

CLAY MINERAL INVESTIGATION OF SEDIMENTS IN THE NORTHERN GULF OF MEXICO¹

By

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ABSTRACT

Clay mineral studies of recent sediments from a diversity of environments in the vicinity of Rockport, Texas, have been made as part of American Petroleum Institute Project 51.

The bulk of the argillaceous material in these sediments is a complex mixture of poorly crystallized three-layer clay minerals. Problems of the identification and nomenclature of the components of such mixtures are considered.

Variations in areal distribution of the clay mineral constituents indicate progressive diagenesis in response to changing chemical environment. The gradual loss of montmorillonitic source material with the ultimate formation of poorly crystalline illitic and chloritic phases has been related to variations in environment. Environmental criteria based on clay mineral compositions are suggested.

INTRODUCTION

The object of this paper is to present the results of clay mineral analyses of a suite of sediments collected in the Gulf of Mexico in a small area near Rockport along the Texas coast (Fig. 1), and to consider the significance of these data in relation to diagenetic changes and environment of accumulation.

The work reported herein was done as part of American Petroleum Institute Research Project 51, which is under the general direction of Professor Francis P. Shepard of the Scripps Institute of Oceanography of the University of California. The clay mineral studies were made at the University of Illinois under contractual arrangement with the University of California. Thanks are due to Professor Shepard for his interest and support of the clay mineral part of Project 51 and for discussions with him which helped very much in analysing the significance of the clay mineral data. The authors appreciate the kind permission of the API steering committee under the chairmanship of Mr. Clarence L. Moody to publish this paper.

The samples were collected by personnel of Scripps Institute and were forwarded to the University of Illinois without drying. The location of

¹ Contribution from the Clay Minerals Laboratory, Department of Geology, University of Illinois.

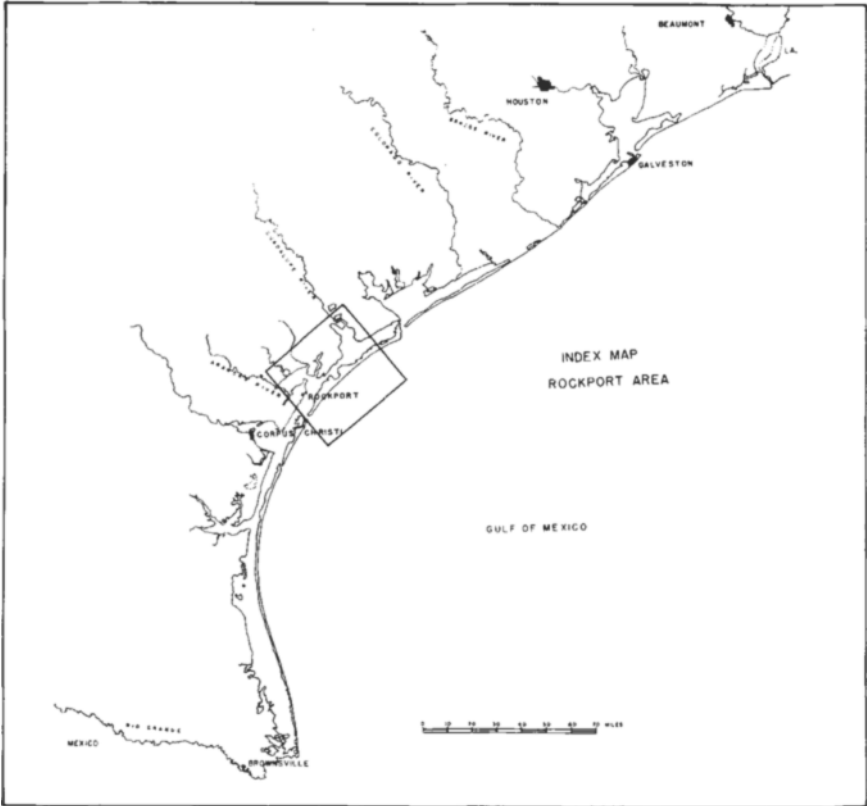


FIGURE 1.—Index map showing the location of the area investigated near Rockport along the Texas coast of the Gulf of Mexico.

the samples studied is given in Figure 2. All of the samples reported herein came from core depths of less than 60 cm.

The area investigated is along the central part of the Texas Coast around Rockport and Aransas Pass. It includes the continental shelf of the open Gulf of Mexico, barrier islands, a series of bays, lagoons, and inlets behind the barrier island, and a deltaic area actively being built by the Guadalupe River into one of the bays. The area was chosen because of its variability, the small scale of industrial activity which might contaminate sediments, and its accessibility.

Shepard and collaborators (1952-53) have described the area and classified the different environments in it. In the present report the classification and nomenclature offered by Shepard et al (1952-53) is considered along with the geographic subdivisions.

Detailed studies of all aspects of the area and the sediment accumulating therein, including rate of sedimentation, character of the water, particle

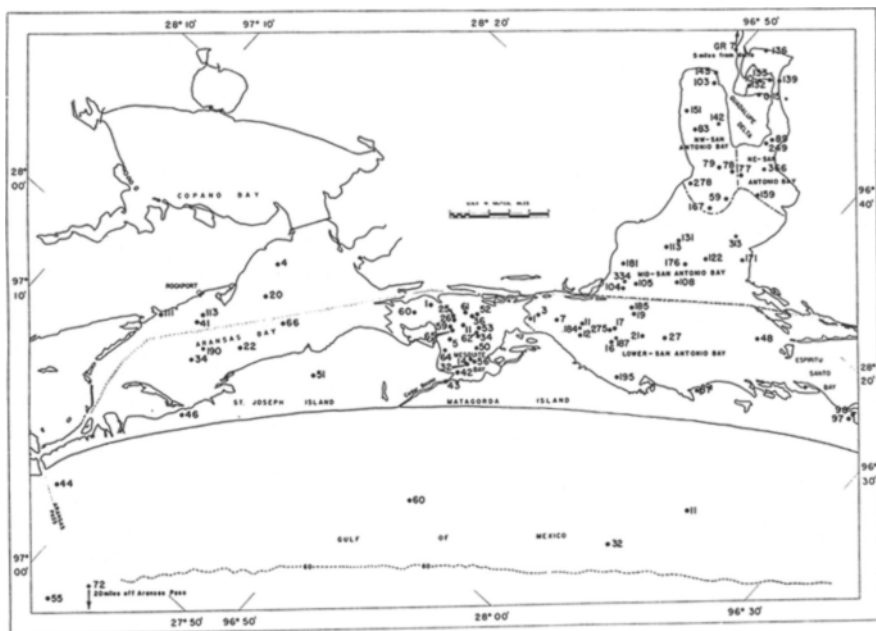


FIGURE 2.—Map of the Rockport area showing the geographic subdivisions, and location of the samples investigated.

size distribution of the sediments, are being made as part of API Project 51. In the present paper only that part of the work concerned with the clay mineral composition is reported.

ANALYTICAL PROCEDURE

Detailed studies by Shepard and Moore (1953) have shown that sediments in the area range from clays to fine sands with great variations in the amount of clay-sized material. Sediments with high percentages of clay-sized material are found chiefly in the vicinity of Guadalupe Delta and the central portions of San Antonio and Aransas Bays. The sandy sediments are found around the edges and southern portions of San Antonio Bay and particularly in Mesquite Bay adjacent to the sandy barriers, i.e., St. Joseph and Matagorda Islands.

Preliminary microscopic examinations were made of samples as received to determine the approximate abundance of the clay minerals, and the particle size and identity of the major nonclay minerals. Carbonate minerals generally are present in particles larger than about 2-5 microns and in greater relative abundance in the finer grained sediments. The quartz grains in the sediments are mostly larger than about 1 micron.

Fractionation of the samples at 1 micron yielded a minus 1 micron size-grade which was essentially free from carbonate and contained only a small amount (about 10 percent) of quartz. The minus one micron fraction contains substantially all of the clay mineral (except the glauconite grains). That is, the clay minerals either are present in particles finer than 1 micron or were broken down to this size easily in the fractionation procedure. This is a point of general significance since in the authors' experience the clay minerals of ancient sediments are larger and less easily broken down to such small size. Postdepositional processes must, therefore, favor the growth of clay mineral particles and/or the formation of more resistant aggregates.

The concentration of the clay minerals in the minus one micron particle-size fraction and the elimination of the carbonate and most of the quartz from this fraction greatly facilitated the identification of the clay minerals. Removal of carbonate by acid leaching was avoided because of the probable detrimental effects on the clay mineral constituents.

Following the microscopic study, a large portion of the raw sample was slurried with distilled water and the pH determined. In every instance pH determinations were made on slurries of about equal clay concentrations (10 percent by weight). Somewhat variable pH values may be obtained depending on sample preparation and, therefore, the values obtained may have no absolute significance. It is believed, however, that they are comparable.

The slurries were subsequently filtered and washed continuously with distilled water until the leachate showed a negative test for chloride ions. The leachates obtained after removal of soluble salts were saved and analyzed for K, Na, Mg, and Ca ions. Determinations of the first two ions were made using a Perkin-Elmer Model 52-C flame photometer, utilizing the direct intensity method. Ca and Mg ions were determined by titration with a "versenate" as recently described by Cheng and Bray (1951). The nature of the washing procedure prevented determination of absolute amounts of the various ions present, but the ratios of ion concentrations expressed in parts per million are significant. The soluble cations thus obtained represent those contained in interstitial water in most intimate contact with the sediment, and perhaps also some few exchangeable cations replaced in the washing process. Significant variations in cation ratios, which are largely independent of total ion concentration, should give indications of ions being subtracted from the sea water by diagenetic processes.

The salt-free sediment was then resuspended in distilled water, and the less than 1 micron fraction was separated by settling, using Stokes' law to compute settling time. Following the removal of the soluble salts, no chemical dispersing agent was required to place the samples in suspension. Fractionation was repeated until substantially complete separation of the size fraction was attained.

In the process of fractionation by sedimentation, it was noticed that a few samples seemed to exhibit initial differential flocculation. In such cases the bulk of the material would flocculate, but an appreciable amount of material would remain in suspension. The flocculated material would, however, ultimately go into suspension with repeated fractionation. It was suspected that the two phases might exhibit different clay mineral suites. Accordingly about 25 samples were studied by collecting an early portion for clay mineral analysis, and a later portion after numerous fractionations. Those samples which had exhibited the initial differential flocculation frequently showed a slightly greater amount of montmorillonite in the fraction collected first. No major characteristics of composition were associated with samples showing differential flocculation.

The clay concentrate was collected and some of it was allowed to settle from suspension on glass slides with the formation of aggregates with parallel orientation of the clay mineral particles (Grim, 1934). The clay suspension was evaporated in an oven maintained at temperatures below 45°C. This temperature is sufficiently low to prevent the irreversible collapse of the expanding clay minerals and, hence, their confusion with the micas.

The clay mineral determinations were based mainly on x-ray diffraction. Differential thermal analyses were also run for many samples.

CLAY MINERAL COMPONENTS AND X-RAY IDENTIFICATION

Clay mineral analyses of complex clay mineral mixtures such as those occurring in sediments from the Rockport area present many difficult problems in the interpretation of x-ray diffraction data, particularly when quantitative evaluations of the components are desired. Such analyses also develop difficult problems of clay mineral nomenclature.

The great bulk of argillaceous materials in these sediments are three-layer silicates (montmorillonite, illite, chlorite) which are all based on the structural scheme of pyrophyllite. The identity of each mineral species results largely from variation in interlayer compositions. Owing to differences in volumes occupied by different interlayer components, differences in c-axis periodicities result.

Diffraction patterns were taken of the prepared oriented aggregates recording 00 l reflections. Patterns for all specimens were film recorded, and x-ray spectrometer traces were also obtained.

Diffraction data were obtained on samples without treatment, with ethylene glycol treatment, and after heating to 450°C. Diffraction data were obtained from powders as well as oriented aggregates. It was found that in some cases spectrometer data were insufficient in resolving several diagnostic maxima occurring over a small angular range, and in such cases film-recorded data were superior for purposes of identification. Once identified, spectrometer data are invaluable in making quantitative estimates of the clay mineral constituents present. The additional reinforcement resulting from focusing conditions from oriented specimens at low angles (within the range where most diagnostic clay mineral reflections occur) allows maximum opportunity for the recognition of minor but important constituents.

It is comparatively simple to determine from the x-ray data that the samples investigated contain components with the general attributes of illite, chlorite and montmorillonite, but it is extremely difficult to determine the precise nature of the components and their relative abundance. This is in large part due to their low degree of crystallinity and to the intimacy of mixing.

An illite phase was identified as a constituent on the basis of characteristic reflections related to a 10 Å periodicity which remained unchanged following treatment with ethylene glycol. The analytical data do not permit its classification beyond that of a natural nonexpanding 10 Å mineral, i.e., illite.

Two distinct types of montmorillonite, probably representing different interlayer compositions were identified in these sediments. The samples of sediment from the Guadalupe River contain a component which at low relative humidities exhibits a 15.5Å basal spacing. This is suggestive of a two-layer hydrate characterized by exchange positions dominated by Ca ions.

The second type of montmorillonite phase is common to almost all samples from the Bay and Gulf environments and is unique in that it exhibits properties common to both montmorillonite and chlorite. In its natural state it exhibits the normal sequence of basal orders of reflection characteristic of a chlorite (14A, 7A, 4.7A, etc.). However, the intensities of the higher orders relative to the first order are rather lower than would be expected for a true chlorite. This is indicative of an interlayer population considerably deficient in brucite as compared to material that can definitely be called chlorite. Thus this component approaches a vermiculite in its attributes. However, unlike either a true chlorite or vermiculite, it imbibes glycol and behaves like a montmorillonite, expanding and displaying an integral series of orders related to a 17 Å periodicity. On the other hand, significant scattering contribution at angles corresponding to 7A indicates an interlayer population in excess of that afforded by exchange cations alone. There is no discrete hydrate of montmorillonite which in its natural state exhibits the observed *rational* sequence of orders related to a

periodicity of 14 Å. The foregoing characteristics suggest the following structural interpretation. The interlayer region consists of occasional "islands" of brucite scattered laterally at random over otherwise hydrated montmorillonite surfaces. These brucite "islands" occur with sufficient frequency to keep the silicate layers separated and permit them to assume a chloritic aspect. Yet they are too few in number to tie succeeding silicate layers strongly together and to prevent glycolation and subsequent expansion, or to prevent almost complete collapse upon moderate thermal treatment. This material is probably similar to the "swelling chlorite" described by Stephen and MacEwan (1951), but because it expands fully as does montmorillonite, it will be referred to herein as montmorillonite. This material could represent incipient chloritization by the aggradation of montmorillonite, or the degradation of chlorite in the source area by the removal of magnesium.

Chlorite has been identified as a common constituent of these sediments on the basis of an integral series of orders related to a 14 Å periodicity which are unaltered following glycolation. Inasmuch as it is very difficult in sediments of this type to distinguish chlorite from kaolinite, the necessity of good and complete analytical data should be emphasized. Kaolinite and chlorite have two characteristic basal reflections in common, the first and second orders for kaolinite and the second and fourth for chlorite, occurring at 7Å and 3.5Å respectively. Diagnostic first and third orders for chlorite occur at 14Å and 4.7 Å. Owing to other components present the 14Å reflection is often masked by a broad and diffuse reflection falling within the same range, even following glycolation. Film-recorded patterns usually resolved the 14Å line from the very broad 17Å reflection characteristic of the glycolated montmorillonite phase. On spectrometer traces the 4.7Å reflection often appears only as a modification of the symmetry of the 5 Å reflection of illite. Again film-recorded patterns are superior in resolving these two reflections. On the basis of such analyses, however, especially in such poorly crystalline materials, detection of small amounts of kaolinite admixed within the chlorite and other components is impossible. It is necessary to modify the phases present by slight thermal treatment to verify the presence of kaolinite. Chlorite upon ignition undergoes stepwise reactions which are useful in identification (Brindley and Ali, 1950). The first change encountered upon heating involves slight partial dehydration of brucite layers between the aluminosilicate sheets. Accompanying this change all basal orders other than the first become weaker or are lost completely. Kaolinite loses all characteristic reflections following heating to about 550°C. The thermal modification of the chlorite constituent of these sediments takes place on heating rapidly (approximately 10°C per minute) to 400-500°C with immediate air-quenching. This is in contrast to chlorites in ancient sediments which are modified between 500-600°C and the well-crystallized metamorphic chlorites which react between 600-700°C. Thus following ignition to 450°C, loss of re-

lections at 7A and 3.5 A indicates that the original component was chlorite rather than kaolinite. No kaolinite has yet been found by the authors which loses reflections when heated rapidly to 450°C and immediately air-quenched. A residual 7 A reflection following thermal treatment (450°C) is attributed to kaolinite. Details of this procedure have been discussed by Bradley (1953).

It seems likely that the chlorite phase in these sediments should be interpreted as having poorly developed brucite layers or variations in the continuity of the interlayer brucite. Such chlorite can be visualized as a kind of mixed vermiculite-chlorite phase, the "mixing" occurring *laterally* between sheets. This component can be considered as differing from the second type of montmorillonite just described by having more brucite "islands" which prevent expansion of the lattice.

The nature of these clay mineral components suggests the possibility of the occurrence of the more usual type of mixed-layer component consisting of randomly alternating layers of two distinct species. Diffraction effects for such components are less well-defined than for discrete phases as described above. Nevertheless, comparison of the observed diffraction data with theoretical scattering distribution curves for various two-component systems in random intergrowth, suggests definitely that montmorillonite, chlorite, and illite mixed-layer sequences are present in many samples. The considerable low-angle scattering associated with these samples is a characteristic of such random mixed phases.

Consideration of (060) reflections from suitably oriented aggregates indicates that all constituents are within the range characteristic of dioctahedral compositions. In spite of this fundamental difference between this sedimentary chlorite and the better known trioctahedral varieties, recognition of the even more fundamental attribute, i.e., a structural scheme based on alternating mica and brucite layers, seems to make it unwise to consider new nomenclature for the dioctahedral chlorite mineral.

Quantitative estimates of the clay mineral constituents were made utilizing x-ray spectrometer data from samples in the air-dried and glycolated states as well as from those subjected to thermal treatment. Because of the poor crystallinity and intimacy of mixing of the components in clay materials of this type, procedures dependent solely upon comparisons with so-called standard reference clay minerals cannot be applied. Utilizing experimentally determined form-factor functions by Bradley (1953), modified by the appropriate correction factor for spectrometer focusing conditions (Bradley et al., 1953), the relative intensities of diagnostic diffraction maxima were compared in determining the relative abundance of each clay mineral constituent in each sample. Estimates given are based on comparisons of all constituents with one component (illite) within each individual sample. This obviates the necessity of making allowances for differences in degree of orientation and film thickness and variation in nonclay components from sample to sample.

Certain unavoidable errors are inherent in analyses of this type. Variations in scattering distribution resulting from minor unknown differences in composition and crystallinity may result in considerable departure of intrinsic absolute intensities from those actually used in making quantitative evaluations for each component. Thus such variations may accompany diagenetic clay mineral changes believed to have taken place in these sediments. It is believed, however, that the present case represents a situation where these difficulties are likely to exert a minimum influence, because the variations are largely due to changes in interlayer composition and can be evaluated. The range of compositional variation among all samples is such that all analyses have been subjected to errors of the same order of magnitude. Thus the quantitative data are sufficiently accurate for comparison of *relative* differences in clay mineral composition from sample to sample.

The estimates given indicate the most probable number of parts in 10 of the *total clay mineral constituents* for each clay mineral phase. In order to make clear the significance of the quantitative data given, an example will be considered. Sample S89 from upper San Antonio Bay in the vicinity of Guadalupe Delta contains 5.5 parts in 10 montmorillonite, 1 part chlorite, and 2.5 parts illite. In comparing components within this sample it should not be inferred that this sample contains precisely 15 percent more illite than chlorite, but rather there is probably a little more than twice as much illite as chlorite; likewise this sample contains more than twice as much montmorillonite as illite. Comparison can be made for each component when considering and comparing different samples. In comparing sample S89 with sample J11 from the open Gulf (3.5 parts montmorillonite, 2.5 chlorite, 3.5 illite), it is probably accurate to say that the latter contains approximately 20 percent less montmorillonite, 15 percent more chlorite, and 10 percent more illite than the former. It will be noted that the summation of the estimates given for each component never adds up to 10. It has been estimated that from 0.5 to 1.5 parts in 10 can be attributed to poorly crystalline components, particularly mixed layer phases which could not be detected or evaluated quantitatively. Detailed consideration of the interpretation of x-ray diffraction data derived from such samples will be presented in another paper by W. F. Bradley and the authors.

DIFFERENTIAL THERMAL ANALYSES

Differential thermal data were obtained for the minus one micron fraction of many samples, and representative examples are given in Figure 3. All samples are characterized by a prominent endothermal effect at 500-600°C (initiated at about 400°C). Accompanying this reaction is another endothermal effect of considerably less intensity occurring between 600-700°C. The former is within the range usually attributed to an illitic phase, whereas the latter is usually considered diagnostic of montmoril-

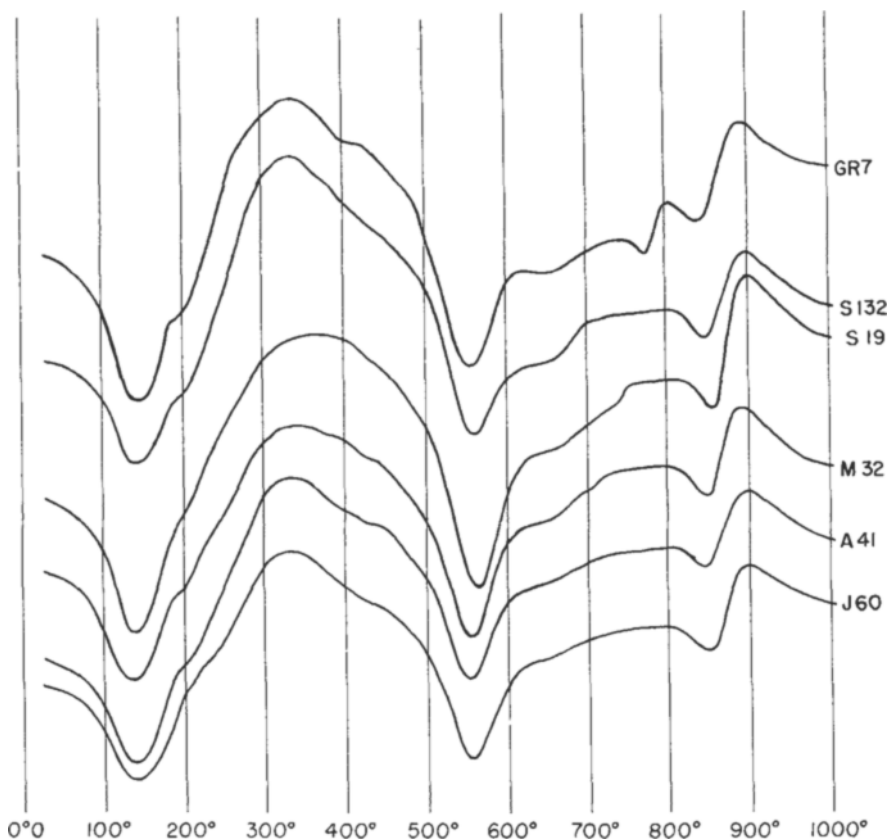


FIGURE 3.— Differential thermal curves of fractions less than one micron of samples characteristic of various environments.

lonite (along with a prominent low temperature endotherm due to loss of interlayer water). However, the relative intensities of these two thermal effects are not commensurate with the relative amounts of illite and montmorillonite as indicated by the diffraction data; nor do they vary relatively from sample to sample as do the clay mineral ratios. In those sediments in which montmorillonite dominates over illite, as well as those exhibiting the reverse order of abundance, the relative amplitudes of the two endotherms show no significant variation. Therefore, in these sediments these endotherms cannot be used to differentiate illite and montmorillonite. The lower temperature endotherm (500-600°C) cannot be explained as resulting solely from illite and must in part be due to montmorillonite. However, it may be concluded that there are two types of montmorillonite present in these samples; one type with the endotherm at 600-700°C

suggests the montmorillonite of many bentonites, the other type with the endotherm at 500-600°C may be an expanding component produced by the degradation of illite or chlorite.

The differential thermal analyses in no case indicate definitely the presence of significant amounts of kaolinite, and in the authors' experience appreciable kaolinite should show in the data for such samples if it were present.

The differential thermal analyses also do not show thermal effects definitely correlative with well crystallized chlorites. However, the analyses of many clay samples containing unquestioned chlorite mixed with other three-layer minerals are substantially like those obtained (Fig. 3). Also the fact that these chlorites are dioctahedral as compared with the trioctahedral character of the well crystallized mineral may account for the failure to recognize them in the differential thermal curves.

It is obvious from the above considerations that differential thermal data for these samples do not permit any quantitative evaluations.

CLAY MINERAL DISTRIBUTION

Clay mineral data are given for each sample in Table 1. A correlation of the clay mineral data and sample locations (Fig. 2) shows that various portions of the Rockport area are characterized by systematic differences in clay mineralogy. In order to indicate these differences it is desirable to subdivide the area geographically into the following units: Guadalupe River; Guadalupe Delta; Upper, Middle and Lower San Antonio Bay; Mesquite Bay; Aransas Bay; and the inner shelf of the open Gulf of Mexico. Although the subdivision of San Antonio Bay appears somewhat arbitrary, each area when considered as a whole emerges as a unit somewhat different from the others. The position of these geographic units in relation to Shepard's (1952-53) general environmental classification is shown in Figure 4 and Table 1. Average values for each clay mineral component for each area have been plotted graphically in Figure 5, and are related to Shepard's classification in Figure 4.

TABLE 1. — CLAY MINERAL COMPOSITIONS
Most Probable Parts in 10 of Total Clay Mineral Constituents

| Sample | Core Depth | Montmorillonite | Chlorite | Illite | Kaolinite |
|-----------------|--------------------|-----------------|----------|--------|-----------|
| GUADALUPE RIVER | | | | | |
| GR7 | 0 cm | 8.0 | 0.5?1 | 0.5 | |
| GUADALUPE DELTA | | | | | |
| S132 | 5-12 cm | 7.0 | 0.5 | 1.0+ | TR. |
| S133 | 12-16 cm | 6.5+ | 1.0 | 1.5 | |
| S136 | 5-15 cm | 8.0 | — | 1.0— | |
| G10 | Poor Data 11-16 cm | Abund. | Slight | Slight | |
| G15 | 0 cm | 6.5 | 1.5— | 1.0+ | TR. |

| Sample | Core Depth | Montmorillonite | Chlorite | Illite | Kaolinite |
|----------------------------|------------|-----------------|----------|--------|-----------|
| UPPER SAN ANTONIO BAY (NE) | | | | | |
| (Bay near river) | | | | | |
| S366 | O cm | 5.5 | 2.0 | 1.5+ | TR. |
| S249 | O cm | 5.5 | 2.0 | 1.5+ | |
| S89 | 5-15 cm | 5.5 | 1.0 | 2.5 | |
| S139 | O cm | 4.5— | 2.0 | 2.5 | |
| S77 | 20-28 cm | 4.5— | 2.0 | 2.5 | |
| S159 | O cm | 4.0 | 2.5 | 2.5 | |
| UPPER SAN ANTONIO BAY (NW) | | | | | |
| (Bay near river) | | | | | |
| S145 | O cm | 4.0 | 2.5 | 2.5 | |
| S103 | 10-25 cm | 4.0 | 2.5 | 2.5 | |
| S151 | O cm | 4.5— | 2.0 | 2.5 | |
| S83 | 10-25 cm | 3.5 | 2.5 | 2.5 | |
| S142 | 70-80 cm | 5.0 | 1.0 | 3.0 | |
| S79 | 10-25 cm | 3.0 | 3.0 | 3.0— | |
| S78 | 25-34 cm | 3.5 | 2.5 | 3.0 | |
| S278 | O cm | 4.0 | 2.5— | 2.5 | |
| S59 | 17-24 cm | 3.0+ | 3.0— | 3.0— | |
| S167 | O cm | 3.0 | 3.0— | 3.0— | TR. |
| MIDDLE SAN ANTONIO BAY | | | | | |
| (Bay intermediate) | | | | | |
| S313 | 40-130 cm | 4.0 | 2.0 | 3.0 | |
| S131 | 50-60 cm | 3.0 | 3.5 | 3.0 | |
| S113 | 10-25 cm | 3.0+ | 3.0— | 3.0— | |
| S122 | 55-59 cm | 3.5 | 2.5 | 2.5 | |
| S171 | O cm | 3.5 | 2.5 | 2.5 | |
| S181 | O cm | 3.0 | 3.0— | 3.0— | |
| S176 | O cm | 4.0 | 3.0 | 2.0 | |
| S334 | O cm | 4.0 | 2.0 | 3.0 | |
| S105 | 22-30 cm | 3.0— | 3.0— | 3.5 | |
| S104 | 10-25 cm | 4.5 | 1.5 | 3.0 | |
| S108 | 10-27 cm | 3.0 | 3.0— | 3.0— | |
| LOWER SAN ANTONIO BAY | | | | | |
| (Bay intermediate) | | | | | |
| S48 | 10-25 cm | 2.5 | 2.5 | 4.0 | |
| S1 | 10-25 cm | 2.5 | 3.0 | 4.0 | |
| S3 | 10-25 cm | 3.0+ | 3.0 | 2.5 | |
| S7 | 10-25 cm | 3.0 | 3.0 | 3.0 | |
| S11 | 10-25 cm | 3.0— | 3.0— | 3.0 | |
| S184 | 90-100 cm | 2.5+ | 2.5— | 2.5 | |
| S12 | 10-25 cm | 2.0 | 3.5 | 3.5 | |
| S275 | O cm | 3.0 | 2.5 | 3.5 | |
| S17 | 20-30 cm | 3.0 | 1.5 | 4.0 | |
| S187 | 25-33 cm | 4.5 | 1.5 | 3.0 | |
| S16 | 25-35 cm | 3.0+ | 3.0— | 3.0 | |
| S195 | 12-20 cm | 3.5 | 2.5 | 3.0 | |
| S185 | 10-25 cm | 3.0 | 2.5 | 3.5 | |
| S19 | 23-33 cm | 3.5 | 2.5 | 3.0 | |
| S21 | 20-30 cm | 3.5 | 2.5— | 2.5 | |
| S27 | 10-25 cm | 3.0 | 2.5 | 3.5 | |

| Sample | Core Depth | Montmorillonite | Chlorite | Illite | Kaolinite |
|----------------------------|------------|-----------------|----------|--------|-----------|
| MESQUITE BAY | | | | | |
| (Bay near inlet) | | | | | |
| M1 | 5-20 cm | 4.0 | 2.0 | 3.5 | |
| M60 | 5-20 cm | 4.0 | 2.0 | 3.5 | |
| M25 | 20-36 cm | 2.0 | 3.5 | 3.5— | |
| M26 | 30-35½ cm | 2.0 | 3.5 | 3.5— | |
| M59 | 0 cm | 4.5— | 1.5 | 3.0 | |
| M65 | 65-72 cm | 1.5 | 4.5 | 2.5 | |
| M5 | 10-22½ cm | 3.0— | 3.0— | 3.0 | |
| M64 | 80-88 cm | 1.5 | 4.5 | 2.5 | |
| M61 | 40-48 cm | 2.0+ | 3.0 | 4.0 | |
| M36 | — | 2.5 | 3.0 | 3.5 | |
| M11 | 5-20 cm | 4.0 | 2.0 | 3.0 | |
| M52 | — | 2.5 | 3.0 | 3.5 | |
| M53 | 0 cm | 3.5 | 2.5 | 3.5 | |
| M62 | 90-96 cm | 1.5 | 4.5 | 2.5 | |
| M34 | 22-30 cm | 3.0— | 3.0 | 3.0— | |
| M50 | 80-86½ cm | 4.0— | 3.0 | 2.0 | |
| M14 | 20-30 cm | 3.5 | 4.0 | 1.5 | |
| M56 | 0 cm | 3.5 | 2.0 | 4.0 | |
| M32 | 20-25 cm | 2.5 | 2.5— | 4.0 | |
| M42 | 25-32 cm | 4.0— | 2.5 | 3.0— | |
| M43 | 25-32 cm | 3.5 | 2.5 | 2.5 | |
| ARANSAS BAY | | | | | |
| (Bay no special influence) | | | | | |
| A4 | 5-21 cm | 2.5 | 4.0 | 3.0 | |
| A20 | 10-25 cm | 3.0 | 3.0 | 3.5 | |
| A66 | 20-30 cm | 3.0 | 3.0+ | 2.5 | |
| A113 | 0 cm | 3.5+ | 2.5 | 3.5 | |
| A190 | 0 cm | 3.5 | 2.5 | 3.0 | |
| A22 | 5-25 cm | 3.0— | 3.0 | 3.0+ | |
| A111 | 21-27 cm | 4.5 | 2.5 | 2.5— | |
| A34 | 0 cm | 2.5 | 3.0 | 3.5 | |
| INNER SHELF | | | | | |
| J44 | 27-32 cm | 2.0 | 3.0 | 4.0 | |
| J72 | 0 cm | 5.0 | 1.5+ | 2.5 | |
| J55 | 40-46 cm | 3.5 | 2.0 | 3.5— | |
| J60 | 0 cm | 3.5— | 2.5 | 3.5+ | |
| J32 | 0 cm | 3.0 | 2.5 | 4.0— | |
| J11 | 0 cm | 3.5 | 2.5 | 3.5 | |
| ST. JOSEPH ISLAND | | | | | |
| (Barrier island flats) | | | | | |
| SJ46 | 5-10 cm | 2.0 | 3.0 | 4.0 | |
| SJ51 | 0-5 cm | 2.0 | 2.5 | 4.5 | |
| MATAGORDO ISLAND | | | | | |
| (Barrier island flats) | | | | | |
| MT87 | 0-5 cm | 3.0 | 3.5 | 3.0— | |
| MT98 | 5-10 cm | 2.5 | 2.0 | 4.5 | |
| MT97 | 3-12 cm | 2.5— | 2.5+ | 4.0 | |

¹ Data insufficient to characterize as chlorite or kaolinite.

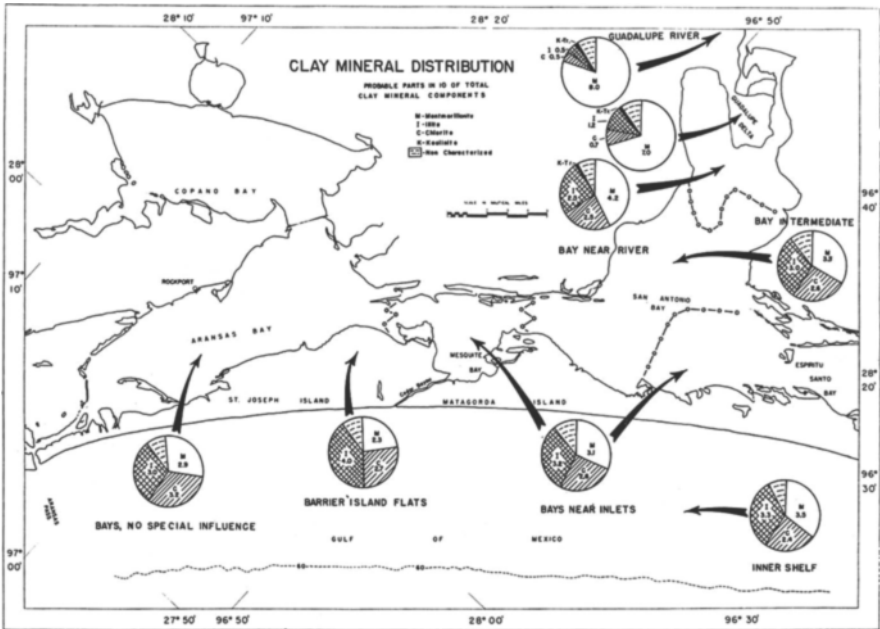


FIGURE 4.— Clay mineral composition of sediments from various environmental divisions of the Rockport area.

The clay mineral data available from each area are for samples taken over a moderate range of core depths down to about 50-60 cm. There is no apparent consistent variation in clay mineral distribution related to depth within the cores.

A systematic variation in the clay mineral composition of the Rockport area sediments is apparent from Figure 5. The source material, Guadalupe River-borne sediment, is characterized by a dominance of montmorillonite with insignificant amounts of illite and a third component indicated as kaolinite and/or chlorite. The only samples in which kaolinite could be definitely identified, and then in very small amounts, came from upper San Antonio Bay.

In the area of initial contact of river-borne sediment and more saline water in upper San Antonio Bay, a rapid decrease in montmorillonite is apparent. In addition there is a suggestion that with regard to the remain-

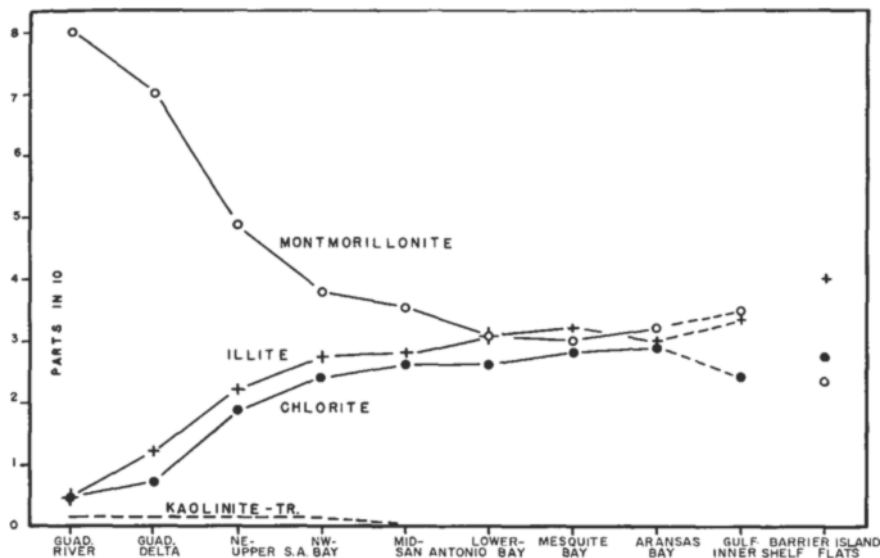


FIGURE 5.—Relation of clay mineral composition to geographical divisions in the Rockport area.

ing montmorillonite in this area, the 15A type decreases relatively and the 14A type increases. In the same area there is a commensurate increase in the illite and chlorite phases as the montmorillonite decreases. Traversing middle and lower San Antonio Bay, Mesquite Bay, and finally into Aransas Bay, montmorillonite decreases and illite and chlorite continue to increase in abundance progressively, although at a much more gradual rate. The small magnitude of differences here are believed to be significant since they are average values.

In passing into the open Gulf an apparent reversal in trend takes place. Here montmorillonite occurs in greater amounts than detected in the lower portions of the "closed-bay" system and chlorite has become a less abundant phase. Illite however shows no decrease similar to that of chlorite. The chlorite phase in the open-Gulf sediments is characteristically better crystallized than its counterpart in samples from the other areas studied. More extensive development of interlayer brucite is evidenced by its greater thermal stability.

The open-Gulf sediments are also characterized by the presence in significant amounts of glauconite in the coarser fractions. This mineral is not present in the other samples studied.

It is noteworthy that the samples from the Barrier Island Flats of St. Joseph and Matagorda Islands have the highest illite and lowest montmorillonite contents of any samples investigated for this area. Perhaps the repeated wetting and drying of the clays in this environment may be significant in the development of illite.

CHEMICAL ANALYSES

Chemical analyses for ten samples representative of various environmental units within the Rockport area are shown in Table 2. The samples are listed in order of increasing salinity for a traverse extending from the Guadalupe Delta into the open Gulf of Mexico. Analyses are for the less than one micron fraction washed free of soluble salts and separated according to the procedures outlined earlier.

TABLE 2. — CHEMICAL ANALYSES*

| | Guad. Delta S132 | San Antonio Bay | | | | Mesquite Bay | | Aransas Bay A34 | Open Gulf | |
|--|------------------------|-----------------|--------|--------------|---------------|-----------------|--------|-----------------------|--------------|--------|
| | | Upper S159 | S167 | Mid- S176 | Lower S275 | M59 | M56 | | J32 | J60 |
| SiO ₂ | 47.46 | 48.34 | 49.13 | 48.66 | 49.80 | 48.01 | 48.05 | 49.44 | 48.50 | 48.14 |
| Al ₂ O ₃ | 18.05 | 18.52 | 18.81 | 18.65 | 18.39 | 18.22 | 18.19 | 18.36 | 19.16 | 19.02 |
| TiO ₂ | .60 | .63 | .60 | .59 | .60 | .60 | .60 | .59 | .61 | .59 |
| Fe ₂ O ₃ ¹ | 6.35 | 6.34 | 6.65 | 6.12 | 6.34 | 6.46 | 6.34 | 5.95 | 7.17 | 7.07 |
| MnO | .06 | .05 | .05 | .05 | .05 | .06 | .07 | .05 | .05 | .05 |
| MgO | 2.45 | 2.53 | 2.62 | 2.98 | 2.77 | 3.17 | 3.20 | 3.36 | 3.25 | 3.37 |
| CaO | 3.32 | 2.64 | 2.56 | 2.29 | 2.80 | 2.54 | 2.50 | 2.08 | 1.25 | 1.34 |
| Na ₂ O | .20 | .10 | .14 | .18 | .18 | .17 | .18 | .18 | .23 | .20 |
| K ₂ O | 1.51 | 1.75 | 1.81 | 1.88 | 1.86 | 1.96 | 1.96 | 2.03 | 2.27 | 2.36 |
| H ₂ O— | 8.91 | 9.15 | 7.47 | 8.39 | 7.19 | 8.74 | 8.78 | 7.95 | 8.22 | 9.10 |
| H ₂ O+ | 8.13 | 8.01 | 7.93 | 8.11 | 7.65 | 7.82 | 7.19 | 8.06 | 7.93 | 7.63 |
| Loss on Ignition ² | 2.99 | 2.09 | 2.26 | 2.09 | 2.37 | 2.38 | 2.30 | 1.83 | 1.18 | 1.13 |
| TOTAL | 100.03 | 100.15 | 100.03 | 99.99 | 100.00 | 100.13 | 100.08 | 99.88 | 99.82 | 100.00 |
| Al ₂ O ₃ /K ₂ O | 11.95 | 10.59 | 10.39 | 9.92 | 9.88 | 9.30 | 9.27 | 9.04 | 8.44 | 8.06 |
| Al ₂ O ₃ /MgO | 7.37 | 7.33 | 7.18 | 6.26 | 6.64 | 5.75 | 5.68 | 5.47 | 5.89 | 5.69 |

* Chemical Analyses made at Rock Analysis Laboratory, Department of Geology, University of Minnesota under supervision of S. S. Goldrich; Eileen H. Oslund, Analyst.

¹ Total iron as Fe₂O₃.

² Loss on Ignition = Total wt. loss on ignition minus total H₂O.

Chemical data of intimate mixtures of clay and nonclay mineral species, although not amenable to quantitative interpretation, are of very considerable value in supplementing the mineralogical data.

Variations in clay mineral distribution, namely the increase in illite and chlorite seaward, are revealed chemically by significant increases in K₂O and MgO content. However, since total K₂O and MgO can vary as a result of differences in the nonclay content alone (chiefly quartz, calcite, and organic matter), it is more revealing to consider Al₂O₃/K₂O and Al₂O₃/MgO ratios in evaluating relative differences in composition from sample to sample. The progressive though gradual decrease in Al₂O₃/K₂O is in accordance with the gradual increase in amount of illite as revealed by the mineralogical determinations. Likewise the variation in Al₂O₃/MgO ratio is in accord with the variation in chlorite content, indicating a

gradual and progressive increase in magnesium through the "closed bay system," followed by a decrease in passing out into the open Gulf of Mexico (compare with Fig. 5). In addition the $\text{Al}_2\text{O}_3/\text{MgO}$ ratios are conclusive in indicating substantial amounts of chlorite rather than kaolinite in these sediments. If this mineral which often can be distinguished from kaolinite only with difficulty, actually was kaolinite, rather than chlorite, an *increase* in $\text{Al}_2\text{O}_3/\text{MgO}$ and probably also $\text{Al}_2\text{O}_3/\text{K}_2\text{O}$ ratios would be expected rather than the observed decrease.

The amount of increase in potassium does not necessarily reflect the exact amount of increase of illite since the content of potassium in illite is variable. All possible K^+ positions need not be filled before the material has the characteristics of illite rather than montmorillonite. Similar statements apply to magnesium and the development of chlorite.

The marked differences in CaO content of Delta, Bay and Gulf samples reflect the known differences in carbonate contents from these three types of environment. Likewise the observed variations in loss on ignition can be at least partially attributed to this factor.

pH AND CHLORINITY

Average sample pH values are plotted in Figure 6 according to geographic divisions. Surface water pH data from Moore (Shepard and colleagues, 1952-53), also plotted in Figure 6, though not directly applicable

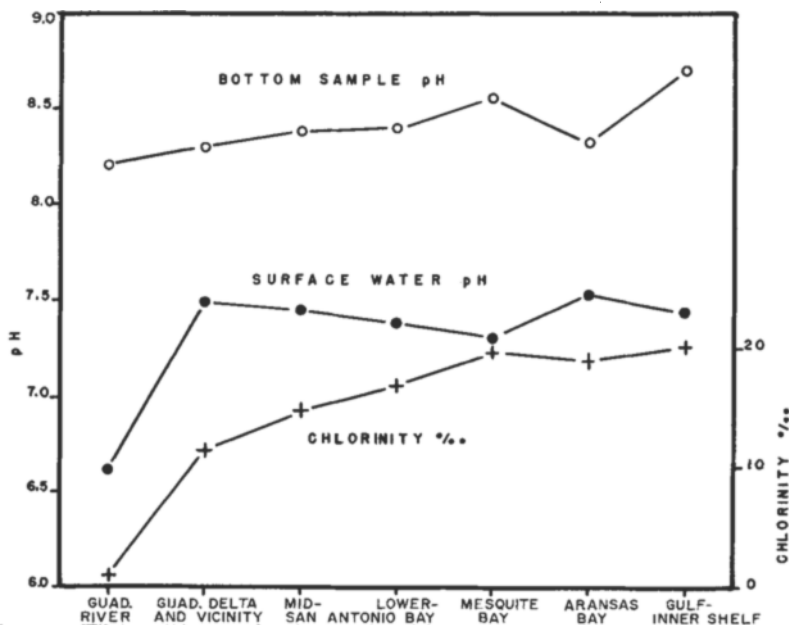


FIGURE 6.—pH and chlorinity data in relation to geographic divisions in the Rockport area.

to the bottom sediments themselves, show the probable order of magnitude of actual pH characteristics of the environment. Although surface conditions are variable, the river and near-delta waters are slightly acid to neutral, grading into mildly alkaline conditions within the bays and open Gulf.

Relative pH values of the bottom sediments show a gradual increase in pH in passing through the bays and across the barrier island into the open Gulf. The anomalous low average pH value for Aransas Bay is not fully explained, although it can possibly be correlated with the higher organic content of sediments in this area.

Comparison of bottom sediment pH with Moore's (Shepard and colleagues, 1952-53) bottom chlorinity data (Figure 6) indicates that variations in pH reflect, in general, changes in salinity conditions. It should be noted that the systematic changes in clay mineral compositions mentioned earlier are correlative with changes in salinity and pH. The conformity between the mineralogical and chemical data is noteworthy, both indicating initial rapid changes followed by more gradual but progressive variation.

INTERSTITIAL WATER

The ratios of cations present in the interstitial water from each sample were computed, and average values for Na/K and Na/Mg for each area are given in Figure 7. These ratios express the relative proportions of each cation present in the static water intimately associated with the sedimentary material. Variations in the ratios give an indication of ions being removed from the interstitial water with respect to other cations. A very appreciable increase in the ratios in the vicinity of Guadalupe Delta and the upper portions of San Antonio Bay indicates a sudden decrease in K and Mg ions relative to Na ions.

It is known that fresh water contains more K and Mg ions relative to Na ions than sea water. Consequently, on mixing fresh and sea water there would be a dilution effect and it could be expected to cause a progressive change in Na/K and Na/Mg values in relation to the geographic divisions. In Figure 7 the dashed lines show the probable dilution effect for Na/Mg. The actual values obtained show a larger reduction in K and Mg ions in the Guadalupe Delta area than would be expected solely on the basis of dilution. These statements refer to ratios of the cations and not to their actual abundance. The total amounts of K and Mg ions in sea water are considerably greater than in fresh water.

The decrease in K and Mg ions in the Delta area is correlated with the increase in relative abundance of illite and chlorite in this area, and can be explained, therefore, by the pick up of these cations in the development of these clay minerals.

It would be expected that the Guadalupe Delta also represents the area of greatest sedimentation; sediment load being transported and deposited

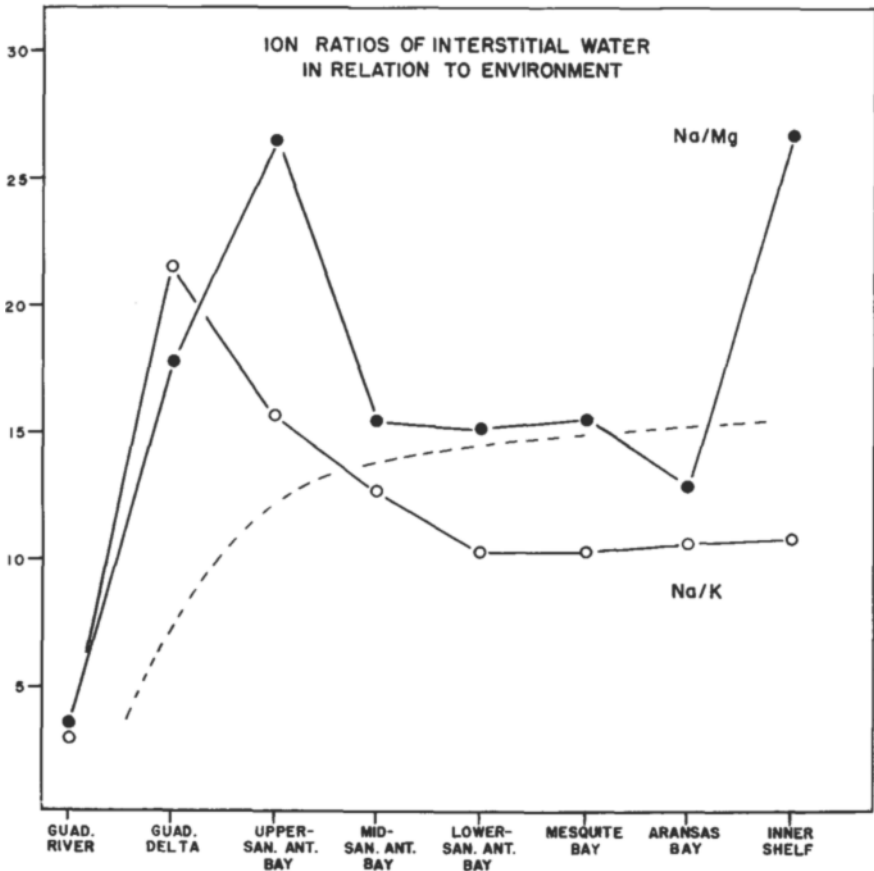


FIGURE 7.—Ratios of Na/Mg and Na/K in the interstitial water in relation to geographic divisions in the Rockport area.

by the Guadalupe River. The sheer bulk of the material would be expected to exert its influence. This is in accordance with studies by Shepard (1953) of depth changes and rates of sedimentation within Texas estuaries and lagoons. His data show an *average* shoaling within San Antonio Bay of 1.23 feet during the last 100 years and an estimated 3 feet total sedimentation. Shepard notes that the greatest amount of shoaling occurs in the vicinity of Guadalupe Delta, so that an average value for this limited area would be much higher. Thus in spite of the very appreciable abstraction of K and Mg ions in this area, the mass of the clay material present is such that only a small percentage would be expected to be converted to illite and chlorite.

Following this initial rapid and extensive removal of K and Mg ions from San Antonio Bay seaward the amount of potassium being removed shows a gradual and progressive relative increase. Magnesium on the other hand shows an additional stage of accelerated loss when passing into the open Gulf. The abnormally low Na/Mg ratio for Aransas Bay cannot be explained, although this portion of the curve seems to be in some way related to pH conditions (Fig. 6).

DIAGENESIS

Several possible explanations for the variation in clay mineral composition in different geographic areas of the Rockport area may be listed as follows:

(a) Differential sedimentation of particular clay minerals in certain areas. Thus Rivière (1952) has argued for preferential sedimentation of kaolinite when fresh-water source material enters a marine environment. (b) The various areas are supplied by source material of different composition. (c) The samples do not all represent materials of wholly the same geologic age. (d) Diagenetic changes.

Explanations (b) and (c) cannot be applied to the Guadalupe Delta area which is receiving sediments from the Guadalupe River. They may, however, explain at least in part the slight variations in clay-mineral composition of some of the Bay areas and particularly the open Gulf area.

Differential sedimentation cannot be completely ruled out, but in the authors' opinion the evidence is overwhelmingly in favor of diagenetic changes to account for the clay mineral variations, particularly in the Guadalupe River, Guadalupe Delta, and adjacent Bay areas. The evidence comes from the detailed character of the clay minerals themselves, structural data regarding the clay minerals which make such diagenetic changes likely, synthetic experiments which show that they are readily possible (Grim, 1953), and data on the distribution of cations in the interstitial water, pH values, and salinity determinations.

The major diagenetic change is the development of illite and chlorite from montmorillonite. Somewhat subtle differences in clay mineral constituents and the presence of randomly mixed species indicate the probable mechanism of early diagenesis. Initial cation exchange reactions taking place in the vicinity of the Guadalupe Delta as the source material first comes in contact with more saline water would result in the acceptance of K and Mg ions in exchange positions, perhaps for Ca ions.

In the chloritization process, Mg ions surrounded by a hydration envelope would develop first between silicate layers. With increasing magnesium content and pH, protons would be subtracted from some of the water and the brucite configuration would develop around the Mg ions. The brucite would develop randomly first between a few montmorillonite layers with the formation of montmorillonite-chlorite mixed-layer sequences. As chloritization proceeded, additional montmorillonite layers

would be effected and more and more magnesium removed from the liquid phase. Ultimately a sufficient number of contiguous montmorillonite layers would be populated with interlayer brucite to develop a 14 Å montmorillonite. With increasing growth of interlayer brucite a definite, though poorly crystallized, discrete chlorite phase would develop.

In the presence of organic material, it would be expected that some organic molecules would be absorbed between the montmorillonite layers blocking the adsorption of the inorganic cations. In areas of abundant organic material, therefore, the development of chlorite and illite in well crystallized forms might be retarded. This is a possible explanation for the relatively high degree of crystallinity of the chlorite in the open Gulf samples.

Simultaneous fixation of K ions between additional montmorillonite layers would result in progressive illitization, with intermediate stages being represented by illite-montmorillonite mixed sequences.

In weathering processes with active leaching, Mg and K ions are progressively removed from chlorite and illite with the development of degraded material (Grim, 1953). When such degraded material is carried to and deposited in a marine environment the process would be reversed with the formation again of chlorite and illite.

Loss of montmorillonite through diagenesis is well established based on a diversity of information. Studies by Dietz (1941) and Grim, Dietz, and Bradley (1949) of Recent sediments from off the California coast have shown the loss of montmorillonite through the formation of illite. Clay mineral environmental studies by Millot (1949) point to a similar trend. The avid potash fixation properties (resulting in illitization) of montmorillonite in alkaline soils has been demonstrated by numerous soil investigators (Reitemeier, 1951). The synthesis of illite and poorly developed chlorites from montmorillonite has been accomplished at room temperature by numerous laboratory investigators (Caillere et al., 1948).

Another diagenetic change which may be taking place is the development of a chloritic mineral from kaolinite. In the Rockport area, no definite evidence for such a change has appeared, but the general absence of kaolinite in the sediments has been somewhat surprising. On structural grounds the transition of a stacking of kaolinite to that of chlorite would involve a shift in silicon positions of every other silicon sheet and the replacement of some Al by Mg ions within the structure. The resulting structure would be dioctahedral, and it is significant that the chlorite in these sediments is dioctahedral.

It is important to emphasize the simplicity of these diagenetic changes and the consequent ease and rapidity with which they probably can take place. With the exception of the kaolinite to chlorite transition, they involve only the exchange and/or addition of components in interlayer positions. There is no necessity to postulate a breakdown to constituent oxides and hydroxides prior to a regrouping and indeed, this seems very unlikely.

It appears likely that the major diagenetic changes would develop about contemporaneously with accumulation or at least very soon thereafter. It is not surprising, therefore, that no variations are found in the clay mineral composition downward for cores of moderate depths.

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DISCUSSION

Thomas F. Bates. — I believe you stated that the change from montmorillonite to illite and chlorite was related only to changes in the inter-layer cation. What is the nature of your evidence that indicates that the 2:1 layer itself was unaffected?

W. D. Johns. — One of the interesting aspects of the clay minerals in these sediments as outlined in the text, is the dioctahedral character of the chlorite (and illite) components. This is of course as expected if chlorite formed from montmorillonite in the manner postulated. The possibility

of changes in the 2:1 layer of a magnitude less than that necessary to change it from dioctahedral to trioctahedral cannot be denied without proof to the contrary. However, the rapidity with which the changes in mineralogy are apparently accomplished would lead us to conclude that only minor changes might occur within the stable silicate layer.