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CLAY DISTRIBUTIONS IN RECENT ESTUARINE SEDIMENTS

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Abstract—The distribution of clay minerals in Recent sediments can be explained by the relative stability of the clays. The rates of particle aggregation for three clays were determined in the laboratory in synthetic estuarine solutions; from the kinetic studies stability values were calculated. The results indicate that illite is more stable than kaolinite which is more stable than montmorillonite. The distribution of the clays in the Pamlico River Estuary can be explained on the basis of relative clay stability where kaolinite which aggregates rapidly (relatively unstable clay) is found upstream of illite.

INTRODUCTION

The transport and deposition of sediments in estuaries are complex processes with various interacting factors affecting the ultimate fate of the sediments. In a review of this subject Meade (1972) considered three influencing factors: dynamic processes that circulate and mix estuarine waters, the agglomeration process (flocculation) which increases the settling velocities of sediment particles, and properties of the particles themselves. Meade concluded that estuarine circulation is the most important process influencing the transport and deposition of sediments while discounting flocculation as having been overemphasized. Meade pointed out that while laboratory experiments demonstrate flocculation of sediment particles due to the effects of salt water, there is no available field evidence which demonstrates the importance of flocculation.

Proponents of flocculation frequently cite the work of Whitehouse *et al.* (1960) as a basis for the deposition of clays in estuaries. As will be discussed in this paper, the results of Whitehouse *et al.* laboratory investigations of the settling tendencies of clays in quiescent saline waters is often inappropriately extrapolated to the field. The purpose of this paper is to discuss the distribution of clay minerals in the surface sediments of estuaries from the viewpoint of clay stability. The relative stability of kaolinite, illite, and montmorillonite (or the relative rates at which these clays undergo particle aggregation) has been evaluated from laboratory studies. The Pamlico River Estuary is used as a specific case to show that the longitudinal distribution of clays in the surface sediments can be explained in terms of clay stabilities.

FLOCCULATION: PARTICLE AGGREGATION

Terminology

Different investigators use various terms to describe the process whereby colloidal particles are aggregated into larger particles. Stated simply, the process is one where very small particles are made into larger particles or into a network of floc particles. Coagulation and flocculation are frequently used to describe this process but these terms have connotations relative to the biases and background of the individual scientist. In spite of the terminology problem the process is easily described. Colloids are particles with large surface areas per unit mass so that the effects of particle surface properties influence their behavior in suspension. The net result being that interparticle physicochemical forces between particles yield stable suspensions (i.e. dispersed suspensions) with little tendency for particle aggregation. It should be noted that a size classification of 2 μm is often used as an upper limit for colloids; however, this is not entirely applicable here since the surface properties of the particles are the key characteristics and cannot be precisely associated with an exact physical classification. The fundamentals of clay colloid stability and particle aggregation kinetics are summarized below. An extensive coverage of clay colloid stability can be found in van Olphen (1963).

Particle stability

Clays carry an electrical charge, usually negative in natural waters, which influences their behavior in suspension. Positive ions in solution are attracted toward the particle surface giving rise to a concentration gradient of ions. The opposing forces of diffusion and electrostatic attraction lead to a density gradient of charges in which the concentration of positive ions is highest adjacent to the particle surface and which decreases exponentially with distance from the particle–

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water interface. The resulting electrical double layers surrounding clay particles in aqueous systems are responsible for the stability of clay suspensions due to the repulsion between similarly charged double layers. Some physico-chemical forces between particles are attractive (van der Waals atomic forces); however, stable clay suspensions usually exist in natural waters because repulsive forces dominate at low ionic strength (low salt content) conditions. One can picture the stability of the clays being attributed to a repulsive energy barrier that inhibits particle collisions and the sticking together of particles to form aggregates or flocs.

The formation of particle aggregates or flocs is often envisioned as a two step process. The first step is referred to as particle destabilization and involves elimination or reduction of the repulsive energy barrier that prevents particles from colliding with each other. The second step involves processes which cause interparticle contacts—i.e. particle transport. Interparticle contacts may be induced by Brownian motion of colloidal particles, by the effects of velocity gradients within the suspending fluid, or by differential velocities of suspended particles which permits larger particles to overtake and collide with smaller particles. In water and wastewater treatment practice, particle destabilization is achieved by the addition of certain inorganic chemicals such as $Al_2(SO_4)_3 \cdot 18H_2O$ or $FeCl_3$. Recently, synthetic organic polyelectrolytes have been added to the stock of chemicals used for the purpose of solids–liquid separation. In natural waters particle destabilization may be accomplished by compression of the electrical double layer surrounding the particles. Verwey–Overbeek and Derjaguin–Landau (1948) have independently developed a quantitative theory —VODL theory—in which the stability of colloids is treated in terms of the energy changes which take place when colloidal particles approach one another. According to the VODL theory, the thickness of the electrical double layer is governed by the electrolyte concentration and the valence of the ions of opposite sign from that of the particle surface. The double layer thickness is compressed with increasing electrolyte concentration and valence of the counterions permitting particles to approach each other. Thus for clays the degree of colloidal destabilization is improved as the ionic strength (salt content) and the charge of the cations increase. This occurs naturally when clays are transported from fresh waters into estuaries.

Particle aggregation kinetics

The rate of particle aggregation depends upon the degree of mixing, particle size and concentration, and the stability of the colloidal particles. A mathematical model describing the aggregation of particles when collisions are induced by fluid motion was developed by Smoluchowski (1917):

$$\frac{dn}{dt} = -\frac{4\alpha\phi Gn}{\pi}$$

where n is the concentration of particles at time t (particles/cm^3), ϕ is the volume of colloidal particles per unit volume of suspension, G is the root mean square velocity gradient (sec^{-1}), π is the mathematical constant, and α is the collision efficiency factor or a measure of colloid stability. A completely destabilized suspension is characterized by $\alpha = 1$ (all collisions lead to agglomeration) while a stable suspension is characterized by $\alpha \ll 1$. This equation is applicable to particle aggregation in water for the case in which particles are initially larger than 1 μm. Brownian motion is responsible for particle collisions where particles are less than 1 μm. A decrease in particle number occurs as particle aggregation proceeds, yielding floc aggregates and the concomitant increase in effective particle size.

Smoluchowski's equation accounts for both particle destabilization and particle transport. The degree of particle destabilization is measured by α and opportunities for interparticle contacts via mixing or velocity gradients are reflected in G, ϕ and n. Furthermore, particle stability (α) depends upon colloid and chemical solution parameters (Edzwald *et al.*, 1974; Hahn and Stumm, 1968). For clays being transported from fresh waters into estuaries the degree of destabilization and thus the α value will depend on the type of clay mineral and on chemical solution parameters such as salinity and pH. Clays should be stable in fresh waters with α approaching zero while in salt waters the clays should be destabilized yielding higher α values.

Laboratory kinetic studies

Three clay minerals* (Kaolinite No. 3, Montmorillonite No. 21 and Illite No. 35) were used in laboratory flocculation kintetic studies. The rate of particle aggregation was determined for each clay under controlled conditions. An outline of the procedures and conditions is presented here; details may be found in previous publications (Edzwald, 1972; Edzwald *et al.*, 1974). The clays were sized using a two-step centrifugation procedure prior to the rate studies so that initially the clay suspensions had narrow particle size distributions. A microscopic check of the initial size distribution of several clay suspensions indicated 80 per cent of the clay particles had an equivalent dia. between 1·5 and 6 μm with a mean of 4·2 μm.

The initial clay particle number was determined and the suspensions were gently stirred to provide opportunities for particle collisions. The rate studies were conducted in a 2 l. stirred-tank reactor and the velocity gradient was determined from torque measurements. The particle aggregation rates were determined by observing the change in particle number concentration using microscopic counting and Coulter Counter techniques. Artificial estuarine solutions were used to evaluate the effect of salinity on particle destabilization. It should be pointed out that mixing enhances flocculation as reflected by G in Smoluchowski's equation. However, there is a limit on the intensity of mixing since vigorous mixing will shear agglomerated particles apart. Krone (1962) examined the relationship

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* Obtained from Ward's Natural Science Establishment, Rochester, N.Y. General data for these clays can be found in American Petroleum Institute Research Project 49, 1949.

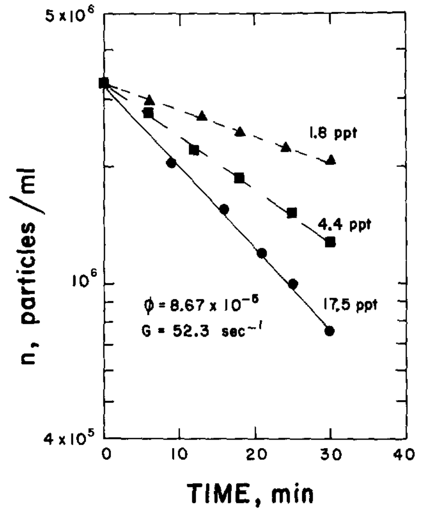

Fig. 1. Flocculation kinetics of kaolinite in synthetic estuarine solutions at three salinities.

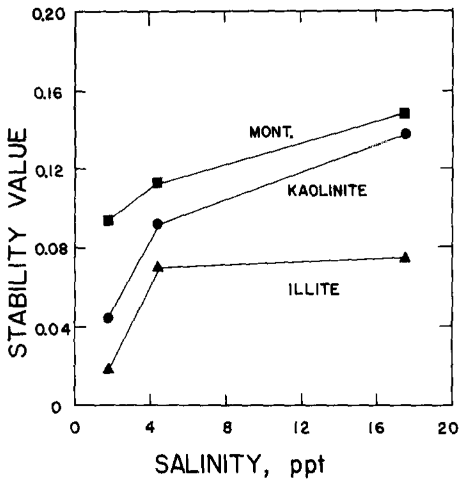

Fig. 3. Stability value (α) as a function of salinity for Kaolinite No. 3, Montmorillonite No. 21, and Illite No. 35.

between particle size and G in a study of shoaling in estuarine systems.

Laboratory results

A series of experiments was conducted to determine the rates of particle aggregation for different clays at various salinities. Fig. 1 illustrates the effect of increasing salinity on the flocculation rate of kaolinite. Fig. 2 shows that illite aggregates at a slower rate than either kaolinite or montmorillonite in solutions with a salinity of 17·5 ppt. The clays had been presized so in spite of the fact that the initial clay particle number concentrations were slightly different, illite is definitely a more stable clay than the others. That is, under similar physical (G and ϕ) and chemical conditions (salinity) illite flocculates at a relatively slow rate. Under conditions where G and ϕ are known, stability values (α) can be evaluated from the slopes of least-squares regression lines (Figs. 1 and 2) in accordance with Smoluchowski's equation.

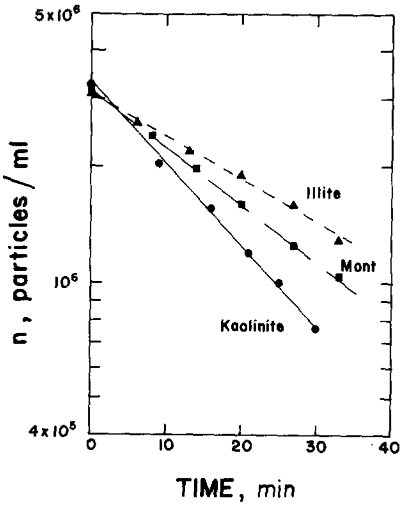

Fig. 2. Flocculation kinetics of Kaolinite No. 3, Montmorillonite No. 21, and Illite No. 35 at a salinity of 17·5 ppt.

Figure 3 is a summary of stability values (α) and demonstrates the effect of salinity on particle destabilization. Clays which are relatively stable (low α values) in waters of low salt content are destabilized to a greater degree in waters of higher salinity. In addition the relative stability depends on the type of clay mineral: illlite is more stable (lower α values) than kaolinite which is more stable than montmorillonite. The results of the laboratory experiments indicate that as clays are transported into estuaries the salinity of these waters provides a mechanism for destabilizing these particles so that the suspensions can become unstable and undergo deposition. In addition the results indicate that clays with slow rates of flocculation (such as illite) would be deposited downstream of unstable clays. A field test of this hypothesis was made by examining the longitudinal clay distributions and flocculation rates of the Pamlico River Estuary sediments.

CLAYS IN THE PAMLICO RIVER ESTUARY

The Pamlico River Estuary flows in an approximate northwest-southeast direction from Washington, North Carolina to the vicinity of Pamlico Point where it enters Pamlico Sound (Fig. 4). The Tar River is the major tributary of the Pamlico River Estuary. The Tar River and Pamlico River Estuary drain approximately 4000 miles^2 of the Piedmont and Coastal Plain of North Carolina. The Pamlico River Estuary is a shallow well-mixed estuary with a maximum width of about 8 miles and an average depth of about 10·5 ft. The 'Outer Banks' of North Carolina have a damping effect on the lunar tide; consequently, the lunar tide is only about 6 in. and is greatly overshadowed by wind tides of up to 3 ft. The average surface salinity for the Pamlico is shown in Fig. 5. The salinity data are based on bimonthly measurements taken from June 1968 to December 1970 (Hobbie, 1970; Hobbie *et al.*, 1972) and from Water Resources Data for North Carolina (1965–1969). Stratification is irregular due to the shallowness of the estuary with no permanent salt wedge.

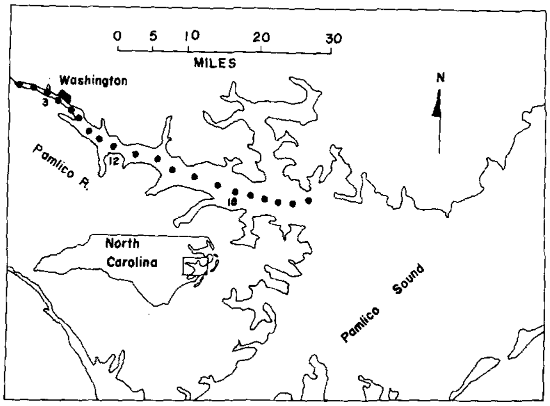

Fig. 4. Map of the Pamlico River Estuary showing approximate sediment sampling stations. No. 3, fresh water sediment; No. 12 upper estuary sediment; and No. 18, lower estuary sediment.

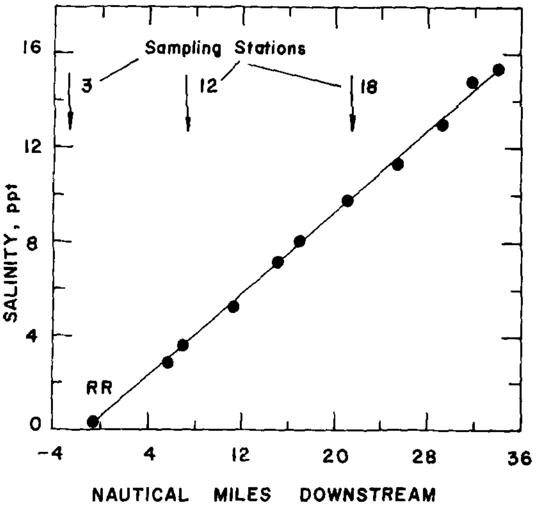

Fig. 5. Salinity of the surface waters of the Pamlico River Estuary as a function of the distance downstream from the railroad bridge at Washington, N.C. (Hobbie, 1970; Hobbie, Copeland and Harrison, 1972; and Water Resources Data for North Carolina, 1965–1969).

An Ekman dredge was used to collect surface sediments from the bottom of the Pamlico River Estuary. The clay size fraction (< 2 μm) of the sediment samples was isolated in the laboratory by centrifugation and the clay mineral composition was determined by X-ray diffraction using a Phillips–Norelco diffractometer. The relative amounts of the clay minerals in each sample were calculated by comparing the ratios of weighted basal peak areas (Park, 1971; Biscaye, 1964; Freas, 1962). The results of such techniques are semi-quantitative; however, the results can be used to indicate trends in the clay mineral composition of the surface sediments. Quartz, kaolinite, illite, montmorillonite, chlorite, and chlorite-like intergrade clay (14Å) were found in the Pamlico sediments. The clay mineral composition of the Pamlico sediments as a function of sediment sample location is plotted in Fig. 6. Kaolinite is the dominant clay in the upper end of the estuary where salinity is lowest and decreases towards the mouth where salinity is highest. Illite occurs in minor amounts in the upper end and increases towards the mouth, while montmorillonite is present in minor amounts along the entire length of the estuary. Chlorite and chlorite-like intergrade clay (14 Å) comprise the remainder of the clay fraction. Dobbins *et al.*, (1970) and Park (1971) have reported similar trends for the clays in the Pamlico sediments.

DISCUSSION

Several models including differential sedimentation, diagenesis, and different source areas for the clays have been proposed and used by investigators to explain the clay mineral composition of Recent sediments. Clay minerals in estuarine and ocean sediments may be derived from weathering profiles on the continents—detrital clays—or they may be formed in their depositional environment—diagenetic clays. Diagenesis is undoubtedly important for deep sediments but would be of minor importance for surface sediments. Grim (1968) has pointed out that all types of clays are present in Recent sediments, but in general the clay composition reflects the climatic conditions of the source area. Grim reports that chlorite and illite are abundant components of marine sediments with kaolinite commonly abundant near-shore in localized areas. Furthermore, the distribution of montmorillonite in Recent sediments is irregular but is associated with volcanism.

The trend for illite in which it is found to be abundant in marine sediments while less abundant in fresh water sediments has been reported by several investigators. Nelson (1960) observed that the amount of kaolinite in the sediments decreased between the upper Rappahannock River and the lower Rappahannock Estuary while in the estuary there was an increase of well-crystallized illite. Griffin and Ingram (1955) found illite to be abundant in the lower end of the Neuse River Estuary of North Carolina while kaolinite was abundant in the fresh water sediments. This same trend was found in this investigation and by others (Dobbins *et al.*, 1970; Park, 1971) for the Pamlico River Estuary.

The distribution of kaolinite and illite in the Pamlico sediments (Fig. 6) is in agreement with the results

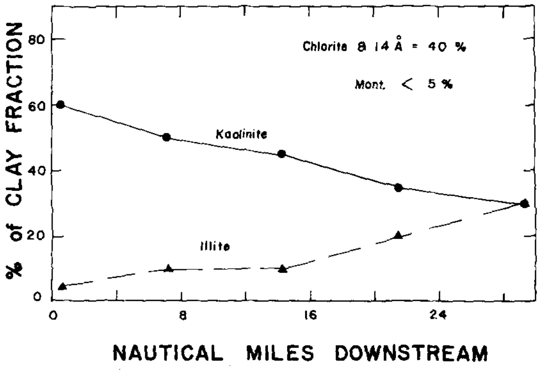

Fig. 6. Clay mineral composition of the Pamlico sediments downstream from the railroad bridge at Washington, N.C.

of the laboratory particle aggregation rate studies. The rate studies indicated that illite is more stable than kaolinite so that under similar physical conditions, illite would be expected to aggregate more slowly than kaolinite and be deposited downstream of kaolinite. Additional laboratory experiments were performed using the Pamlico sediments to test our proposed mechanism for the distribution of clays according to their relative stability. Three Pamlico sediments (Nos. 3, 12 and 18) were sized and subjected to particle aggregation rate studies from which α values were evaluated according to the procedures previously described. The three sediments used are representative of fresh water (No. 3), upper estuary (No. 12), and lower estuary (No 18) sediments. The results are summarized in Fig. 7 which shows the relative stability for the three sediments. For any given salinity the fresh water sediment is relatively unstable compared to downstream sediments (i.e. upstream sediments have higher α values and thus aggregate rapidly relative to downstream sediments under similar chemical conditions). It can be concluded that the stability of the Pamlico sediments is as follows: lower estuary sediment is more stable (lower α values) than the upper estuary sediment which is more stable than the fresh water sediment. The sediments deposited upstream have undergone particle aggregation more rapidly than those deposited downstream which is in agreement with the clay mineral distribution.

The mechanism 'differential flocculation' is often invoked to explain clay distributions in surface sediments, where the work of Whitehouse et al., (1960) on the differential settling velocities of clays in quiescent sea water is cited. The results of Whitehouse *et al.* are summarized in Table 1 and indicate that illite has a higher settling velocity in quiescent sea water than the other clays. Extrapolation of Whitehouse's results to explain clay distributions often results in an anomaly for illite since it has been reported in this investigation and by others that illite tends to dominate downstream (or in marine sediments) of other clays. This is not surprising since Whitehouse's data is applicable to settling velocities of various clays in quiescent sea water but does not account for the time of particle aggregation—i.e. the flocculation time.

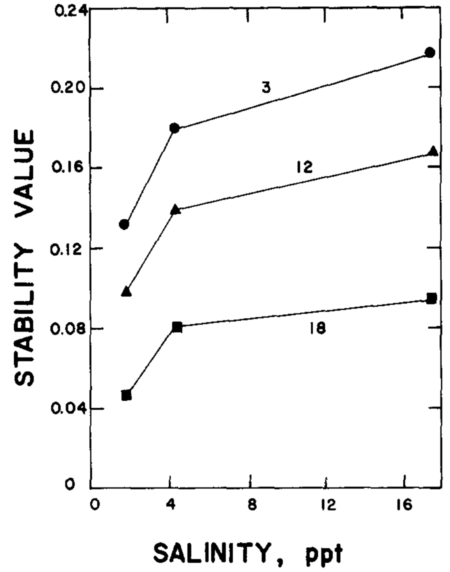

Fig. 7. Stability value (α) as a function of salinity for the clay size fraction of three Pamlico sediments.

Whitehouse *et al.* used several techniques to determine the settling velocities of clays but most of the work was based on gravitational settling analyses. Clay suspensions (< 2 μm fraction) were dispersed initially in a Hamilton Beach dispersion apparatus at 14,000 rpm for periods of 5–10 min for kaolinite and illite and 20 min for montmorillonite. Settling columns were used from which samples were withdrawn over time at a fixed depth below the surface so that settling velocities could be calculated. However, after each sample was withdrawn the suspensions were reagitated prior to the withdrawal of the next sample at a longer settling time. This repeated intense agitation certainly permits determination of settling velocities as shown in Table 1 but it also redisperses the particles during the course of the experiments. As pointed out previously, gentle mixing enhances particle aggregation (flocculation) but mixing is limited in intensity since flocculated particles are sheared apart under extreme mixing conditions resulting in redispersion of the suspension. Effects of particle aggregation were essentially eliminated by Whitehouse *et al.* except that which could occur between agitation periods from Brownian motion or inherent differential settling. Their results do show that the illite particles were larger in their experiments. In fact, for a particle density of 2·5 g/cm^3 and at a salinity of 32·5 ppt the results of Whitehouse *et al.* indicate that the Stokes equivalent diameters for illite, kaolinite, and montmorillonite were 14·2, 12·2, and 4 μm, respectively.

As pointed out by Nelson (1972), even particles as large as 16 μm and at current velocities as low as 25 cm/sec will be transported great distances prior to settling from the water. Consequently, estuarine circulation processes will influence the transport and deposition of suspended sediments (Meade, 1972) such as

Table 1. Representative Settling Velocities in Quiescent Sea Water* (cm/min)

Clay mineral	Salinity (ppt) 0·9	1·8	3·6	10·9	18·1	32·5
Illite	0·89	0·90	1·05	1·10	1·10	1·10
Kaolinite	0·80	0·81	0·81	0·81	0·81	0·81
Montmorillonite	0·0023	0·0036	0·0078	0·041	0·076	0·088

* Data from Whitehouse *et al.* (1960).

clays and other colloids since these particles will be transported with little tendency for sedimentation until the particles are aggregated to such a size that gravitational settling velocities can overcome current velocities. The results of our work can explain the longitudinal distribution of clays in Recent sediments by considering the combined effects of flocculation rates and settling. Those clays which are relatively stable (low α values) will be transported farther downstream due to slow aggregation rates before deposition can occur. Illite was shown to be a stable clay undergoing particle aggregation relatively slowly compared to kaolinite and montmorillonite. Hahn and Stumm (1970) have considered the deposition of clays in natural waters using theoretical values for clay stability whereas in this investigation clay stability was determined experimentally.

The stability of illite has, in a sense, been observed by others. Jacobs and Ewing (1969) investigated the source and transport of clay minerals in the Gulf of Mexico and Caribbean Sea. The authors reported that the montmorillonite-rich sediments of the Mississippi River appear to be flocculated and deposited near the front of the Delta leaving very little montmorillonite in suspension. On the other hand, they reported that the influence of discharge from the Amazon River extends into the Caribbean Sea yielding suspended clays in the Gulf of Mexico and Caribbean Sea which are predominantly mica-like (illite).

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