CLAY DIAGENESIS IN THE CHESAPEAKE BAY AREA

By

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ABSTRACT

The rivers of the Chesapeake Bay area carry in suspension predominantly a well formed to degraded illite with minor amounts of kaolin and accessory degraded chlorite. Montmorillonite is rare.

Electron microscope photographs of suspended and bottom sediment clays in the James estuary indicate a decrease in floccular size and an increase in crystal size with increasing salinity.

A chlorite-like clay is forming in the Chesapeake Bay estuaries. Its thermal stability increases with increase in the salinity of the environment and with depth in the sediments. This material seems to arise from the diagenesis of degraded illite in the Chesapeake Bay area, but it has also been observed to result from diagenesis of a montmorillonoid in the Atchafalaya region of the Gulf Coast.

The geochemical relations of chloride, sodium, calcium, potassium, and magnesium in the clays of the James estuary support the hypothesis that chlorite is forming in the estuarine and marine environment.

INTRODUCTION

During the past two years the author has been studying the physico-chemical properties of the sediments in the Chesapeake Bay area. Some of the information coming out of this work has an important bearing on the origin and diagenesis of clay minerals. The present paper concerns the results of this research to date. Work on the clays is still under way, and will not be completed for another few months.

The x-ray unit, electron microscope, and chemical analyses have proved most useful in investigating the clays, and these three methods of investigation will be taken up in the order given.
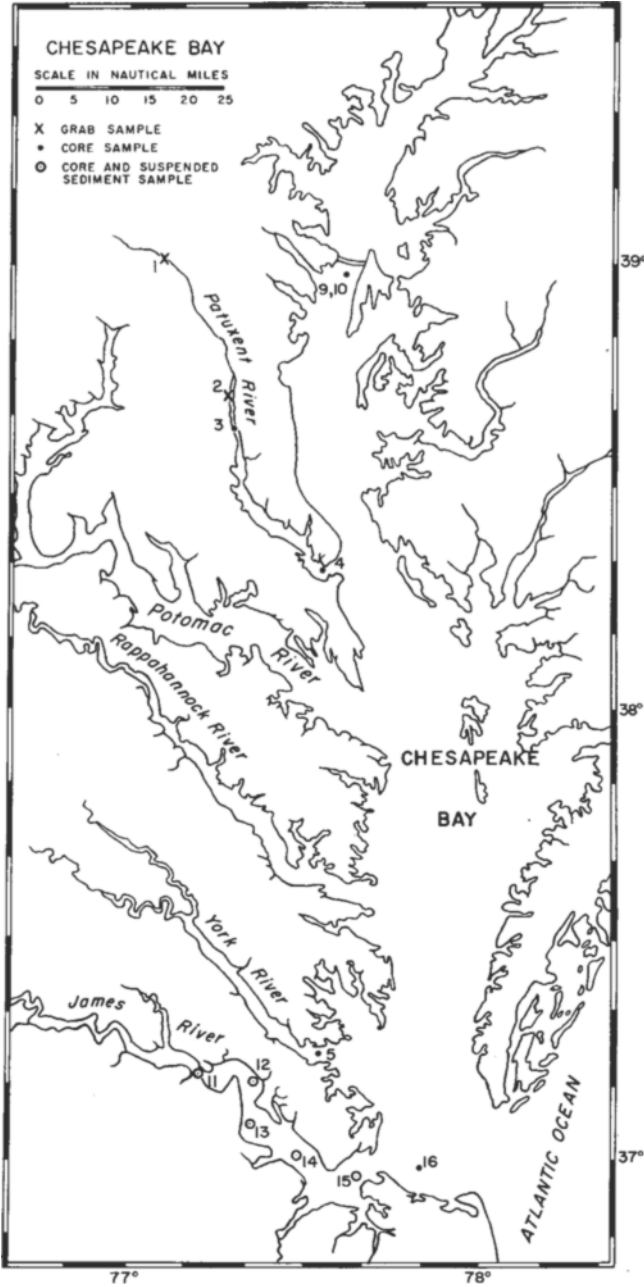
ACKNOWLEDGMENTS

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FIGURE 1. — Map of Chesapeake Bay showing location of samples.

core, and water samples from the Chesapeake Bay area, and for allowing the writer to pursue the laboratory investigations while under employment there.

INVESTIGATION BY X-RAY

Sampling Program

A modified Kullenberg corer (Silverman and Whaley, 1952) and a small grab sampler were used to collect samples from the Patuxent River and estuary, the York estuary, the Chesapeake Bay, and the continental shelf in the latitude of the mouth of Chesapeake Bay. Samples from the continental slope and deeper ocean areas in the latitude of Chesapeake Bay were supplied by Mr. D. Ericson of the Lamont Geological Observatory. About 100 samples from the Chesapeake Bay area have been investigated but only a few of these need be described.

Table 1 contains a list of the samples discussed with the approximate salinity of the overlying bottom water, water depth, and depth of samples below the bottom surface. Location of the offshore cores is given in the table. Figure 1 shows the location of the inshore cores and grab samples.

TABLE 1. — FIELD DATA ON SAMPLES USED IN X-RAY

Sample number	Type sample	Depth of sample below surface (inches)	Water depth (feet)	Salinity of bottom water (0/00)*	Location of offshore cores
1	Grab	0-6	10	Fresh	
2	Grab	0-6	24	1-3	
3	Core	0-6	24	5-7	
4	Core	0-6	49	17	
5	Core	0-6	40	23-25	
6	Core	0-6	110	30-34	50 miles east of Cape Charles
7	Core	0-6	1,656	35-36	80 miles east of Cape Charles
8	Core	0-6	15,700	35-36	396 miles east of Roanoke Island
9	Core	0-6	80	5	
10	Core	415-420	80	5	

* Parts per thousand.

Source of the Clays

A careful study of the sediments in the Patuxent estuary shows that erosion of its banks is negligible. The deposition of the river-borne sediments therefore constitutes practically the entire mud volume found in the Patuxent estuary channel from whence samples were collected; thus any differences found in the clays in a downstream direction have resulted from the alteration of the clays carried to the estuary by the river. The

clays in the Chesapeake Bay channel are likewise brought in by its estuaries, most of the clays having their origin in the Piedmont rather than in the banks of the estuaries or on the shore of Chesapeake Bay.

Sample Preparation

The samples were x-rayed after the following preparations:

1. Clay size particles were separated from bulk sample by sedimentation in water and x-rayed as an oriented aggregate and capillary tube mount.
2. The oriented aggregate was saturated with glycerine and x-rayed.
3. Untreated oriented aggregates were x-rayed individually after heating to 300°, 350°, and 500°C.
4. Four samples were x-rayed as oriented aggregates after first boiling in ammonium chloride, then after boiling in magnesium acetate, and again after boiling in potassium acetate.

This combination of preparations enables the observer to differentiate among vermiculite (Walker, 1951, p. 203), chlorite, and hydrous mica (Rolfe and Jeffries, 1952, p. 599-600). The temperature treatments allow a rough determination of the thermal stability of the minerals.

Results from X-Ray

Where percentages of clay minerals in a sample are given they are to be considered approximations. The author fully recognizes the difficulties in attempting to estimate relative percent of clay minerals in such complex samples as these and particularly where mixed layer structures exist. For a more detailed discussion of this problem see Grim and Johns (1953, p. 16-18).

Sample 1. — This sample is from the Patuxent River at Laurel, Maryland, above the estuary. The clay minerals are 50 percent illite, 35 percent degraded illite, 15 percent kaolinite, and a trace of chlorite. A sample located 15 miles farther downstream in the Patuxent, but still in fresh water, showed the same sequence of clay minerals.

The illite shows up as a band from 10 to 14 A with strong peak at 10 A. This band is concentrated around 10 A by digesting the sample in potassium acetate, thereby suggesting that it is due to an expanded or degraded illite. The amount of degraded illite was estimated by comparing the relative intensity of the 10 A peak before and after digestion in potassium acetate.

A very weak but narrow band with its center at 14 A could be seen after digestion in potassium acetate. This band may be a degraded aluminum chlorite of metamorphic origin.

When the sample was heated to 300°C, the photograph cleared up leaving only a strong peak at 10 A and 7 A. The 7 A line disappeared at 500°C while the 10 A line persisted as the only (00l) reflection.

Sample 2. — At this location the salinity may reach one to three parts per thousand. A weak band from 10 to 14 A remains after heating the sample to 300°C, but disappears when heated to 350°C.

Sample 3. — This sample is from Lower Marlboro, five miles downstream from Nottingham, where the salinity may reach 5 to 7 parts per thousand. The diffraction pattern showed a stronger 14 A line than did sample 2, and the band from 10 to 14 A is also stronger. A strong 14 A line persists after heating the sample to 300°C and a weak line persists after heating to 350°C. The relative percentages of the clays in this sample are illite, 50 percent; degraded illite, 15 percent; chlorite, 20 percent; kaolinite, 15 percent.

Sample 4. — At this location salinity of the overlying water has increased to approximately 17 parts per thousand. The x-ray photograph showed a strong line at 14 A after the sample was heated to 350°C. The line collapsed at 500°C leaving only a 10 A line.

Sample 5. — This sample is located near the mouth of the York estuary where the salinity may reach 23 - 25 parts per thousand. There is a slight decrease in the intensity of the 10 A line at this location, and a slight increase in the intensity of the 14 A line. This sample reacted to heat in the same way as did sample 4.

Sample 6. — The location of this sample is opposite the mouth of Chesapeake Bay about 50 miles offshore. The salinity here is around 35 parts per thousand. Heating this sample to 500°C decreased the intensity of the 14 A line but did not completely collapse the brucite structure.

Samples 7 and 8. — Near the base of the continental slope, from where these samples were collected, the salinity is approximately 35-36 parts per thousand. Heating the samples to 500°C intensified the 14 A line. Furthermore, these samples do not display bands in the 10 and 14 A regions as do the samples from closer inshore. The percentages of clay minerals in these samples are illite, 40 percent; trace of degraded illite; chlorite, 45 percent; and kaolinite, 15 percent.

Summary of X-Ray Observations

Going from the river clays to the deep ocean clays the following steps have been observed:

1. Kaolinite and a band from 10 to 14 A with a strong peak at 10 A.
2. Kaolinite and a band from 10 to 14 A with strong peak at 10 A and lesser peak at 14 A.
3. Kaolinite and a band from 10 to 14 A with strong peaks at 10 and 14 A and a slight diminution of the 10 A peak.
4. Finally kaolinite, illite, and chlorite accompanied by a sharpening of the lines associated with the 10 and 14 A positions.
5. Thermal stability of the 14 A line increases over a range of 200°C with increase of salinity from zero to 37 parts per thousand.

Diagenesis in Surface Sediments

It is strongly suggested from these observations that a chlorite is forming from illite in the surface sediments of the Chesapeake Bay area. The mineral is probably a true chlorite since it does not react to heat or ammonium chloride in the way that vermiculite does; nor does the chlorite expand when saturated with glycerine unless previously treated with a strong oxidant such as H_2O_2. However, the chlorite is unique and differs from metamorphic chlorite which generally has a thermal stability of 600 to 700°C. The chlorite apparently forms from a degraded illite by the addition of brucite to the illite basal surfaces. The brucite structure continues to grow across the illite surface with increasing time and salinity, tying the silicate layers together and thus increasing thermal stability.

The chlorite may form via a mixed-layer stage with illite but there is no proof that the brucite structure alternates randomly with illite on the $(00l)$ surfaces.

Most of the chlorite that forms in the marine environment seems to assume its "embryonic" form fairly soon after becoming exposed to the salt water environment. The illite reaching the estuary varies in its crystallinity from a well-formed illite which holds its interlayer potassium tenaciously, to a very weak crystal which may readily undergo interlayer exchange of ions. It is this weakest set of crystals that is first susceptible to $Mg(OH)_2$ interlayer adsorption. The partially degraded illite repels the magnesium-potassium exchange until higher concentrations of magnesium are encountered farther down the estuary. The well-formed illites may completely repel the magnesium so that very little to no chlorite will form from them. The amount of chlorite formed and its thermal stability is a function in part of the concentration of magnesium in solution and the ratio of illite to degraded illite reaching the estuarine environment.

Rate of Diagenesis

The question naturally arises as to the effect of time on the diagenesis of the clays.

Samples from the top and bottom of about 50 cores were investigated to determine the effect of time of exposure to a given salt water environment on the increase in amount and thermal stability of the chlorite. A description of one of these cores will suffice to illustrate the effect of time. This core was taken in a homogeneous mud just below the Chesapeake Bay bridge where the salinity of the bottom water is about 5 parts per thousand. The core was 35 feet long. Sample 9 from the top of this core showed a 14 A line which disappeared almost completely upon heating the sample to 300°C. Sample 10 from the bottom of the core (35 feet deep) showed a 14 A line which persisted only faintly after heating the sample to 350°C. This increase in thermal stability reflects a build-up of the brucite structure on the basal surfaces of the chlorite with depth in the sediment. Based on the present rate of sedimentation in this area,

sample 10 should be about 4,000 years older than sample 9 and the 50°C increase in thermal stability observed is rather small for this time interval. On the other hand there is a 200°C increase in thermal stability from salinity of zero to 37 parts per thousand, and the time involved is only a matter of weeks. The concentration of magnesium in solution, and not time, is therefore the most important factor in clay diagenesis. Grim (1951, p. 229) has suggested that there would be little vertical change of clay composition in a core.

In the Atchafalaya region of the Gulf Coast chlorite is developing primarily from a montmorillonoid, and to a lesser extent from degraded illite. The increase in thermal stability of the chlorite is greater for a given distance seaward than for clays in the Chesapeake Bay area, and it is very probably due to the much steeper salinity gradient found in the Atchafalaya area. There is a strong suggestion that a close relation exists between the steepness of the salinity gradient and rate of diagenesis.

INVESTIGATION BY ELECTRON MICROSCOPY
Suspended Sediment Sampling Program

It was desired to determine the floccular and crystal size of clays at different points in an estuary and the shapes of crystals present.

Six suspended-sediment samples were obtained from the upper and lower water layers in the James estuary. The location of the samples is shown in Figure 1.

Specimen screens covered with a collodion supporting membrane were placed on a brass block that was partially embedded in dry ice. As each water sample containing the suspended material was brought up, a drop of the water was quickly dropped onto one of the specimen screens. The drop of water froze immediately, thus trapping the clay particles in a rigid state in the ice. The ice was then sublimed off. In this way the floccular size of the clays in suspension was preserved on the specimen screens. Several salts from the water did not sublime off and remained on the specimen screens along with the clays. These salts were almost completely removed by floating the screens on distilled water and allowing the salts to diffuse through the collodion supporting membrane.

Observations

Two important observations were made from these samples. Floccular size decreases and crystal size slightly increases with increasing distance down the estuary. The observed decrease in floccular size was to be expected in view of the following logic. Large volumes of clays brought in by rivers tend to flocculate rapidly upon reaching salt water of very low salinity. This early flocculation produces large aggregates because there are many chances for collision of particles. The larger floccules settle out rapidly so that the sediment load farther downstream is depleted in quantity. Collisions are therefore less likely downstream, and floccules become smaller and smaller in that direction.

The observation that crystal size showed a slight increase in a down-stream direction seems to upset the idea held by some geologists that there is selective transport of clay types owing to settling out of larger particles upstream. Growth of crystals while in suspension would hardly be adequate to account for the slight increase in size observed, in view of the fact that suspended sediments are flushed through the James in about 10 days (Pritchard, 1952, p. 122).

Bottom Sediment Sampling Program

A set of samples from the bottom sediment surface was collected in the James estuary. These samples were taken from the same locations from which the suspended samples were collected (Fig. 1). Another sample was supplied by D. Ericson from the bottom sediments 397 miles east of Roanoke Island in 15,700 feet of water. Clay-size particles (<3.9 microns) were separated from these samples and cleaned with ethylene diamine tetra-acetic acid. They were then dispersed in 0.001 N Calgon solution. The dispersed samples were prepared for microscopy using the freeze-dry technique mentioned above.

Observations

Three different shapes discerned in the photographs were hexagon flakes, rods, and rectangular to irregular flakes (Plates 1 and 2). The hexagon flakes are probably a kaolin mineral. Most of the rods are very likely halloysite, since x-ray work suggests the presence of this mineral in small quantities. Some of the rods may be magnesium clays or flakes curled by heat in the microscope. The rectangular to irregular flakes probably represent the illite and chlorite fractions. It is hoped that before long a program utilizing electron diffraction will enable the author to make more positive statements about the relation of crystal shape to clay type.

Definite crystal shapes become more abundant in a seaward direction, probably because of crystal growth. Crystal size shows a definite increase in a seaward direction for rectangular to irregular flakes and no change in size for rods or hexagons.

Fifty samples taken through the Chesapeake Bay estuary showed better crystal boundaries but a negligible change in crystal size in a downbay direction.

Current velocities in a coastal plain-type estuary and on a continental shelf are undoubtedly high enough to keep particles which are smaller than about 2 microns in suspension almost indefinitely. Therefore Stokes' law of settling velocities cannot be applied to these small particles. It would seem then that bottom muds at least as far out as the outer edge of the shelf have most likely resulted from the settling of *floccules* of clays rather than particles, and these floccules are not necessarily selective as to crystal size or clay type, until proven otherwise.

The observation that crystal size did not decrease seaward may of course be a chance occurrence and future work may prove otherwise. It
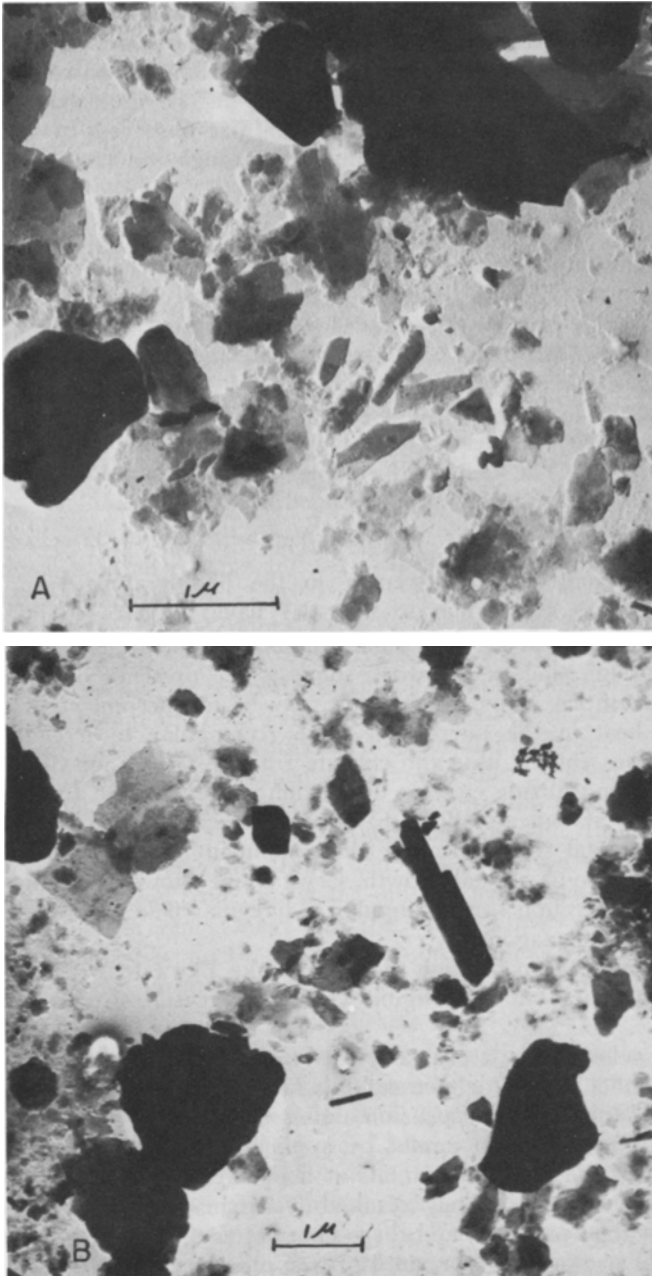
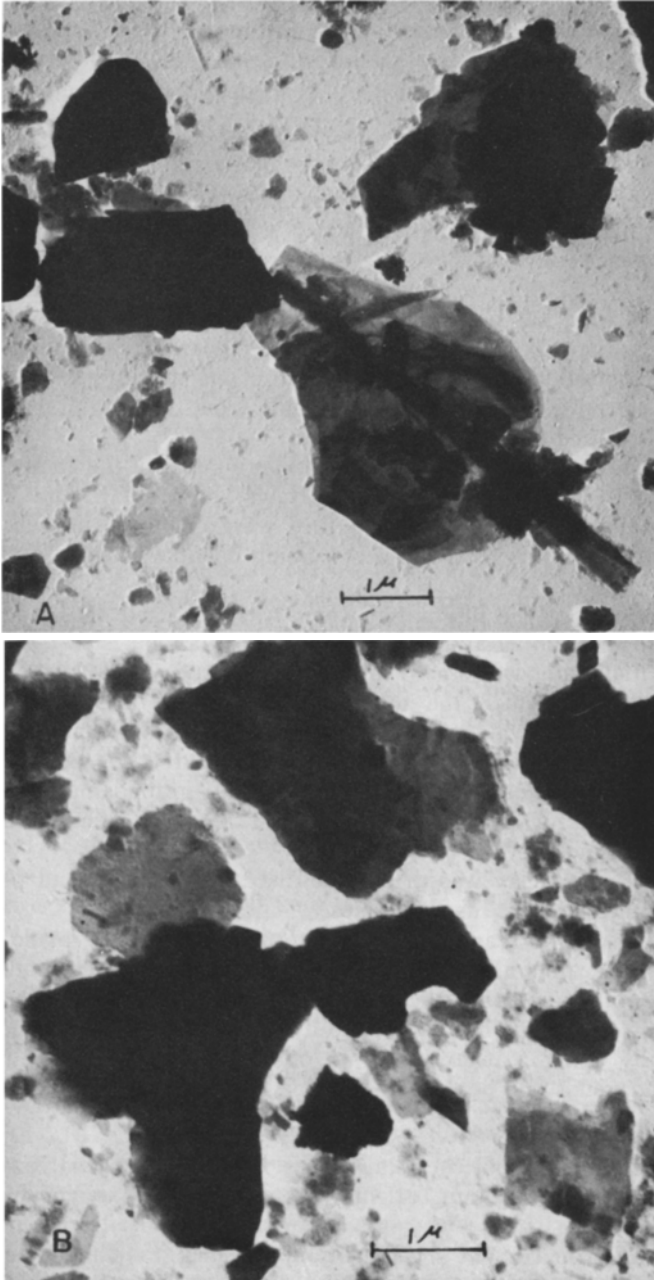PLATE 1. — Electron micrographs of clay from top of core 14.

Plate 2. — Electron micrographs of clays from top of cores 13 (A) and 15 (B).

seems more probable, however, that differential size settling of clay particles is limited to deep water areas with extremely low bottom current velocities.

INVESTIGATION BY CHEMICAL ANALYSES

Sampling Program and Laboratory Technique

The James River estuary is ideal for studying estuarine sediments, as it is not contaminated by tributary water from its head to where it flows into Chesapeake Bay. Based on a study of its bottom sediments and a comparison of old and recent navigation charts it was found that five to eight feet of mud has been deposited in the channel during the past 100 years. The estuary is filling somewhat faster near its head than near its mouth. If vertical compaction by squeezing out the interstitial water is taken into account, it is found that a sample from the bottom of a 10-foot core was deposited some 800 years ago.

Six cores to be used for chemical work were taken in the James estuary. Location of the cores, numbers 11 to 16, is shown in Figure 1. When the cores were brought aboard ship they were cut into six-inch sections and put into glass jars to which a sterilizing agent was added in order to stop bacterial activity.

In the laboratory the interstitial water was extracted from samples by using a Buchner funnel attachment on an International size-1 centrifuge. The interstitial water was stored in wax-lined bottles for analysis.

The mud from which the interstitial water had been collected was dispersed in distilled water and the clay fraction smaller than 2.0 microns was collected. This clay was washed with distilled water until the wash water was free of chloride and potassium. A half-gram sample of the clay was then leached for 1 hour with 25 cc of 1.0 N HCl. The leachate was stored in wax-lined bottles for analysis.

The HCl-leached clay was dried and fused. Magnesium and potassium were determined on the fused samples.

Sodium, potassium, and calcium determinations were made with a Beckman flame photometer. One percent analyses were obtained for sodium and potassium, while the calcium was a four to five percent analysis. Magnesium was precipitated with 8-hydroxyquinoline and determined titrimetrically using a polarograph to obtain the end point in titration. This method yields one percent analyses.

Results from Interstitial Water

Several hundred partial chemical analyses of the interstitial water have been run. Chloride, sodium, calcium, potassium, and magnesium were determined.

The chloride ion content shows only slight changes with depth in any given core. This constancy of chlorinity together with textural similarity indicates that the sediments in a given core had a fairly restricted depositional environment.

All of the elements show an increase in abundance with distance downstream. The ratio of the cations to chloride is fairly constant for any given level below the bottom surface in a downstream direction.

TABLE 2. — RELATION OF RATIOS OF Na^+, Ca^{2+}, K^+, AND Mg^{2+} TO Cl^-
IN INTERSTITIAL WATER TO DEPTH IN CORES

$+$ = Increase with Depth in Core
$-$ = Decrease with Depth in Core
O = Very Slight to No Change with Depth in Core

Core number	11	12	13	14	15	16
Na/Cl	$+$	$+$	$-$	$+$	$-$	O
Ca/Cl	O	$+$	$-$	O	$+$	$-$
K/Cl	$+$	$+$	O	O	$+$	$+$
Mg/Cl	$-$	$-$	$-$	$-$	$-$	$-$

Table 2 summarizes 93 analyses, and shows the relation of Na/Cl, Ca/Cl, K/Cl, and Mg/Cl ratios to depth in cores. The table shows that magnesium content decreases with depth in each core. The minimum decrease in magnesium from the surface sample to a sample 10 feet deep in the core was 10 ppm; the maximum decrease was 273 ppm. This decrease in magnesium is very probably due to its adsorption into the clays where it adds to the growth of the "embryonic" brucite structures on the (00l) surfaces of the diagenic chlorite.

Potassium generally shows an increase with depth. The difference in potassium concentration for the first 10 feet of the cores varies between zero and forty ppm.

Calcium and sodium do not show any particular trend of change in concentration with depth in the cores.

The pH of the cores was measured as soon as the cores were extruded aboard ship. The pH values were confined to the narrow range of 7.3 to 7.5. This is slightly more acid than the pH of most estuarine muds which generally ranges from 7.5 to 8.0.

Results from HCl Leachate

In poorly crystallized clays such as those found in an estuary no sharp line can be drawn between the exchangeable and nonexchangeable ions. At best one can determine the desorbed ions for a given leaching medium for a given time interval. For this work the clays were leached for one hour with 1.0 N HCl. This method allows one to determine the relative abundances of "available" ions for depth in cores and position in the estuary. The leached samples contained between 1600 and 4800 ppm of "available" magnesium. Sodium and potassium varied in much the same way between 100-550 ppm, and 250-600 ppm respectively. There was no general increase or decrease in magnesium, potassium, or sodium with depth in the sediments or position in the estuary, indicating that the amount "available" is a function of neither salinity nor time.

The ratio of magnesium to potassium in the interstitial water samples has a range of 2.0 to 3.0. Seventy percent of the HCl-leachate samples had a ratio of magnesium to potassium ranging from 6.0 to 8.0; the other 30 percent ranged from 4.9 to 10.2. These ratios suggest strongly that magnesium is adsorbed onto the clays preferentially to potassium, and supports the hypothesis that chlorite is forming in the James estuary.

Results from Fused Samples

The residue from HCl leaching was washed, dried, and fused. The magnesium and potassium in these samples represent that part which is held in the crystals more strongly relative to the "available" elements; they are referred to as the "unavailable" elements. Table 3 shows the "unavailable" potassium and magnesium in six fused samples.

TABLE 3. — RELATION OF PERCENTAGES OF Mg^{2+} AND K^+ IN FUSED SAMPLES TO Cl^- IN INTERSTITIAL WATER

Core number		11	12	13	16
Top	$\%Mg^{2+}$	0.01			3.18
six	$\%K^+$	0.29			0.05
inches	$Cl^- (^0/_{00})$	0.84			15.42
9 to	$\%Mg^{2+}$	0.07	0.15	0.39	3.97
10	$\%K^+$	0.12	0.21	0.12	0.17
feet	$Cl^- (^0/_{00})$	1.85	4.44	6.52	15.41

Potassium varies only slightly in the samples analyzed, while magnesium shows a considerable increase with depth in the sediment and chlorinity of the interstitial water. This increase in magnesium content very likely reflects the lateral growth of the brucite structure across the basal cleavage faces, and the consequent stronger bonding results in increased resistance of the magnesium to attack by dilute acid.

REFERENCES CITED

Grim, R. E. (1951) *The depositional environment of red and green shales:* Jour. Sed. Pet., v. 21, p. 226-232.

——, and Johns, W. D. (1953) *Study of near shore recent sediments and their environments in the northern Gulf of Mexico:* A.P.I. Project 51, Rept. VIII, p. 13-18.

Pritchard, D. W. (1952) *Salinity distribution and circulation in the Chesapeake Bay estuarine system:* Jour. Marine Research, v. 11, p. 106-123.

Rolfe, B. N., and Jeffries, C. D. (1952) *A new criterion for weathering in soils:* Science, v. 116, p. 599-600.

Silverman, M., and Whaley, R. C. (1952) *Adaptation of the piston coring device to shallow water sampling:* Jour. Sed. Pet., v. 22, p. 11-16.

Walker, G. F. (1951) *Vermiculites and some related mixed-layer minerals:* In "X-ray identification and crystal structures of clay minerals," Mineralogical Society of Great Britain Monograph, Chap. 7, p. 199-223.