CLAY MINERALOGY OF THE BOTTOM SEDIMENTS, RAPPAHANNOCK RIVER, VIRGINIA

by

BRUCE W. NELSON

Virginia Polytechnic Institute, Blacksburg, Virginia

ABSTRACT

Bottom sediment clay mineral assemblages from the Rappahannock River and estuary contain kaolinite, illite, unorganized illite, dioctahedral vermiculite, 12.4 Å montmorillonite, 14.2 Å montmorillonite, chlorite, feldspar and quartz. The x-ray diffraction characteristics of these species and their thermal modifications at 25–500°C are described and illustrated. Progressive changes in the mineralogical composition of bottom sediments occur between the fresh-water and saline-water portions of the Rappahannock system. Chlorite and feldspar occur exclusively in the saline portions of the estuary. Illite shows progressive increase in crystallization quality. There appears to be less kaolinite, proportionately, in the estuarine sediments of the most saline zone. x-Ray diffraction diagrams showing these progressive changes are illustrated.

INTRODUCTION

This report describes the mineralogy of clay-sized fraction of bottom sediments from the Rappahannock River and estuary of northeastern Virginia. The data are interesting chiefly because they describe sediments of the fresh-water–marine transition zone. The mineralogy of the coarse fraction, the mineralogy of suspended sediments, and certain chemical measurements will be reported elsewhere. This is the first of several papers that will deal with problems of sedimentation in the Rappahannock River area.

ACKNOWLEDGMENT

GEOGRAPHY

The Rappahannock River drainage basin is a relatively small one, about 2400 miles^2 in area. Headwaters of the Rappahannock rise on the east side of the Blue Ridge Mountains, and its tributaries drain parts of the Blue Ridge and Piedmont physiographic provinces in northeastern Virginia. Most of the sediment carried by the Rappahannock River is derived from weathered felsic crystalline rocks in the Blue Ridge and Piedmont, a source area of about 1600 miles^2. The Rappahannock River crosses the Fall Line at Fredericksburg, 94 naut. miles from its mouth. From Fredericksburg the river flows for about 45 naut. miles in a narrow incised valley across the

10   135

Coastal Plain physiographic province. In the lower 45 naut. miles of its course the Rappahannock forms a somewhat sinuous but funnel-shaped estuary which debouches into Chesapeake Bay. The estuary is about 3 miles wide at its mouth. Within the Coastal Plain area the Rappahannock River and estuary are bordered by Cretaceous and Tertiary sedimentary rocks, but the tributary streams entering from the Coastal Plain are very small and carry almost no sediment.

Sampling stations referred to throughout the text and on the illustrations are numbered with reference to their distance in nautical miles from the mouth of the estuary. Fredericksburg is at station R–94, the head of the estuary is at about R–45, and the mouth is at R–2.

The water overlying the bottom sediments is fresh, generally, as far downstream as station R–50, the lower part of the river. The salinity increases gradually downsteam in the estuary until at the mouth the bottom water has a salinity of about 20‰.

Sediment is transported by tidal currents which reach their maximum velocities in the lower part of the river between stations R–68 and R–45. The maximum observed velocities are 1.4 knots for ebb tide and 1.1 knots for flood tide during the high runoff period of early spring. The tidal velocities decrease downstream in the estuary.

SAMPLING PROCEDURE

Field work was carried out in the Rappahannock River area in August and September 1956. Control sampling sections were established at 4 mile intervals for most of the distance between Fredericksburg and the mouth of the estuary, but at 2 mile intervals in the low salinity transition zone between stations R–50 and R–37. At each control section bottom samples were obtained in a line across the stream. From six to ten bottom cores were spaced evenly across the width of the stream, the number depending on the width at that point. A Trask-type coring instrument modified to hold a plastic liner was used to obtain the samples.

The cores were collected in such a way that a few inches of water overlay the sediment in the plastic liner when the liner was removed from the coring tube. The cored mud was removed from the liner and sampled at depths of 1, 3, 6, 12 and 18 in. below the sediment–water interface. The samples were bottled in glass jars and preserved against bacterial activity with 1 percent phenol.

A total of 90 sampling stations were occupied in the Rappahannock River system below Fredericksburg, and the bottom sediment cores yielded approximately 300 sediment samples. The remarks below summarize the mineralogical observations made on these samples.

IDENTIFICATION OF CLAY MINERAL SPECIES

Clay mineral identifications are based upon x-ray diffraction characteristics of $<4\mu$ oriented aggregates and their response to glycolation and

various heat treatments. The size fractions were obtained by sedimentation after washing the naturally associated water through bacteriological filters until a chloride-free leachate was achieved. The muds were not treated in any way other than washing with distilled water. Glycolation was accomplished by the method of Brunton (1955). The oriented aggregates were heated successively at 200, 300, 400 and 500°C for from 12 to 24 hr. A General Electric XRD–5 diffractometer was used to record the diffraction characteristics using a linear scale range of 1000 counts/sec and Ni-filtered Cu radiation. x-ray diffractograms are illustrated in Figs. 1–9.

Most of the sediment samples contain several different clay mineral species. The relative proportions of the different species vary from sample to sample. In addition certain species vary with respect to hydration state and degree of crystal perfection. The presence of varying proportions of organic matter in various forms, the presence of undefined inorganic constituents such as sulfides and iron hydroxides, the variation of qualitative mineralogy, and the variability of crystallization quality precludes estimates of quantitative mineral composition. An effort has been made, however, to characterize as specifically as possible the qualitative constituents of these mixtures. The minerals identified are indicated below.

Kaolinite

This mineral is identified by its strong characteristic diffraction maxima at 7.2 and 3.58 Å. These maxima are unaffected by glycolation and thermal treatment to 300°C. At 400°C the kaolinite peaks show slight diminution in intensity, as might be expected from prolonged thermal treatment under anhydrous conditions near the maximum hydrothermal stability temperature (405°C), and at 500°C they are completely gone. This characteristic response to thermal treatment may be seen by examination of the 12° 2θ peaks in Figs. 1, 3, 4, 7 and 8.

The first-order kaolinite peak has an intensity of 500–600 counts in well oriented kaolinitic specimens. A well oriented aggregate is one that gives a background intensity at 2° 2θ of 800–900 counts.

Illite

All samples contain mineralogical skeletons related to the muscovite crystallization. Those that show a definable 10 Å diffraction maximum which is not affected by glycolation are here distinguished as " illite " no matter how poorly the maximum is defined. The 10 Å peak may be resolved from the background scattering at 8° 2θ by as little as 50 counts or as much as 200 counts in untreated well oriented aggregates. The variation in the degree of resolution is related, of course, to the degree of crystallite organization in aggregates of good orientation. This property varies among different samples as the text figures show and as is discussed in a later section for specific examples. So long as it is possible to observe a peak in the 10 Å region the micaceous constituent is referred to as illite.

Unorganized Illite

Different samples have varying amounts of micaceous skeletons that do not yield definable peaks at 10 Å. They show instead diffraction effects best described as bands above background extending from 10 Å to somewhat higher spacings. They may be well enough defined to be called shoulders beginning at 10 Å. These diffraction effects are not resolved from the background scattering at 8° 2 θ. Usually, mild thermal treatment up to 200–300°C does not concentrate the scattering near 10 Å and digestion in potassium salts is similarly without effect. Presumably the crystallite organization of such micaceous skeletons as are represented by these diffraction effects shows such poor periodicity that it fails to give coherent scattering. Figs. 1 and 2 (R–68 and R–58) show diffraction effects attributable to unorganized illite.

Dioctahedral Vermiculite

One of the products of muscovite weathering in the Rappahannock tributary basin and source area is a mineral giving its most prominent diffraction maximum at about 14.2 Å. The evolution of this phase from weathered muscovite has been described by Rich and Obenshain (1955) and Rich (1958), who studied weathering profiles in the Virginia Piedmont. The 14.2 Å peak is not affected by glycolation or saturation with potassium salts, but it is modified by thermal treatment (Fig. 1). At 200°C the peak shifts to about 13.6–13.8 Å and broadens. At 300°C it shifts to 13.3–13.4 Å. At 400°C it shifts to 11.8 Å and broadens further. At higher temperatures the peak fades into the 10 Å region and eventually forms a well defined sharp peak at 10.1–10.3 Å. The decrease in d-spacing is gradual and regular with progressive increase in temperature. Rich and Obenshain called this phase dioctahedral vermiculite and Rich has shown that basic aluminum ions occupy the interlayer positions of the degraded muscovite lattice. The basic aluminum ions expand the silicate sheets to 14.2 Å, and as they are decomposed by thermal treatment the lattice contracts. The dioctahedral vermiculite apparently contributes diffraction effects to the 7 Å and 4.7 Å regions. The 7 Å scattering probably contributes to the low-angle asymmetry of the kaolinite diffraction maximum, but a separate peak is never resolved from that of kaolinite. The 4.7 Å maximum is always broad, diffuse, and of low intensity. It shows as a modification on the high-angle side of the second-order illite peak, but it is never itself well defined.

Distinction from other minerals.—It is important to emphasize the distinctions between diffraction effects arising from dioctahedral vermiculite and those that might be attributed to chlorite, kaolinite, montmorillonite or chloritic montmorillonite (montmorillonite with interlayer islands of brucite). The chlorite in these sediments gives sharp integral orders of the 14 Å reflection, and the first-order reflection is intensified at 14 Å by thermal treatment at 500–600°C. In contrast the dioctahedral vermiculite shows a progressive collapse with increasing temperature of heat treatment, and at 500–600°C a sharp 10 Å peak replaces the original peak at 14 Å. The existence

of both constituents can be detected (Fig. 8). The dioctahedral vermiculite contributes to 7 Å scattering along with kaolinite, as discussed above, but comparatively a small amount. The form factor for dioctahedral vermiculite shows contributions to the scattering at 7 Å, 4.7 Å, and 3.5 Å, but such scattering is very weak in terms of that at 14 Å. The 7 Å diffraction maximum obtained for these sediment samples is contributed to predominantly by kaolinite, except perhaps where true chlorite makes some contribution. Diffraction effects at 7 Å have been described by Grim and Johns (1954) and attributed to chloritic montmorillonite. No separate evidence for such effects has been found in the present data. Similarly the diffuse reflections at 4.7 Å are thought to be due to dioctahedral vermiculite in Figs. 1–5 and not to chlorite, degraded chlorite, nor chloritic montmorillonite. Where chlorite is present the 4.7 Å reflection is sharp and well defined, as in Figs. 6, 8 and 9. In favorable instances the detection of both montmorillonite and dioctahedral vermiculite in the same sample can be made after glycolation. Figs. 4 and 7 show the 14 Å dioctahedral vermiculite peak resolved from the glycolated montmorillonite peak. Elsewhere the results of progressive heat treatment serve to distinguish montmorillonite from dioctahedral vermiculite.

Thermal effects from illite, unorganized illite and dioctahedral vermiculite.— Diffraction effects in the 10 Å region arising from illite, unorganized illite, and dioctahedral vermiculite when subjected to thermal treatments are more difficult to assign to individual components. That thermal treatment of the unorganized illite does not result in intensification of the 10 Å diffraction maximum up to 400°C can be ascertained by a close examination of Fig. 1. In the other figures apparent intensifications are due to montmorillonite in the samples. Such an instance is apparent for the 300°C heat in Fig. 3. The constituent referred to as illite seemingly retains its inherent character at all temperatures up to 400°C, since the intensification effects observed may be referred equally well to montmorillonite impurity or dioctahedral vermiculite collapse.

12.4 Å *Montmorillonite*

A mineral that in the untreated state gives a diffraction maximum at 12.4 Å and after glycolation expands to about 17.4 Å is related to the montmorillonite clan. The 12.4 Å spacing suggests that the mineral possesses but a single water layer between the silicate sheets. In untreated specimens the 12.4 Å peak is resolved individually, as in Fig. 5 (R–37 and R–31), occasionally, but it normally occurs as a shoulder or diffuse modification on the high-angle side of the 14 Å dioctahedral vermiculite peak. That this species occurs in addition to 14 Å montmorillonite is apparent from Fig. 2 in the diagrams for sample R–58, R–50 and R–50–glycol. Thermal treatment at 200–300°C collapses the hydrated sheets to 9.9 Å.

14.2 Å *Montmorillonite*

There is in many samples a montmorillonite giving in the untreated state a diffraction maximum at about 14.2 Å which expands to about

17.5 Å after glycolation. The 14.2 Å spacing suggests that this mineral in the natural state has two layers of water between the silicate sheets. The untreated specimens have their principal peak in the same angular position as the dioctahedral vermiculite, and both species occur together. That the 14.2 Å montmorillonite exists individually is shown by a greatly enhanced diffraction peak in some specimens (not illustrated) and by Figs. 6, 8 and 9 where the 14.2 Å montmorillonite occurs without associated 12.4 Å montmorillonite in all samples marked R–2. The hydrated layers collapse to a 9.9 Å spacing after thermal treatment at 200–300°C. Neither this species nor the preceding one shows any abnormal departures from montmorillonitic response to the various thermal or glycol treatments. Neither this species nor the preceding 12.5 Å montmorillonite collapses upon saturation with potassium salts. They both appear to be related truly to the montmorillonite clan.

Chlorite

Some samples contain a mineral that gives an integral series of sharp diffraction maxima based upon a 14.2 Å periodicity. In untreated specimens the only order that is clearly distinguishable is the third, which in chloritic specimens is always well resolved from the second-order illite reflection. The first-order peak is masked by the presence of montmorillonite and dioctahedral vermiculite. Figs. 6 and 9 show typical untreated chloritic assemblages. Upon heat treatment the nonchloritic members of these assemblages collapse and at 500°C the first-order chlorite reflection is intensified. Detection of true chlorite in these samples is based upon the appearance of an intensified 14.2 Å peak after heat treatment at 500°C. Fig. 8 shows the characteristic behavior referred to and Fig. 7 indicates the lower limit at which the presence of chlorite may be detected with confidence.

Since the chlorite is associated with several more abundant clay minerals in all samples it is impossible to determine whether or not it is a trioctahedral species. The distinctions between this species and dioctahedral vermiculite, which in its x-ray diffraction characteristics shows some chloritic attributes, have been discussed under " dioctahedral vermiculite."

Thermal stability.—Many mineralogists studying Recent sediments have distinguished between chlorite and kaolinite on the basis of modifications in the 7 Å reflection after thermal treatment at 400–500°C. Some have attributed quantitative significance to the results. Experience with the Rappahannock River samples suggests that here, at least, this procedure is likely to lead to treacherous interpretative results. The thermal modifications of the first-order kaolinite reflection at 400°C already have been discussed, and it was shown that the 7 Å peak already begins to decrease in intensity when the sample is heated for long periods at this temperature. Roy and Osborn (1954) have shown that the maximum thermal stability of natural kaolinites under hydrothermal conditions is 405°C, and the rate of decomposition is dependent only on grain size and other kinetic factors. We should expect a

lower thermal stability under anhydrous conditions, particularly if the grain size is small. This is borne out by the data described under " kaolinite." The thermal stability of the chlorite in the Rappahannock samples, in terms of its 7 Å reflection, persists up to 400°C (Fig. 8). The decrease in intensity of the 7 Å peak at 400°C is no more than would normally be attributed to kaolinite. At 500°C the 7 Å peak is gone, so both the chlorite and the kaolinite have been modified. The data are not illustrated, but progressive heat treatment at 10°C intervals within the range 400–500°C shows that the thermal breakdown of kaolinite and chlorite in these sediments occurs at essentially the same temperature and the effects on the intensity of the 7 Å peak due to one cannot be separated from the effects due to the other. These results indicate that great reliance cannot be placed upon the interpretation of intensity losses of the 7 Å reflection upon heat treatment in the range 400–500°C, at least for the Rappahannock sediments. If this is true for the static heating method employed here, one might be even more conservative in interpreting the results of dynamic heating where both chance and human error possibly may enter in.

The results just described and those discussed under " dioctahedral vermiculite " underline the fact that interpretation of the 7 Å diffraction peak is very difficult and frequently ambiguous. The Rappahannock samples generally can be interpreted using the *principles* outlined by Bradley (1954), but the presence of dioctahedral vermiculite adds a complicating factor. Here three phases have scattering amplitudes that contribute significantly to the 7 Å maximum. This fact must be remembered when the variation of kaolinite content between samples is discussed in a later section.

Feldspar

In some samples from the lower part of the estuary relatively weak diffraction peaks are observed at 3.21 Å and 3.26 Å. The intensity of such peaks is commonly 20–30 counts and occasionally as much as 50–80 counts. Normally both peaks are present, but occasionally only one is observed. Fig. 9 shows typical examples. The diffraction effects at 3.21 Å and 3.26 Å are attributed to feldspar and probably they arise from two different feldspars. The strongest peaks for albite and microcline fall in the required positions. However, the data are too scanty to make certain identification possible.

Quartz

Quartz is universally present in all the samples, but in most samples the size fractionation has minimized its abundance. Figs. 2, 5, 6 and 8 show weak peaks at 4.27 Å attributable to quartz and, of course, the strongest quartz line is superimposed on the third-order illite reflection.

PROGRESSIVE VARIATIONS IN MINERAL COMPOSITION

Changes in the character of bottom sediment mineral assemblages occur along the Rappahannock River and estuary. Typical x-ray diffraction

diagrams for bottom sediments at several positions along the stream are illustrated in Figs. 1, 2, 3, 5 and 6. These diagrams have been selected from the 300 available to show a representative sample from each station. Each diagram represents an oriented aggregate with approximately the same degree of orientation, as shown by the background scattering at $2°$ $2\,\theta$. Comparison between diagrams, therefore, has some validity.

Upper Rappahannock River

Between Fredericksburg (station R–94) and station R–64 the bottom sediments contain only kaolinite, unorganized illite and dioctahedral vermiculite. Fig. 1 shows a typical diffraction diagram for this interval. In no samples is a well-defined illite present. Similarly there is no evidence for the presence of feldspar nor chlorite, even degraded chlorite. In Fig. 1 the diagram for the 500°C heat shows a residual hump at $12°$ $2\,\theta$, which is due to the kaolinite anhydride, and an obscure feature at $5°$ $2\,\theta$, if anything more than an erratic movement of the recording pen. The latter does not correspond to a chlorite first-order reflection, and from no samples in the upper part of the Rappahannock River is there any evidence that chlorite is present. The broad peak at 4.7 Å and the low-angle asymmetry of the 7 Å peak are interpreted as due to dioctahedral vermiculite. No expandable clay minerals are present.

Lower Rappahannock River

Between station R–64 and station R–50 the bottom sediment mineral assemblage consists of kaolinite, unorganized illite, dioctahedral vermiculite, and 12.4 Å montmorillonite. Fig. 2 shows typical diffraction diagrams. In some specimens from the lower part of this interval the illite peak is resolved partially. The montmorillonite apparently is derived from the bordering Coastal Plain rocks. Neither chlorite nor feldspar is present.

Upper Rappahannock Estuary

The interval between station R–50 and station R–37 is a transition zone from fresh-water to brackish-water conditions (salinity about 2–3‰ at R–37). Typical diffraction diagrams for the bottom sediments are illustrated in Figs. 3 and 5. A most notable addition to the mineral assemblages is 14.2 Å montmorillonite. The assemblage consists of kaolinite, unorganized illite, illite, dioctahedral vermiculite, 12.4 Å montmorillonite and 14.2 Å montmorillonite. The 14.2 Å montmorillonite is derived from the Coastal Plain sedimentary rocks bordering the stream. The illite is well enough defined for all samples in this interval that illite may be considered a member of the mineral assemblage. In glycolated specimens the 10 Å peak is resolved by 50–100 counts from the $8°$ $2\,\theta$ background. No chlorite or feldspar has been detected in any of the samples.

The relative proportions of kaolinite, dioctahedral vermiculite and 14.2 Å montmorillonite are quite variable in different samples. In general, kaolinite

is most abundant where 14.2 Å montmorillonite is least abundant, and conversely as shown in the diagrams for R–44, R–42, and R–37. The variability is due apparently to inhomogeneous contamination by sediment carried in from Coastal Plain tributaries.

Middle Rappahannock Estuary

Between station R–37 and station R–20 the sediment samples are much more homogeneous with respect to mineral composition than in the preceding interval. It is as if the heterogeneity had been eliminated by effective mixing processes. The diagrams for stations R–31, R–26, and R–21, and Fig. 4 are typical. The water in this interval is brackish (salinity 2–10‰).

The mineral assemblage consists of kaolinite, illite, unorganized illite, dioctahedral vermiculite, 12.4 Å montmorillonite and 14.2 Å montmorillonite. Neither feldspar nor chlorite has been detected as far downstream as station R–25. At station R–21 an occasional sample shows a suggestion of the presence of feldspar, but the presence of chlorite is problematical. In Fig. 6 the diagram for R–21 shows a third-order chlorite reflection which is partly resolved from the illite reflection, although no 14 Å line was produced by 500°C heat treatment. At this station, therefore, a trace of chlorite may occur in a few samples. The illite 10 Å reflection is resolved by about 40–75 counts in most glycolated specimens. In untreated aggregates the 10 Å peak may occur only as an unresolved shoulder, but more commonly it is resolved from the 8° 2 θ background by 30–50 counts. The second-order illite peak is always poorly defined. The 7 Å peak has an intensity of 250–300 counts in aggregates of good orientation. The montmorillonites normally are present in small amounts.

The 14 Å reflection from dioctahedral vermiculite usually is the most prominent feature of these diagrams. As Fig. 4 shows, the dioctahedral vermiculite peak begins to fade into the 10 Å region after heat treatment at 400°C, but it does not add significantly to the 10 Å diffraction maximum at that temperature. At 500°C a large number of dioctahedral vermiculite layers have collapsed to 10 Å.

Lower Rappahannock Estuary

Between station R–20 and the mouth of the estuary the salinity of the bottom water increases from about 10‰ to about 20‰. Within this interval, too, the character of the bottom sediment mineral assemblages undergoes marked change. Typical x-ray diffraction diagrams are illustrated in Figs. 6 and 9.

Illite.—Between stations R–21 and R–2 the first- and second-order illite peaks are resolved progressively from the background scattering. At R–21 the first-order peak is resolved from the 8° 2 θ background by 10–50 counts, at R–17 by 50–100 counts, at R–13 by 70–130 counts, and at R–2 by 150–200 counts. At R–17 the illite peak rises 250–300 counts above true background, and it thus has intensity about equal to that of the 7 Å peak. At

station R–2 the illite peak rises about 350 counts above true background and is stronger than the 7 Å peak by about 100 counts on the average. The second-order illite peak exhibits similarly increased resolution. The above observations are for aggregates of approximately equal orientation. If apparent abundance may be correlated with absolute peak intensity, illite shows progressive increase in abundance between stations R–21 and R–2. At any rate, illite shows progressive increase in crystallization quality.

Unorganized illite.—There appears to be progressive decrease in the amount of unorganized illite in the lower Rappahannock estuary, since the x-ray diffraction diagrams have a much cleaner look in the angular range 9–7° 2 θ. It is hardly possible to estimate this property, except very qualitatively.

Dioctahedral vermiculite.—The amount of dioctahedral vermiculite seems to be about constant between stations R–21 and R–2. There is a suggestion, however, that between R–26 and R–2 the dioctahedral vermiculite is progressively less stable to heat treatment. Figs. 4, 7 and 8 show the difference in thermal stability. At R–26 there is no contribution to the 10 Å peak from collapsed dioctahedral vermiculite between the 300 and 400°C heat treatments. At R–17 the contribution amounts to about 50 counts. At R–2 the contribution amounts to about 100 counts. It is even possible that some of the dioctahedral vermiculite layers collapse to 10 Å between 200 and 300°C as a close examination of Fig. 8 will show.

Montmorillonites.—In Fig. 6 some 12.4 Å montmorillonite is detectable for station R–21, but none is certainly detectable at station R–2. In Fig. 9 it is apparent that little, if any, 12.4 Å montmorillonite is present at station R–2. This suggests that the single water layer montmorillonite occurs with decreasing abundance in the lowermost part of the estuary. The 14.2 Å montmorillonite occurs always as a minor constituent, in all samples in the lower part of the estuary.

Chlorite.—Chlorite is first identified with certainty in the sediments of the lower Rappahannock estuary, and its apparent abundance increases progressively towards the mouth. At station R–21 the occurrence of chloritic material is problematical in occasional samples. At station R–17 about 40 percent of the bottom sediment samples contain a chloritic mineral. In these samples the 14 Å peak that appears after 500°C heat treatment is not so intense nor so well resolved from the background scattering as for samples farther downstream. Fig. 7 shows a typical result after heat treatment, although the 4.7 Å peak is not so well resolved here as for some specimens (see Fig. 6, R–17). At station R–13 slightly more than 50 percent of the bottom sediment samples contain good chlorite, and at station R 2 some 80 percent of the samples contain a well-defined chlorite. At R–2 the thermally enhanced 14 Å peak is resolved 40–80 counts above background scattering. The third-order chlorite reflection is progressively resolved between R–17 and R–2.

Kaolinite.—There is no decrease in the absolute intensity of the 7 Å diffraction peak between stations R–21 and R–2 (Figs. 6 and 9). Between
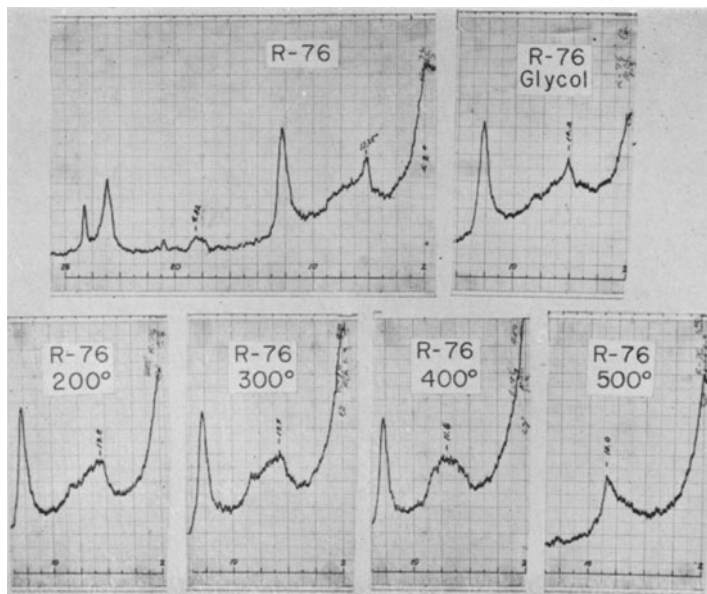
FIGURE 1.—x-Ray diffractometer traces for bottom sediment at station R–76, mid-channel, 1–3 in. depth ; CuK, filtered ; range, 1000 c/s ; 2°/min.
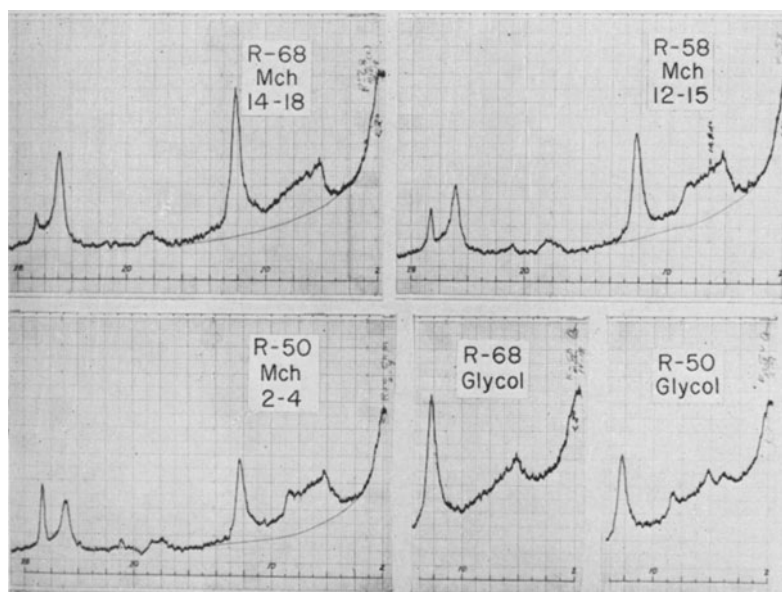

FIGURE 2.—x-Ray diffractometer traces for bottom sediments at stations R–68, R–58 and R–50, mid-channel, depths as indicated ; CuK, filtered ; range, 1000 c/s ; 2°/min.
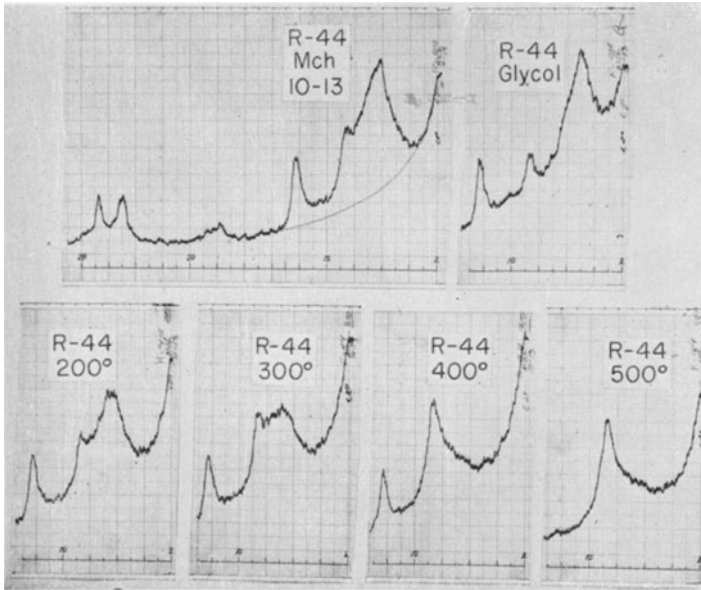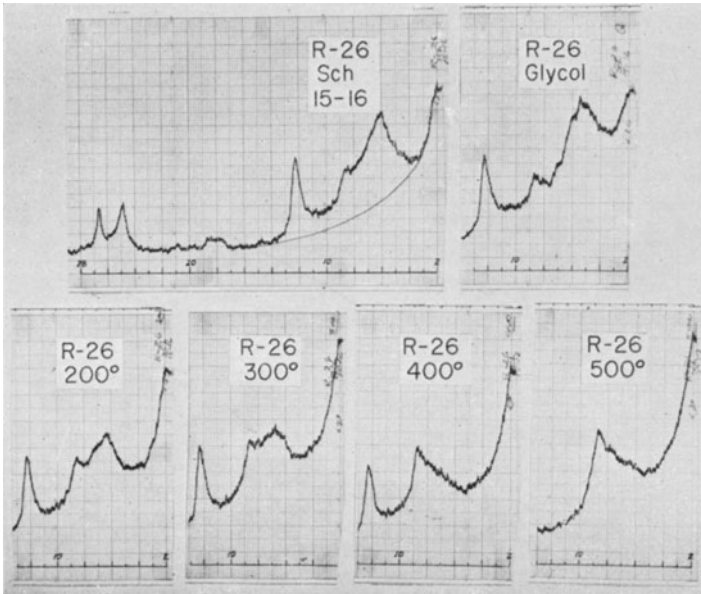
(*To face p.* 144)

FIGURE 3.—x-Ray diffractometer traces for bottom sediment at station R–44, mid-channel, 10–13 in. depth ; CuK, filtered ; range, 1000 c/s ; 2°/min.

FIGURE 4.—x-Ray diffractometer traces for bottom sediment at station R-26, south side of channel, 15–16 in. depth ; CuK, filtered ; range, 1000 c/s ; 2°/min.
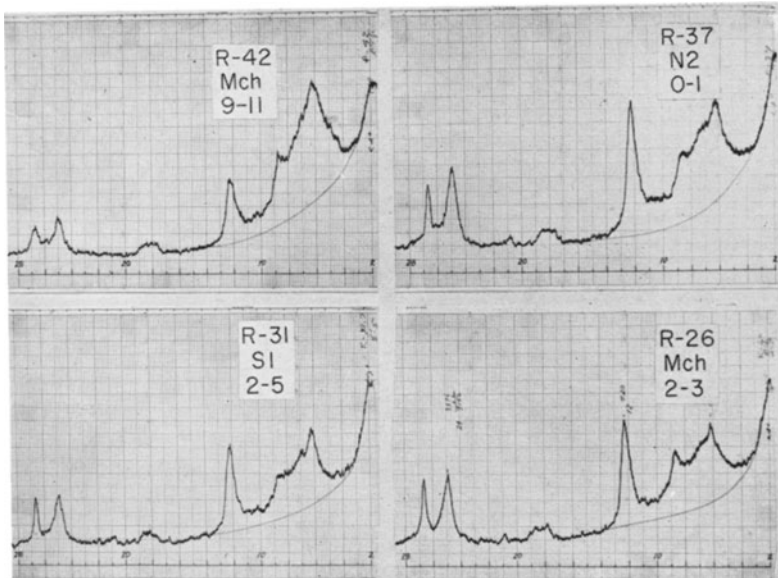
FIGURE 5.—x-Ray diffractometer traces for bottom sediment at stations R–42, R–37, R–31 and R–26, depths as indicated, MCh = mid-channel, N2 = north of channel, 7 ft water, Sl = south of channel, 7 ft water ; CuK, filtered ; range, 1000 c/s ; 2°/min.
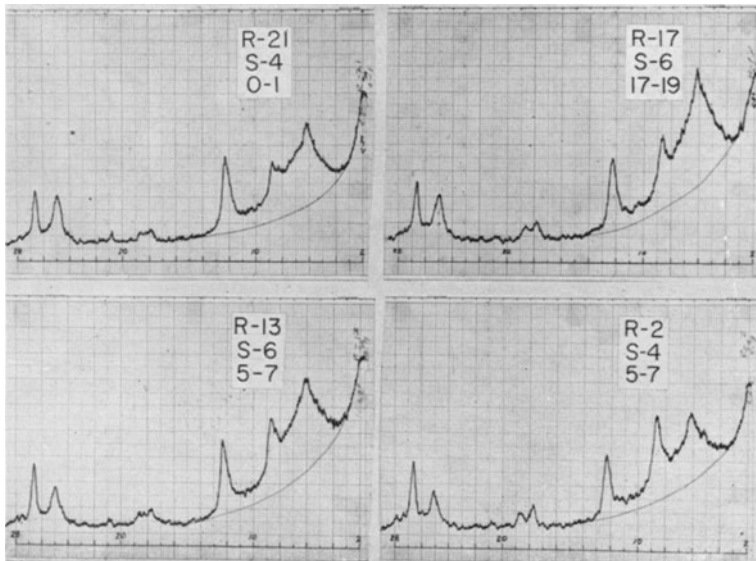

FIGURE 6.—x-Ray diffractometer traces for bottom sediment at stations R–21, R–17, R–13 and R–2, depths as indicated, S6 = south of channel, 40 ft water, S4 = south of channel, 15 ft water ; CuK, filtered ; range, 1000 c/s ; 2°/min.
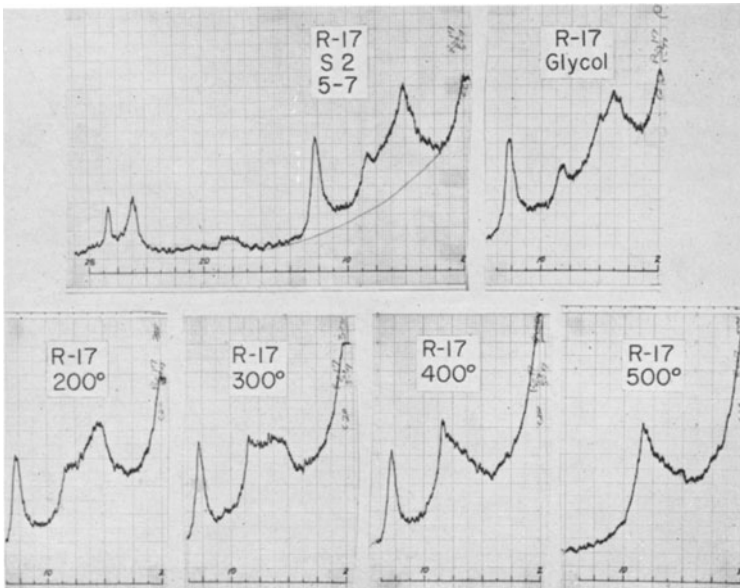
FIGURE 7.—X-Ray diffractometer traces for bottom sediment at station R–17, south of channel, 25 ft water, 5–7 in. depth ; CuK, filtered ; range, 1000 c/s ; 2°/min.
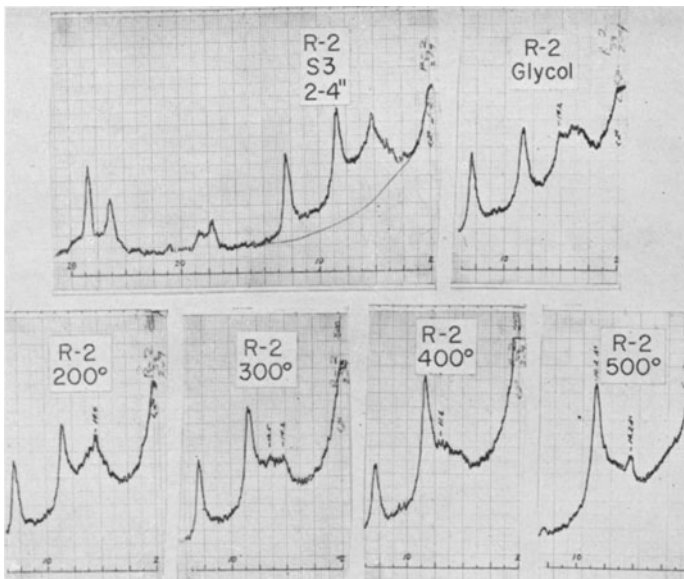

FIGURE 8.—X-Ray diffractometer traces for bottom sediment at station R–2, south of channel, 30 ft water, 2–4 in. depth ; CuK, filtered ; range, 1000 c/s ; 2°/min.
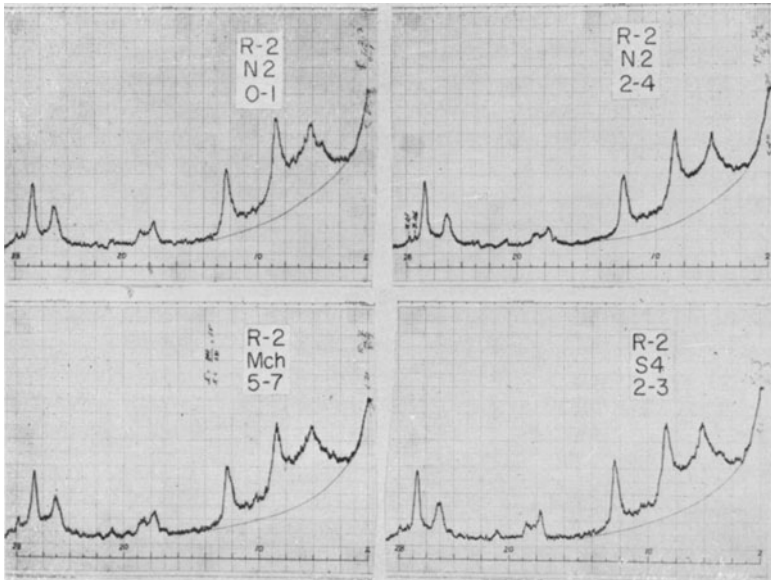
FIGURE 9.—x-Ray diffractometer traces for bottom sediment at station R–2 ; depths as indicated, MCh = mid-channel, N2 = north of channel, 45 ft water, S4 = south of channel, 15 ft water ; CuK, filtered ; range, 1000 c/s ; 2°/min.

the upper Rappahannock River (Figs. 1 and 2) and the mouth of the estuary there is an absolute decrease in the intensity of this peak, but the decrease is due to admixture of other constituents with the upper river assemblage. Evaluation of the kaolinite abundance between R–21 and R–2 must include consideration of the contribution to 7 Å scattering made by dioctahedral vermiculite (whose abundance remains essentially constant) and chlorite (which apparently increases in abundance), as discussed above under " chlorite." Furthermore, should the apparent loss of thermal stability in dioctahedral vermiculite be related to a decreased ion population in the interlayer position, the scattering amplitude at 7 Å for dioctahedral vermiculite will be reduced. This would partly compensate for any increased scattering attributable to a second-order chlorite reflection. There might still be a net increase in 7 Å scattering attributable to the progressively increasing amount of chlorite between R–21 and R–2, and on this basis one might say that kaolinite is present in decreasing amount. The above interpretation is not unreasonable, although the effect appears to be small.

Feldspar.—The occurrence of feldspar in the bottom sediments is confined to the lower part of the estuary. At station R–2 about 70 percent of the samples contain feldspar in the clay fraction. Upstream feldspar is less consistent in occurrence. It has never been identified in the clay fraction of bottom sediments upstream from station R–21. Fig. 9 shows four typical x-ray diffraction diagrams with identifiable feldspar from R–2. In Fig. 8 feldspar is not identifiable.

MINERALOGICAL VARIATIONS WITH DEPTH

No consistent mineralogical variations with depth occur in any part of the Rappahannock River or estuary. The bottom sediments were sampled regularly at depths to 18 in. and for every core a sample from the interval 0–0.5 in. was obtained and analyzed. In all instances the surface sample shows the same mineralogical composition and character as do samples from greater depth. There is no consistent variation in the degree of crystallinity with depth. Some of the surface samples show poorer orientation than deeper samples, but this is not related to mineralogical character.

DISCUSSION

Other workers who have described the clay mineralogy of recent sediments from the Atlantic coastal area include Powers (1954), Murray and Sayyab (1955), and Griffin and Ingram (1955). Of these Powers' study of the Chesapeake Bay sediments brackets the area covered in the present work, but his results correlate least well with those presented here. Powers did not report feldspar or montmorillonite from his samples. The material called " chlorite " by Powers apparently has the same properties as that here called dioctahedral vermiculite, and its distribution does not at all correspond to the result here reported. Griffin and Ingram working in the Neuse estuary, North

Carolina, recognized a " chlorite " having the same properties as diocta-
hedral vermiculite, and many of their results are similar to those reported
here. They did not, however, identify feldspar or a true chlorite in their
samples. Murray and Sayyab studied sediments from the continental shelf
and slope off North Carolina. They detected montmorillonite, illite, kaolinite
and " chlorite," but their data are insufficient to determine if they were
dealing with true chlorite or dioctahedral vermiculite. Murray and Sayyab's
x-ray diffractometer traces clearly show the presence of feldspar in their
samples, and this is confirmed by Murray (oral communication). Each of
the above authors attributed the observed changes in mineralogy and min-
eral crystallinity to diagenetic processes.

Although the present data clearly show basic mineralogical changes in the
bottom sediments between the fresh-water and saline portions of the Rappa-
hannock system, it seems prudent for several reasons to delay interpreting
these changes until the effects of other sedimentary processes operating in
the Rappahannock system can be evaluated. Elsewhere the writer (Nelson,
1958) has discussed observations on the mineralogy of Rappahannock River
suspended sediments and shown that diagenesis is an attractive explanation
for the bottom sediment mineralogical changes. Nevertheless, all the pro-
cesses that operate to produce sediment in the lower estuary are by no means
clearly understood. Until they are, a discussion of the significance of these
data shall be deferred. Instead some anomalies and possible sources of con-
fusion will be described.

The presence of feldspar in the clay fraction confined to the lowermost
estuary should be an excuse for caution. If this mineral forms authigenically,
it should occur in the 1μ and $\frac{1}{2}\mu$ size fractions, too. These samples have not
been analyzed in such detail yet. The occurrence of one feldspar in some
samples and two in others suggests that the feldspar may have a detrital
source, although none is known. If it does, well-crystallized illite and chlorite
may have such sources too. The possible sources of detrital feldspar have not
been thoroughly evaluated.

Coastal Plain rocks might contribute feldspar, chlorite and illite to the
lower estuary. The writer has studied samples of these rocks and found no
clay-sized feldspar, chlorite or well-crystallized illite, but the mineralogy of
these rocks is not exhaustively described.

Seasonal variations in sediment supply have not been evaluated entirely
yet. Furthermore, the mechanism of sediment transport and dispersal in the
estuary is still incompletely understood. Until these aspects of Rappa-
hannock sedimentation are clearly defined, interpretation of the present
results is equivocal.

All the presumed mineralogical changes involve chemical changes in the
sediment, and adjustments chemically between the sediment and the over-
lying estuarine waters. Until good chemical data that illustrate these effects
are obtained, the changes must be considered inferential only.

The preceding discussion has been presented to suggest how fallible may
be conclusions pertaining to process when they are based upon good but in-

complete data. Until a natural process is understood fully, it is difficult to understand it truly at all. Work on this problem continues, and as pertinent results are found they will be reported.

REFERENCES

Bradley, W. F. (1954) X-ray diffraction criteria for the characterization of chloritic material in sediments : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 324–334.

Brunton, G. D. (1955) Vapor pressure glycolation of oriented clay minerals : *Amer. Min.*, v. 40, pp. 124–126.

Griffin, G. M. and Ingram, R. L. (1955) Clay minerals of the Neuse River estuary : *J. Sed. Petrol.*, v. 25, pp. 194–200.

Grim, R. E. and Johns, W. D. (1954) Clay mineral investigation of sediments in the northern Gulf of Mexico : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 81–103.

Murray, H. H. and Sayyab, A. S. (1955) Clay mineral studies of some Recent marine sediments off the North Carolina coast : in *Clays and Clay Minerals*, Natl. Acad. Sci. —Natl. Res. Council, pub. 395, pp. 430–441.

Nelson, B. W. (1958) Relative effectiveness of clay-mineral diagenesis in the Rappahannock River, Virginia : *Bull. Geol. Soc. Amer.*, v. 69, p. 1623 (Abstract).

Powers, M. C. (1954) Clay diagenesis in the Chesapeake Bay area : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 68–80.

Rich, C. I. (1958) Muscovite weathering in a soil developed in the Virginia Piedmont : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl Res. Council, pub. 566, pp. 203–212.

Rich, C. I. and Obenshain, S. S. (1955) Chemical and clay mineral properties of a Red-Yellow Podzolic soil derived from muscovite schist : *Soil Sci. Soc. Amer., Proc.*, v. 19, pp. 334–339.

Roy, Rustum and Osborn, E. F. (1954) The system Al_2O_3–SiO_2–H_2O : *Amer. Min.*, v. 39, pp. 853–885.