

CLAY MINERALOGY OF RECENT SEDIMENTS FROM THE MISSISSIPPI SOUND AREA¹

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ABSTRACT

Recent mud sediments of Mississippi Sound, Mobile Bay and contributory rivers contain a clay mineral assemblage composed essentially of kaolinite and montmorillonite. Illite is present as a minor component.

The montmorillonite in these sediments appears to be at least partially complexed with organic material. This association is particularly evident in river and river mouth deposits and seems to be modified or partially destroyed in sea water. Organic material has been leached from river sediments with a sodium hydroxide solution and combined as a clay-organic complex with montmorillonite from Clay Spur, Wyoming.

The clay mineralogy of sediments from Mobile Bay and areas outside of the barrier island chain is very similar to that of the river sediments. Within Mississippi Sound an apparent increase in the montmorillonite-illite content of the sediments relative to kaolinite from east to west is attributed to the invasion of mud from the Mississippi Delta into the western part of the Sound.

Chemical analyses of these sediments along a section from fresh water to Mississippi Sound localities have shown a progressive increase in magnesium, potassium, and sodium, and a decrease in calcium.

INTRODUCTION

A study of the clay mineralogy of mud samples from the Mississippi Sound Area has been undertaken to evaluate the effect of source material and environment of deposition on the distribution of clay minerals. Mississippi Sound is located to the east of the Mississippi Delta, between the Mississippi-Alabama coast and a chain of barrier islands extending westward from Mobile Bay (Fig. 1). The Sound and Mobile Bay, at the present time, are accumulating mud and silt deposits carried in by local rivers. Sediment in Mobile Bay is supplied by the Mobile-Tombigbee-Alabama river system, while that in the Sound presumably originates from several smaller rivers. The average water depth in these depositional areas is 15 feet. The eastern end of Mississippi Sound is almost cut off from Mobile Bay by shoals so that little sediment enters from this point. It is probable that mud from the Mississippi Delta contributes to deposition in the western part of the Mississippi Sound. Some fine-grained sediment is carried out through passes in the barrier island chain and deposited in an irregular pattern immediately outside the islands.

Samples from three rivers that contribute sediment to the area have been included. These rivers, the Wolf, the Pascagoula, and the Mobile, were selected

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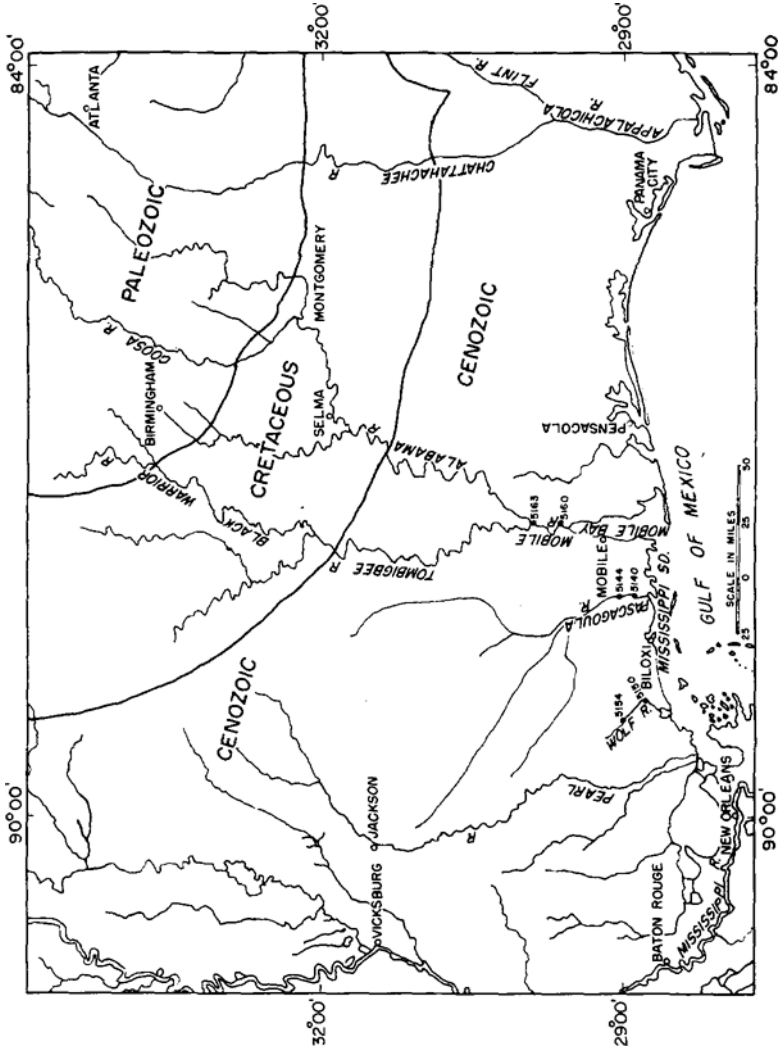


FIGURE 1. — Mississippi Sound area, Gulf of Mexico.

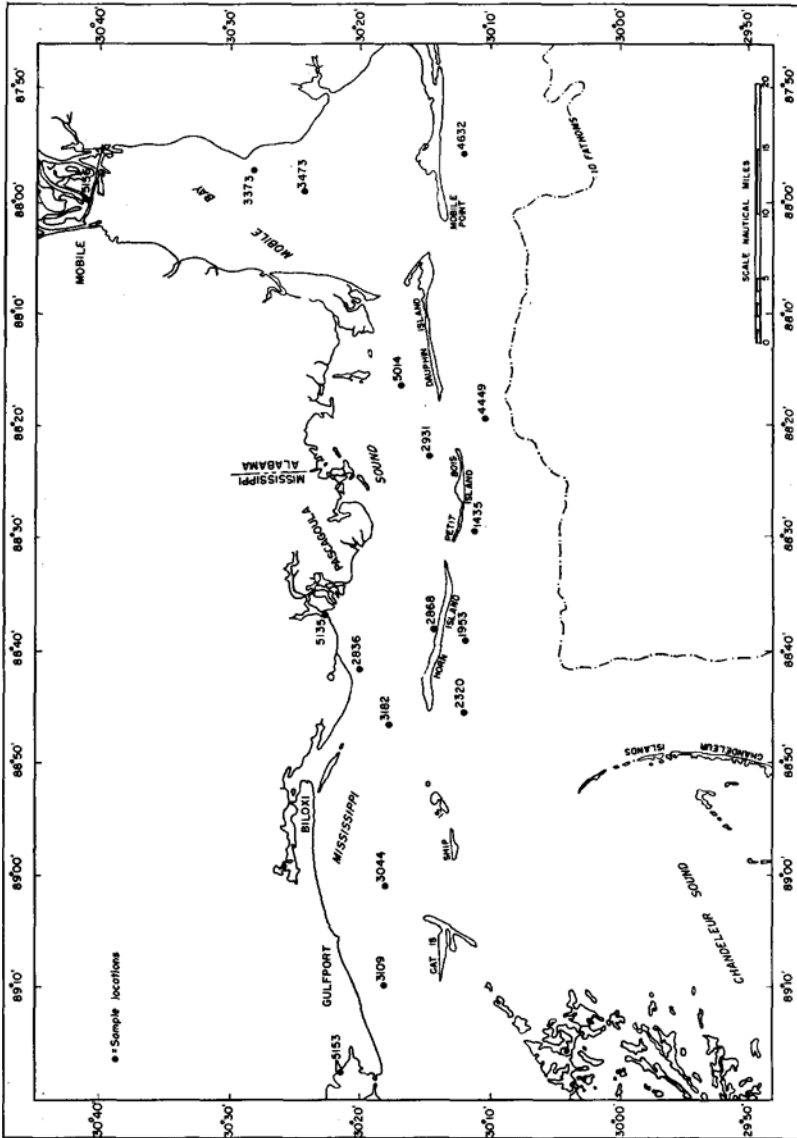


FIGURE 2. — Sample location map.

to represent a short, intermediate, and long drainage system, respectively.

During the course of this study, reference has been made frequently to papers on the clay mineralogy of Recent sediments by Grim and Johns (1954) and Griffin and Ingram (1955).

SAMPLE COLLECTION AND PREPARATION

The river samples were collected in October 1953, while the rivers were at low stage. Sample stations were located at the mouth of each river, at a point well above any possibility of salt water invasion and at an intermediate point where the environment probably alternates under tidal influences between fresh and salt water conditions. These samples will be referred to as the river mouth, fresh water, and intermediate samples, respectively. The remaining samples were collected during the summer months of the last five years. All samples were collected with an "orange-peel" dredge and stored in sealed glass jars. Sample locations, except those of river samples from the fresh water and intermediate zones, are shown in Figure 2. The fresh water and intermediate river sample locations are indicated in Figure 1.

The preparation procedure for these samples was varied. Some samples were washed with distilled water until free of chloride ion while others were first washed with neutral sodium acetate solution followed by distilled water. This variation in preparation, although not ideal, has been found to have no significant effect on the sample comparisons that have been made during the course of this study. The washed samples were dispersed with distilled water and separated into sized fractions by settling and centrifugation. Three centrifuge fractions, 2.6 to 0.5, 0.5 to 0.2, and 0.2 to 0.5 μ , were prepared from each sample and dried at 65°C. Most of the mineralogical and chemical data have been obtained from the 0.5 to 0.2 μ fraction. This fraction has been found particularly suitable for clay studies because of its relatively low content of quartz and amorphous material.

Oriented aggregates for x-ray diffraction study were prepared from the 0.5 to 0.2 μ fraction of each sample by dispersing a small portion in water and allowing a few drops of the suspension to dry slowly on a glass slide. Some care was taken to ensure reasonable constancy in the amount of clay spread over a fixed area marked on the slide.

X-RAY DIFFRACTION STUDIES

The x-ray diffraction properties of the oriented aggregates were determined initially under laboratory temperature and humidity conditions. Diffraction maxima observed at approximately 14, 10, and 7A from all the samples give rise to the usual problems of identifying montmorillonite, chlorite, illite, and kaolinite. Montmorillonite has been identified as contributing largely to the 14A basal spacing by observing expansion and contraction of this spacing to 15.5 and 11.8A under moist and dry air conditions, respectively, and by

obtaining a 17.7A basal spacing as a result of glycerol saturation. In addition, saturation of the samples with the monovalent cations, sodium or lithium, permits the expected collapse of the 14A spacing to 10A or less under dry conditions. Kaolinite has been identified by observing diffraction evidence of the thermal breakdown of the 7A structure in direct comparison with well-characterized pure kaolinite at temperatures above 400°C. Illite has been identified with the 10A basal spacing which remains substantially unchanged under varying humidity conditions. Chlorite has not been identified in these samples, but a poorly crystallized structure is present which appears as a diffraction maximum at 12 to 13A after heat treatment of the samples at 250°C. This spacing collapses slowly to 10A at higher temperatures. Further observations of the chemical and thermal properties and distribution of this component have suggested that it is a natural montmorillonite-organic complex.

The diffraction records of oriented aggregates of the fresh-water samples at room temperature and relative humidity are reproduced in Figure 3. Under these conditions it is apparent that the clay mineralogy of the fresh-water samples is very similar from river to river. Furthermore, samples taken from the river mouths where salt water conditions prevail, show no differences under these conditions of room temperature and relative humidity. However, heat treatment of the samples in stages up to 450°C has revealed significant differences in the succession from fresh- to salt-water environment. A comparison of the shape of the montmorillonite basal diffraction peaks at various temperatures is given for the Pascagoula River samples in Figure 4. At 250°C the original 13.5 to 14A peak has collapsed in part to 10A but a remnant peak

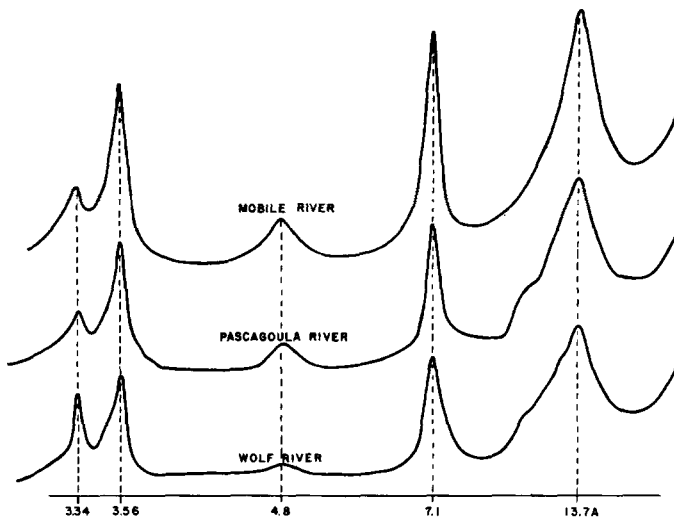


FIGURE 3. — X-ray diffractometer patterns of fresh-water river samples; 0.5-0.2 μ ; room temperature and relative humidity.

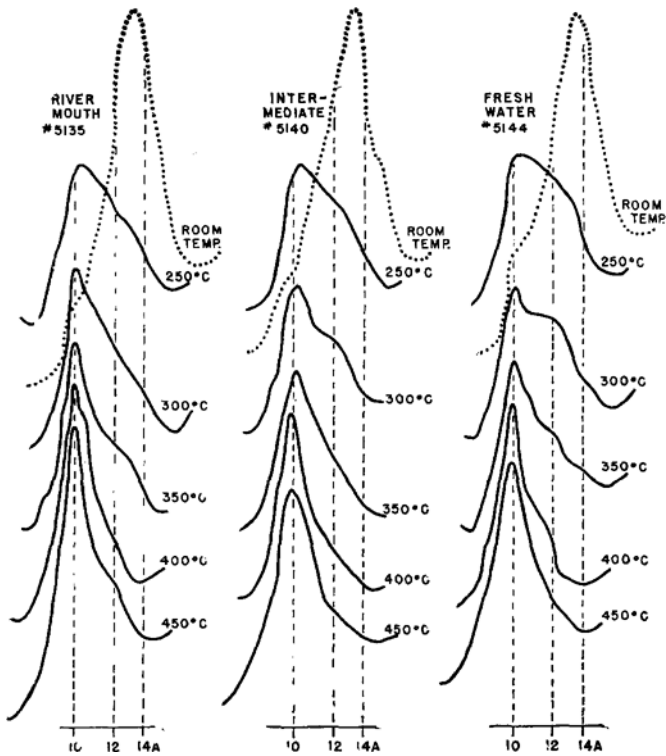


FIGURE 4. — X-ray diffractometer patterns of Pascagoula River mud samples, 10 to 14A; 0.5 to 0.2 μ ; heated to indicated temperatures, 18 hours.

remains at 12A approximately. At 300°C the remnant peak is most evident in the fresh-water sample and seems to show a continuous decrease in intensity relative to the normal montmorillonite and illite components through the intermediate and river-mouth samples. Higher temperatures up to 450°C apparently collapse the 12A structure to 10A in each sample. The variation of this component is again illustrated in Figure 5 where the montmorillonite-illite diffraction peak at 300°C for each of the samples from the three rivers is reproduced. It is obvious that the thermal stability and relative proportions of the 12A component decrease from a fresh- to a sea-water environment. It is difficult to infer the presence of a poorly developed chlorite structure from these observations since sea water containing abundant magnesium would be expected to increase the stability of such a structure. It is suggested as an alternative that this component is an organic-clay complex of montmorillonite and natural organic constituents of the mud.

Some additional evidence pointing toward the existence of a clay-organic complex has been obtained indirectly. The Pascagoula River-mouth sample

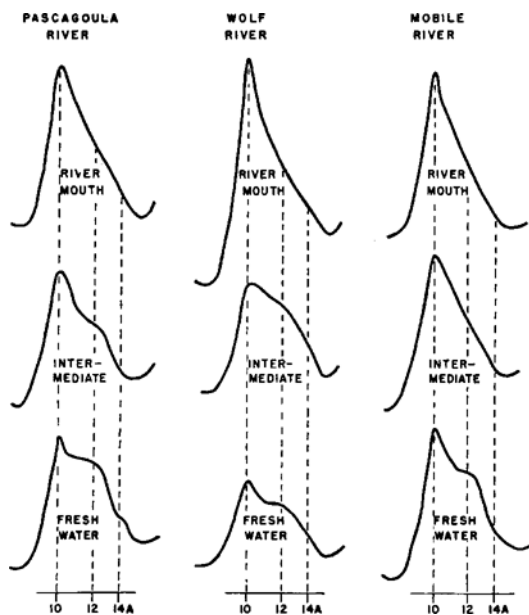


FIGURE 5.—X-ray diffractometer patterns of river mud samples, 10 to 14Å; 0.5 to 0.2 μ ; heated 300°C, 18 hours.

has been leached with water until free of chloride ion, followed by continuous leaching with a one percent sodium hydroxide solution until the effluent was practically colorless. The dark-colored organic extract was precipitated with HCl at pH 2.0. The organic precipitate was separated and washed with dilute HCl. The washed precipitated material was neutralized with NaOH solution to render it soluble. A portion of this solution was added to a suspension of hydrogen-saturated bentonitic montmorillonite from Clay Spur, Wyoming. The system was precipitated by addition of hydrochloric acid and finally washed with distilled water until free of chloride ion. At this point the mixture of montmorillonite and organic material slowly flocculated on standing. An oriented slide of this material was prepared and subjected to x-ray diffraction analysis after various heat treatments. The effects of this treatment are illustrated in Figure 6. It is fairly evident that a complex of the clay and organic material is formed and that it is reasonably stable at 250°C, with an approximate basal spacing of 12Å. Heat treatment at 350°C and 450°C seemingly oxidized the organic material slowly and collapsed the clay structure toward 10Å. It must be realized that the extracted organic material represents only a small part of the total organic material in the original mud and that it has been subjected to a fairly strong chemical treatment. However, this evidence does indicate that organic constituents of mud can form clay-organic complexes under certain conditions.

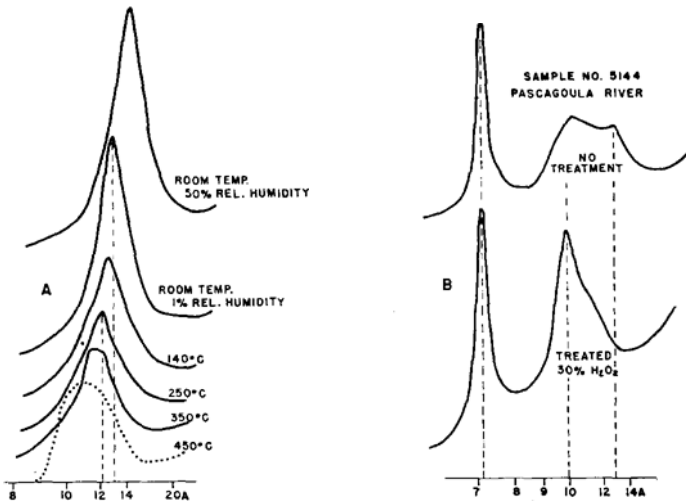


FIGURE 6.—X-ray diffractometer patterns of montmorillonite-organic complexes, 10 to 14A. A. Artificial complex of montmorillonite, Clay Spur, Wyoming, and extracted organic material, heated to 450°C in stages. B. Fresh-water river mud, before and after H₂O₂ treatment, heated to 250°C 18 hours.

Some further indication that the 12A material in these muds is a clay-organic complex is given by the fact that prolonged oxidation of a sample of the fresh-water mud with hydrogen peroxide appears to remove the material which gives this spacing. This is illustrated in Figure 6.

The clay material carried by the three rivers thus appears to be almost constant in composition, consisting of montmorillonite, kaolinite, minor illite, and montmorillonite complexed with organic material. It is quite possible that the montmorillonite of the complex is different from the noncomplexed type. The constant composition of these sediments probably reflects their common origin from the Appalachian Region.

Diffraction records, obtained under room temperature and humidity conditions, of selected samples from Mobile Bay, from the area outside the barrier islands, and from Mississippi Sound are presented in Figure 7. An examination of relative intensities of basal diffracton peaks suggests that samples from the west end of Mississippi Sound, illustrated by no. 3044, show a greater content of montmorillonite relative to kaolinite than is indicated in the remaining samples. Heat treatment at 250°C reveals in all these samples a 12A component which is relatively minor in comparison with that which is present in the fresh-water river samples. Samples heated to 350°C (Fig. 8) show a complete collapse of the 12A component to 10A, except in the Mississippi Sound samples where a minor 12A peak persists. The apparent increase of montmorillonite relative to kaolinite in the west end of the Sound is even more evident in the samples which have been heated to 350°C. This information is presented in Table 1 where peak heights at 10A and 7A for all samples after heat treatment

at 350°C have been measured and combined in a ratio I (montmorillonite-illite)/ I (kaolinite). This ratio, abbreviated I_{M+I}/I_K , has meaning only in a relative sense. It illustrates the basic similarity of samples from the rivers, Mobile Bay, and the area outside the barrier islands and also shows the differences between samples from the east and west sections of Mississippi Sound.

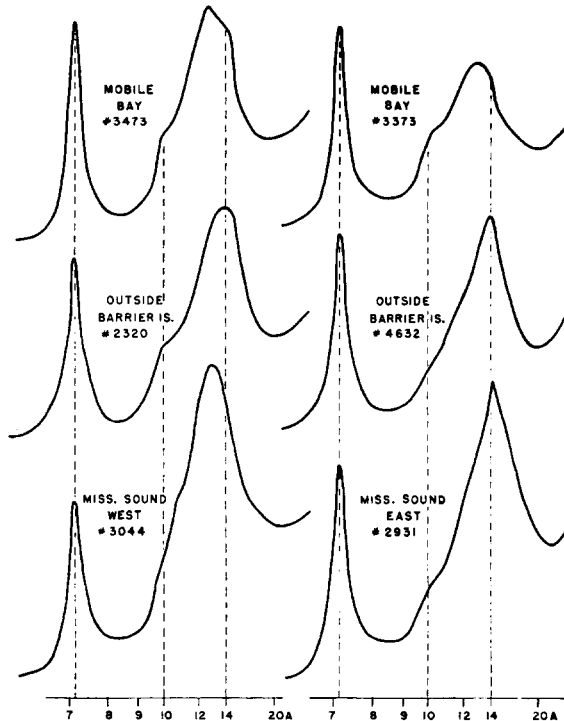


FIGURE 7.—X-ray diffractometer patterns of mud samples from Mississippi Sound area, 7 to 14A; 0.5 to 0.2 μ ; room temperature and relative humidity.

Mud originating from the Mobile River and carried into Mobile Bay and outside the barrier islands seemingly undergoes little change in clay mineralogy other than that associated with the montmorillonite-organic component. It is difficult, therefore, to see how the increased montmorillonite content of muds from the west end of Mississippi Sound can be related completely to the influence of sea water since the Sound in general has a lower salinity than the open Gulf areas. A more plausible explanation is obtained by considering the proximity of the western section of Mississippi Sound to the Mississippi Delta. The delta muds have a high montmorillonite content relative to kaolinite and the invasion of some of this material into the western part of Mississippi

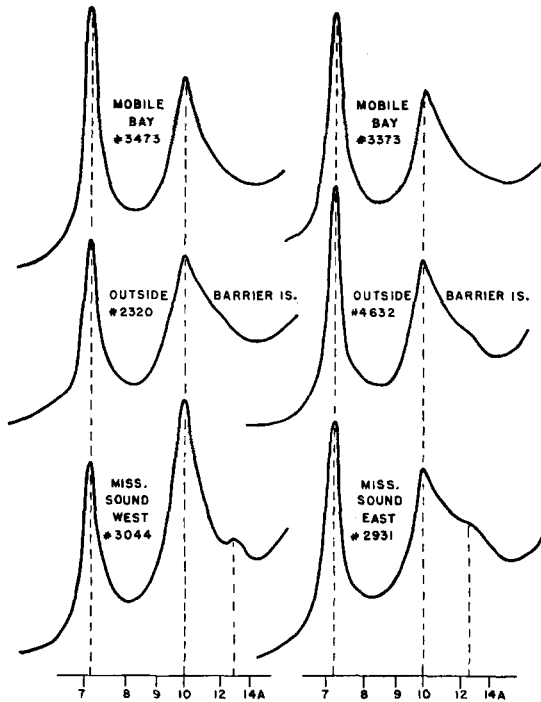


FIGURE 8.—X-ray diffractometer patterns of mud samples from Mississippi Sound area, 7 to 14A; 0.5 to 0.2 μ ; heated to 350°C 18 hours.

Sound can account for the increased montmorillonite-illite/kaolinite ratio of muds from this area.

CHEMICAL ANALYSES

Partial chemical analyses of the three samples from the Pascagoula River and a sample from Mississippi Sound off the mouth of this river are given in Table 2. The analyses were obtained from the 2.6 to 0.5 μ fraction of each sample, prepared by washing with distilled water and by centrifugation. The data of Table 2 indicate that sodium, potassium, and magnesium increase while calcium decreases progressively in passing from fresh water through the intermediate and river-mouth zones to the salt-water environment of the Sound. These are observations which might be expected as a result of changes in the equilibrium of the solid-liquid system, probably involving cation-exchange reactions.

The carbon content of these samples may be considered to be derived from organic and clay-organic complexed material since carbonate is not present. The carbon content is fairly constant in all the river samples but shows a pro-

TABLE 1. — X-RAY DIFFRACTION DATA, MUD SAMPLES, MISSISSIPPI SOUND AREA, ORIENTED AGGREGATES, 0.5-0.2 μ FRACTIONS; HEATED 350°C 18 HOURS

Sample Number	Montmorillonite + Illite		Kaolinite		Ratio I_{M+I}/I_K
	dA	I	dA	I	
Rivers (Fresh water)					
5163 (Mobile)	9.9 A	28	7.1 A	55	0.5
5144 (Pascagoula)	9.9	21	7.1	31	0.7
5154 (Wolf)	9.9	16	7.1	27	0.6
River Mouth					
5156 (Mobile)	9.9	35	7.1	46	0.5
5135 (Pascagoula)	9.9	27	7.1	47	0.6
5153 (Wolf)	9.9	30	7.1	46	0.8
Mobile Bay					
3373	9.9	17	7.1	26	0.6
3473	9.9	19	7.1	24	0.8
Outside Barrier Island					
4632	9.9	19	7.1	27	0.7
4449	9.9	28	7.1	38	0.7
1435	9.9	19	7.1	26	0.7
1953	9.9	14	7.1	20	0.7
2320	9.9	18	7.1	22	0.8
Mississippi Sound					
5014	9.9	20	7.1	25	0.8
2931	9.9	20	7.1	21	1.0
2868	9.9	24	7.1	25	1.0
2836	9.9	30	7.1	22	1.4
3182	9.9	24	7.1	25	1.0
3044	9.9	27	7.1	21	1.3
3109	9.9	27	7.1	20	1.4

nounced decrease in the Sound sample. The change in characteristics of the suggested montmorillonite-organic complex, which begins with the intermediate river sample is not, therefore, related directly to the total carbon content of the muds. The characteristics of the montmorillonite-organic complex appear to be altered as soon as the mud reaches the intermediate river zone where the first effects of the increased pH and salinity of sea water are encountered. The total carbon content of the mud probably is dependent on additional factors which become important only in the Sound environment.

DISCUSSION

The clay material being carried into Mississippi Sound and Mobile Bay by local rivers is a fairly constant assemblage of montmorillonite and kaolinite with minor illite. Included with the montmorillonite of these source sediments is a poorly crystallized component which gives a basal spacing of 12A approximately at 250°C to 300°C. Evidence has been presented which indicates that the structure is undergoing modification (or destruction) in the presence of sea water. Since a degraded chlorite structure might be expected to become

TABLE 2.—PARTIAL CHEMICAL ANALYSES OF MUD SAMPLES:
PASCAGOULA RIVER AND MISSISSIPPI SOUND

Sample	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Total H ₂ O	C as CO ₂	C	Total C + H ₂ O
5144 (Fresh Pascagoula River)	19.88	7.73	0.83	0.17	1.15	0.36	1.06	15.84	8.68	2.37	18.21
5140 (Intermediate Pascagoula River)	21.17	7.23	0.87	0.26	1.23	0.30	1.12	15.59	8.23	2.25	17.84
5135 (Mouth Pascagoula River)	21.02	7.61	0.85	0.31	1.32	0.25	1.45	15.15	9.50	2.59	17.74
3182-D (Mississippi Sound)	19.87	7.80	0.92		1.56			12.84	6.21	1.70	14.54
Analyses Adjusted to Water + Carbon Free Basis											
5144	24.31	9.45	1.01	0.21	1.41	0.44	1.30				
5140	25.76	8.80	1.06	0.32	1.50	0.37	1.36				
5135	25.55	9.25	1.03	0.38	1.60	0.30	1.76				
3182-D	23.25	9.13	1.08		1.83						

more stable in sea water, the suggestion has been made that this material is a clay-organic complex. It has been found that organic material extracted from mud may be combined with bentonitic montmorillonite to give a structure with basal diffraction properties similar to those encountered in these muds. strong oxidation of the fresh-water river muds reduces or destroys the 12A structure. Minor indications of a similar material have been noted in samples from Mobile Bay, Mississippi Sound, and the area outside the barrier island chain. The modification (or destruction) of the montmorillonite-organic component by sea water probably results in a small increase in the normal montmorillonite content of the sediment as illustrated by the slight increase in the I_{M+1}/I_K ratio in Mobile Bay relative to Mobile River material.

Within Mississippi Sound there is evidence of an increased montmorillonite content in the muds of the west end as compared with those of the east end. This may be due partly to release of montmorillonite from the organic-clay complex as a result of the effect of alkaline sea water in the more open western part of the Sound. However, the negligible effect of the same conditions on the muds outside of the barrier islands indicates that additional factors must be considered. The proximity of montmorillonite-rich muds of the Mississippi Delta almost necessitates the conclusion that they are being carried into the west end of the Sound in sufficient quantity to modify the clay mineralogy of this area.

This study has not revealed major mineralogical changes in the clay materials of this area as they are transported from fresh to saline environment except those concerned with the suggested complex of organic material and clay. It is possible, of course, that burial and diagenesis of these sediments may reveal

differences which are not now apparent at the present depositional surface. It seems probable, however, that major variation in the clay mineralogy of a depositional area will be related to source variations rather than to depositional environment.

ACKNOWLEDGMENTS

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