth of 15 cm. there is a zone of red clay in which the clay minerals are of better crystallinity (Fig. 7) and there is a relatively lesser proportion of illite and chlorite-montmorillonite intergrowths. At a depth of 45 cm. the clay again is greenish-gray and the X-ray spectrogram (Fig. 7) shows a decrease in crystallinity of the clay minerals as compared to those in the red clay. At a depth of 320 cm., which is the bottom of the core, the crystallinity of the clay minerals has increased slightly from that of the clays at a depth of 45 cm., but the mineralogy is unchanged.

Discussion of the Results

The X-ray spectrograms have shown in every case that the clay minerals in red clays are very well crystallized in comparison with greenish-gray

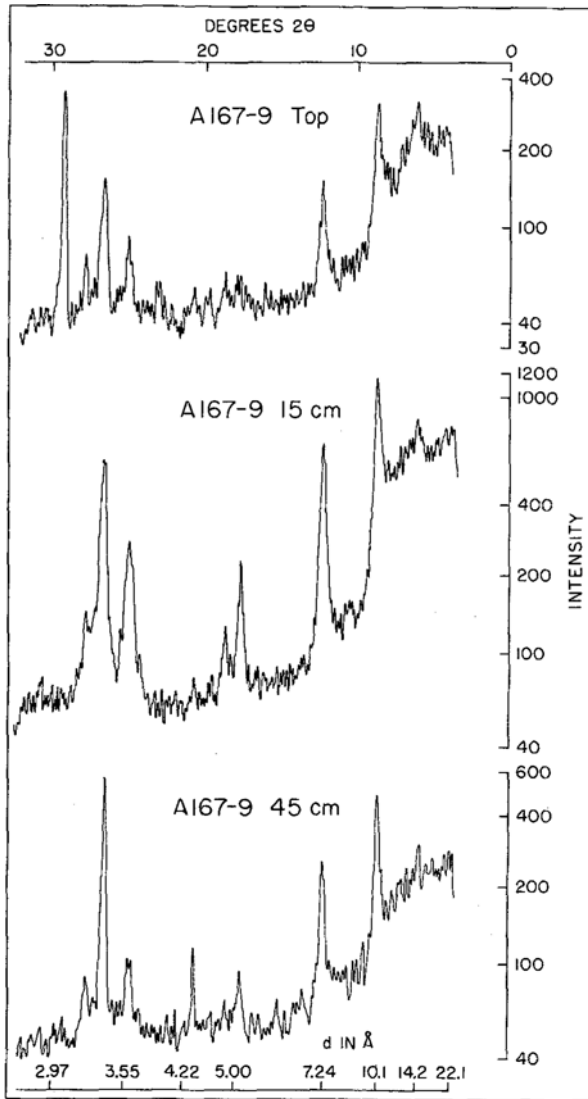


FIGURE 7.—X-ray spectrograms of three clay fractions in Core A167-9.

clays. The red zones contain a better crystallized chlorite and illite and a relatively lesser amount of intergrowth of these minerals. In the Gulf coast region red clays are interpreted as Pleistocene in age (LeBlanc and Bernard, 1954, p. 190), and the red color is attributed to oxidation of the sediment during glacial time when sea level was very low and the sediment was exposed to air. The red clays in Recent sediments off the coast of North Caro-

lina are probably not of this origin because they are found at water depths of some 3,000 to 5,000 meters which is much too deep to have ever been exposed during the Pleistocene. However, these clays could have been brought in by turbidity currents from the shelf during the Pleistocene; much more detailed work on the sediments would have to be done before this could be proved. Another explanation may be that cold water contains more oxygen and that during deposition of the red clay zone the water was very cold and the clays were oxidized as they formed.

The better crystallinity of the clay minerals and the decrease in intergrowths of illite and chlorite-montmorillonite in red clays in contrast to green clays may be a consequence of either (1) the oxidation state of iron at the time of formation of clay in deep basins or (2) a different source area which supplied a better crystalline oxidized clay complex of detrital mica and chlorite. The first hypothesis is favored at the present time because there are no data to indicate that there was a different source, and because the total mineralogy is similar, except that crystallinity of the clay minerals is better. The ionic radii (Ahrens, 1952, p. 168) of ferrous iron is 0.74 Å, of ferric iron 0.64 Å, of magnesium 0.66 Å and of aluminum 0.51 Å. The majority of iron in the clay mineral structures in the green clay zone is probably in the ferrous state. If ferrous iron is in octahedral positions in chlorite, it would be proxying for magnesium and, due to its larger ionic radius might induce strains in the structure which would result in smaller crystals, less order, and therefore, poorer crystallinity. If ferrous iron were present in illite, it would be proxying for aluminum in octahedral positions and again might result in poorer crystallinity due to the same causes. The presence of this larger ion of ferrous iron might favor intergrowths of illite and chlorite which seems to accompany poor crystallinity. Ferric iron, probably present in red clay zones, can proxy for magnesium and aluminum more easily because of its smaller ionic radius, and, therefore tend to form better crystalline illite and chlorite and less intergrowths of the two minerals.

As shown by this study, there is a change in crystallinity of the clay minerals from the top of the core to the bottom which is probably due to diagenetic changes. It may be suggested that this is a reflection of the type of material being brought from the source area, but there is no evidence to support a separate source area and, therefore, the diagenetic change seems the most logical assumption.

CONCLUSIONS

(1) The Recent marine sediments off the coast of North Carolina contain a predominance of the clay minerals illite and chlorite along with intergrowths of illite and chlorite-montmorillonite clays. There are small amounts of poorly defined expandable clay, montmorillonite, and a small amount of kaolinite dispersed throughout the samples.

(2) The type of clay minerals does not change in relation to water depth

or distance from shore, but the crystallinity of the clay minerals changes — with crystallinity increasing with water depth and distance from shore.

(3) The type of clay minerals does not change significantly from the top to bottom of each individual core, but the crystallinity does change — the clay minerals becoming better crystalline with an increasing depth below the clay water interface. The crystallinity of the clay minerals in the top of the cores taken from abyssal depths is better than those which are deepest below the clay-water interface in the shallowest cores.

(4) The crystallinity of the clay minerals in red clays is much better than that in greenish-gray clays probably because the ionic radius of ferric iron is such that it can fit into octahedral positions of chlorite and illite much more easily than ferrous iron. Also the amount of intergrowths of illite and chlorite-montmorillonite material decreases in the red clays.

(5) On the basis of this study, diagenetic changes appear in the form of changes in the crystallinity of clay minerals rather than changes in basic clay mineral types.

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