

# DIFFERENTIAL SETTLING TENDENCIES OF CLAY MINERALS IN SALINE WATERS<sup>1</sup>

*by*

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## ABSTRACT

Differential settling velocities of individual clay mineral types and clay mineral mixtures in quiet saline water are reported for ocean water chlorinity range 0–18 ‰, brackish water ionic strength range 0.0–0.686 moles—(unit charge)<sup>2</sup>/kg, temperature range 6–26°C, clay mineral concentration range 0.01–3.6 g/l., and pH range 6.5–9.8. The materials employed included natural deposit clay minerals and clay minerals extracted from marine sedimentary matter and from terrestrial soils.

Settling velocities at 26°C for illitic and kaolinitic materials reached values of 15.8 and 11.8 m/day, respectively, at an ocean water chlorinity of 18‰ and exhibited little dependence upon chlorinity above a chlorinity of 2‰. Settling velocities for montmorillonites were found to be functions of chlorinity over the entire chlorinity range 0–18‰ and to increase exponentially to a limit of 1.3 m/day at 26°C. The settling velocities were determined by pipette analysis, Oden balance techniques, Kelley–Wiegner manometer methods, and spectrophotometric methods, using artificial sea-water and filtered Gulf of Mexico water.

In quiet brackish water, variations in ionic ratio composition alter the settling rates of illites and kaolinites less than 15 percent from such rates in ocean water, at constant, brackish water, ionic strength of 14 or greater. In contrast, montmorillonitic settling rates in such water varied by 40 percent or more from ocean water rates, at constant ionic strength unless the magnesium–potassium or magnesium–strontium ionic ratios of the brackish water were kept constant. These induced variations were not sufficient in magnitude, however, to change the general relative order of settling rates for the clay minerals.

Decreasing temperatures over the range 26°–6°C decreased settling rates (of all clay types) progressively up to about 40 percent in accordance with temperature-induced changes in the viscosity and density of the saline water medium.

The influences of fifty-seven different organic compounds or materials (carbohydrates and proteins dissolved or dispersed in the water) upon the settling velocities are cited. In general, carbohydrates increased the settling rates of montmorillonitic materials as much as 25 percent, and proteins decreased such rates a maximum of 1–5 percent. Kaolinitic materials suffered a 30–40 percent decrease in settling velocity under the influence of some proteins. So-called “humic acids,” derived from quinone and soil fractions, decreased kaolinitic and montmorillonitic settling rates to lesser extent. No significant alterations of illitic settling rates by organic materials were noted.

Chlorite–montmorillonites were found to settle slightly faster than sodium and calcium montmorillonites. Potassium-saturated montmorillonites settled from two to three times as rapidly as the reference montmorillonites. Chlorite settling rates, of magnitude comparable to rates found for kaolinites, and vermiculite settling rates, comparable at higher chlorinities to illite settling rates, are also reported.

<sup>1</sup> A joint contribution from the Department of Oceanography and Meteorology and the Electron Microscopy Laboratories, A. and M. College of Texas; Oceanographic and Meteorological Series No. 144 and Electron Microscopy Series No. EM-58-1-10.

The apparent interaction of illite and montmorillonite to form illitic-montmorillonitic settling entities in some clay mineral mixtures was noted. Other mixtures, exposed to artificial sea-water for 3-6 years, exhibited a tendency to transport 5-20 percent kaolinite within a developed illitic-chloritic mix, when reagitated.

Evidence is also presented to support the argument that clay minerals do not settle in single solid particulate units in saline waters. The effective settling unit, after flocculation, is described as a coacervate, i.e. as a thermodynamically reversible assembly of solid clay particles or strands within a settling solid-rich liquid unit phase. Settling rate increases are thereby not a consequence of any irreversible formation of larger solid particles or solid aggregates by coalescence of fresh water particles at or beyond the fresh-water-saline-water interface.

Differential transport of clay minerals by the turbulent flow of saline water in a pipe is quantitatively described. Flow rates of about 6 miles/hr were required to eliminate differential transport of the clay minerals. Clay mineral concentrations over the range 0.01-15.0 g/l. were considered.

Chemical data, electron and x-ray diffraction data, base exchange data, and electron micrographs support the settling velocity information.

## INTRODUCTION

The differential settling tendencies of clay minerals in saline water are important to the understanding and interpretation of many geological, oceanographic and tidal hydraulic engineering considerations.

It is generally recognized (Sverdrup, Johnson and Fleming, 1942 ; Landes, 1951) that the determination of specific relationships between the mineralogical, chemical and physical nature and properties of Recent marine sediments and present depositional environments should facilitate the recognition and understanding of environments of the past. In this regard, information relative to the occurrence and distribution of clay minerals in marine sedimentary matter, terrestrial soils and rock formations continues to accumulate. Various hypotheses as to the origin of clay mineral content and the causative factors for variations in the relative clay mineral type contents within clay mineral suites have been presented. Weaver (1958) has emphasized that two dominant, somewhat opposing, zones of thought have developed: the detritus school and the diagenesis school.

Weaver (1958), Rivière (1953) and others consider the clay mineral content in sedimentary rocks and marine deposits to be largely detrital in origin, to reflect the character of the source material, and to be only slightly modified by depositional environments. The early experimental work of Whitehouse and Jeffrey (1952) and Whitehouse (1955) on the differential transport of clay minerals provided data that support some aspects of this argument. However, the latter investigators emphasized that no direct relation necessarily exists between the *relative* clay mineral type contents within a possible source material and such *relative* contents in a deposit or formation. On this basis, the *types* of clay minerals found may have direct source significance from the detrital point of view but the *relative amounts* of clay minerals are changed along the transport path by differential settling.

On the other hand, many investigators including Nelson (1959), Grim and Johns (1952, 1954), Grim (1953), Powers (1954), Millot (1949), Dietz (1941),

and Grim, Dietz and Bradley (1949), have offered explanations of clay mineral origin that depend upon partial to complete chemical transformations of the source clay material by marine environments. Such mineralogical transformation is often called "diagenesis." These investigators consider such mineralogical alteration and development as the most reasonable interpretation in the specific situations studied. Detrital influences are not ruled out but are considered subordinate to diagenetic processes in some environments. Weaver (1958) suggests that this contention is only a consequence of insufficient data relative to source material and to the extent and permanence of the cited transformations.

Whitehouse and McCarter (1958), Barshad (1950), Caillère, Hénin and Mériaux (1948), Aleshin (1948), and Volk (1938) have presented evidence, based on laboratory studies, that transformations of at least one type of clay, montmorillonites, can be initiated to significant extent by saline-water media. However, Whitehouse and McCarter (1958) suggest that no more than 25 percent (wt./wt.) of a source montmorillonite is likely to undergo complete transformation to illitic and chloritic material in an ocean-water environment and that such transformation may be inhibited to pronounced degree by preferential adsorption of organic matter by the clay material. The possible initiation, acceleration, or modification of such transformations by biological activity was also suggested, but not demonstrated, by Whitehouse and McCarter (1958). Anderson, Jonas and Odum (1958) have recently reported that certain species of Mollusca and Echinodermata inhibit the development of chloritic characteristics and possibly abet the development of illitic characteristics in sea-water treated montmorillonite clays via digestive processes utilized to extract organic matter from the clay. Whitehouse and McCarter (1958) reported a similar preferential modification to illitic products when montmorillonites are periodically resuspended and settled in sea-water over a 5 year period, but the total discrete illitic development considered possible was less than 10 percent of the total weight of clay involved.

Glass (1958), Glass and Groot (1959), Keller (1958, 1959) and others have adopted an intermediate view and have utilized both detrital and diagenetic concepts in interpretations of clay mineral distributions in rock formations. Whitehouse and Jeffrey (1952) and Whitehouse and McCarter (1958) also have not negated either concept in interpretations of clay-bearing marine deposits.

Other consequences of marine sedimentation processes influence the investigations of the oceanographer, the geochemist and the tidal hydraulic engineer. The transport and differential settling of clay minerals, silt and sand lead to shoaling of tidal waterways, effect formation of the great river deltas, modify the physical and sonic response of estuarine and marine deposits, and often indirectly govern chemical interactions both in the sea water and within the bottom deposits (Whitehouse and Jeffrey, 1954).

When considerable quantities of finely divided clays are carried into tidal waters, shoaling processes different from those in fresh-water streams

arise (Blackman, 1950). The salt water not only induces flocculation of the clay material but also governs, to significant extent, the subsequent movement and later deposition of the material in the tidal waterway. Variations in sediment physical characteristics such as effective density, shear strength, thixotropic and dilatant character, bearing strength, plastic nature, penetration resistance and sonic response are initially related to the processes of flocculation and adsorption along the transport path to site of deposition. By controlling the chemical nature, distribution and available surface area of the initial deposit, these processes exert directional influence upon later modifications brought about by chemical transformations (diagenetic or authigenic reactions), katamorphic changes, and biological activity, contribution, or disturbance.

Extensive bibliographies on these aspects of sedimentation problems have been compiled by the Committee on Tidal Hydraulics, Corps of Engineers, U.S. Army (1950, 1954, 1955, 1957). Other surveys of existing knowledge on particular problems are given by Rankama and Sahama (1950), Kuenen (1950), Marshall (1949), Sverdrup, Johnson and Fleming (1942), and Whitehouse and Jeffrey (1954). The colloid science of clay minerals has been reviewed by Hauser (1955) and colloidal chemistry of clay mineral-water systems has been extended by the work of Verwey and Overbeek (1948), Van Olphen (1956), Kahn and Lewis (1954), Oakes and Burcik (1956), Marshall (1956), Whitehouse and Jeffrey (1955), Overbeek (1953), Abrikosova and Derjaguin (1956) and others. Some significant results relative to the effects of sea-water upon clay minerals recently have been reported by Carroll (1958) and Carroll and Starkey (1959).

Despite the recognized importance of the initiation of flocculation of finely divided material in tidal waters and the associated sedimentation effects, few investigators have given the process specific attention.

Revelle and Shepard (1939) employed the words "thoroughly coagulated suspensions" in a general sense relative to the distribution of sediments off the California Coast.

Gripenberg (1934) in a study of fine-grained sediments of the North Baltic and adjoining seas, has estimated that such fine material mixed with sea-water flocculates into units having settling rates of 1-20 m/day. Nomitsu and Takegami (1937) obtained variable rates of clearing of suspensions of collected Japanese river sediment samples in separate saline solutions containing potassium, sodium and magnesium ions as flocculating agents. Dreveskracht and Thiel (1941) extended such investigations to selected samples of marl, shale, silt, kaolinite, illite, fire clay, varved glaciolacustrine clay, volcanic ash, bentonite and diatomaceous earth.

The rates of clearing obtained by the last-named investigators were within the range of settling velocities cited by Gripenberg (1934). However, no attempt was made to determine the relative difference in initial particle size distribution of the samples below 250-mesh. Consequently, the different rates of clearing were considered to be a dominant function of initial size before flocculation. It was also noted that bentonites did not exhibit a pro-



nounced fluffy flakelike coagulation when mixed with the ionic media but apparently settled more rapidly than other samples with complete stepwise clearing of the suspension. Settling tubes of 50 cm length and 28 mm diameter were employed. Concentrations of 1 g of sample per 200 ml of solution were used. Such concentration selection was designed to minimize concentration gradient effects and was based upon the work of Rubey (1930, 1933) and Landenburg (1907). However, the conclusions of Rubey have specific application to lyophobic systems. Suspensions of clays, particularly bentonite, are lyophilic (Hauser and LeBeau, 1938). Bentonite exhibits pronounced affinity for interlamellar water and surface water (Grim, 1953). On this basis the bentonite rate of clearing obtained by Dreveskracht and Thiel was significantly influenced by hydration and clay concentration effects, i.e. a coacervated bentonitic mass was settling. Consequently, in order to study the differential rates of settling of kaolinitic, montmorillonitic, and illitic clays in sea-water, Whitehouse and Jeffrey (1953) selected the Andreason pipette (Andreason and Berg, 1935) and the Kelley-Wiegner tube methods of analysis and decreased the clay concentrations to less than 4 g/l.

Since surface activity plays a dominant role in the colloidal action of individual clay minerals (Hauser, LeBeau and Pevear, 1951), Whitehouse and Jeffrey (1953) believed and established that clay particles of similar size but different surface type would exhibit differential flocculation effects and settling tendencies in sea water. In lyophilic clays, such flocculation can be considered governed by both the electrostatic effects and dehydrating effects of the ionic constituents of the water (Hauser, 1951). Van Andel and Postma (1954) accounted satisfactorily for the distribution of clay minerals in the Gulf of Paria by utilizing the results of this early work by Whitehouse and Jeffrey (1953).

In the physicochemical approach to the understanding of marine sedimentation processes, introduced by Whitehouse and Jeffrey in 1951-1952, the evaluation of the influence of eleven general factors upon the flocculation and settling of clay minerals in saline water was considered essential to the understanding of the distribution and diagenesis of clay minerals in marine environments. These factors were: (1) concentrations and interactions of the various ions in sea-water and the associated pH of such water; (2) temperature of the sea-water; (3) initial chemical composition and crystalline structure of the wet clay source material; (4) clay mixture composition of the source material; (5) concentration of clay material per unit volume of sea-water; (6) chemical and statistical lattice structure of the clay and clay-water ionic system; (7) shape and statistical orientations of the clay "floculates"; (8) initial state of division of the clay material before entry into sea-water; (9) type and concentration of dissolved or dispersed organic matter in the sea-water; (10) vertical and lateral movements, turbulence, velocities and general mixing of both fresh-water and sea-water; and (11) vertical concentration gradients of the clay materials in sea-water.

This approach is designed to obtain knowledge of the more probable magnitudes and directions of alterations that may be induced into sedi-

mentary processes by shifting environmental conditions. It is distinct from, but supplements, the use of models of specific environments (Simmons, 1950). Even a partial duplication of an environment from a marine sedimentation point of view is difficult. The information gained is valuable but not necessarily applicable to the understanding of other environments.

Exact duplication of specific natural environments has not been attempted by the present writers. What has been and is sought is an increase in ability to comprehend how nature acts, may act, and has acted. Laboratory study of selected simple units under limited variations of selected parameters that simulate, in part, marine conditions is utilized in this exploration. Such experimental systems are made more complex at a rate commensurate with the developed understanding of systems of lesser complexity. In this connection an environment may be considered as any part, no matter how large or small, of the ocean and its boundaries that may be selected for investigation.

The present report summarizes the most important results derived from the use of this approach in studies of differential transport of clay minerals in saline water. However, much detail of interest to the structural mineralogist, chemist, physicist and engineer is omitted and reserved for later release.

#### ACKNOWLEDGMENTS

This research was initiated under American Petroleum Institute Project 51 through the Scripps Institution of Oceanography, University of California, and was continued under the joint sponsorship of the U.S. Office of Naval Research on Contract N7 onr—48702, Project NR 083 036, Texas A. and M. Research Foundation Project 24, and the Agricultural and Mechanical College of Texas.

Professor R. E. Grim of the University of Illinois contributed advice on clay mineralogy and furnished some of the illitic clay materials studied. Professor G. W. Kunze of the Agricultural and Mechanical College of Texas rendered assistance in the x-ray diffraction analysis of some of the clay materials utilized.

The assistance of the National Kaolin Products Company, the United Clay Mines Corporation, the American Colloid Company, the Harshaw Chemical Company, the El Paso Natural Gas Company, the J. T. Baker Chemical Company, English Clays Lovering, Pochin, and Company, Ltd., Ward's Natural Science Establishment, the Georgia Kaolin Company, the Filtrol Company, the Zonolite Company, the Illinois Clay Products Company, the Baroid Company, the Société Kaolin des Collettes, Echassieres, Allier, and the Amberger Kaolinwerke G.m.b.H., Hirshau, Bavaria, in the procurement of materials is also acknowledged.

Evaluation of results and preparation of the manuscript would have been greatly delayed without cooperative statistical and drafting assistance of Mrs. Margaret Adams, Mr. W. T. Williams, Mrs. Doris S. Whitehouse, Mrs. Mary Bradley, and Mrs. Shirley Griffith.

## GENERAL DISCUSSION

*Terminology*

In the presentation of the results and interpretations in this manuscript, an attempt has been made to commingle the terminology of many scientific disciplines to best advantage. This choice of terminology was considered necessary in order that the discussion might serve investigators in many fields of endeavor to reasonable extent. However, brief explanations of the meaning of a few terms is given herein to expedite perusal and evaluation of the text by investigators not familiar with chemical and oceanographic terminology.

*Chlorinity* is the mass in grams of "atomic weight silver" just necessary to precipitate all the halogens (chloride, bromide, iodide and fluoride ions) in 0.3285233 kg of sea-water sample. Chlorinity is usually expressed as parts per thousand (‰) by weight. This term is employed herein as a relative measure of the constant ionic ratios for the major ions of ocean water (Dittmar, 1884; Lyman and Fleming, 1940) and of brackish water of different ionic ratios herein cited. The term "salinity" is avoided since it tends to imply total salt content and such content is more realistically defined, for the purposes of this investigation, as "ionic strength."

The term "salinity", as used in oceanographic terminology, does not represent the total quantity of dissolved solids, even though it is closely related thereto, and depends by definition upon the chlorinity of ocean water of constant ionic composition. "Salinity" was defined by Forch, Knudsen and Sorensen (1902) as the total amount of solid material in grams contained in 1 kg of sea-water when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine, and all organic matter completely oxidized. Interested investigators may convert the chlorinity values given herein, for ocean water only, to salinity as follows:

$$\text{salinity} = 0.03 + 1.805 \times \text{chlorinity}$$

"Ionic strength" is one-half the sum of the product of the gross molalities of each cation and each anion present in the solution by the square of the respective corresponding ionic charges (valences) (Harned and Owen, 1950, p. 37). It is expressed mathematically as follows:

$$I. S. \text{ (often designated } \mu) = \frac{1}{2} \sum_1^s m_i z_i^2$$

wherein  $s$  is the total number of cations and anions,  $m_i$  is the molality (moles/kg of solution) of any ion,  $z_i$  is the corresponding charge of any ion, and  $I. S.$  is the ionic strength.

"Coacervates" are solid-rich liquid phases that are not spontaneously birefringent. The mechanism of coacervation is sometimes explained by the assumption that protective films of liquid, surrounding and occluded by an association or assembly of suspended or settling solid particles, are in the

form of diffusely orientated liquid molecules. As the ionic concentration of the liquid media increases, dehydration by ions is said to proceed. The diffuse liquid layers are progressively removed by this dehydration process or squeezed out as the solid particles draw closer together, and the effective density of the settling phase increases without change in the amount of solid per unit phase (Bungenberg De Jong and Kruyt, 1930 ; Hartman, 1939, p. 380). A coacervate is thermodynamically reversible and rehydration of a sol in a coacervated condition produces redispersion of the solid particles in the assembly or settling phase. The water in the coacervate is not bound as a whole by hydration forces but to a large extent may be considered occlusion water or water that exists in reversible equilibrium with water outside the coacervate. The solid assembly is dynamic, not static, and is effectively held together and drawn together by ionic coulombic forces as the ionic concentration of the settling medium increases. Actually, at low ionic concentrations the amount of water in the coacervate first increases and then decreases at higher ionic concentrations as the coacervation is suppressed and flocculation, or more rapid settling, follows.

“Lyophilic” is a term applied to solids that tend to associate intimately with the dispersing medium. When the dispersing medium is water the term “hydrophilic” is sometimes employed. In contrast, “lyophobic” materials, or “hydrophobic,” implies lack of association with the dispersing medium. The use of these terms is subject to argument (Thomas, 1934, p. 65 ; Kruyt, 1952) and the categorical classification of clay minerals in this classical way is also subject to debate (McBain, 1950, p. 380).

“Flocculated” is applied to the state of complete coagulation under the existing conditions. The time dependence for complete coagulation is a part of the experimental procedure adopted for preparation of the clay material before settling rates were measured.

The terms *monodisperse* and *monodispersivity*, apply herein to systems in which the settling entities are all of the same effective size, or in which the effective settling velocities are all in a very narrow velocity range.

### *Clay Materials*

Clay minerals from terrestrial clay deposits, soils and marine sediments were studied in these investigations. The procedures employed to separate and classify these materials are described briefly herein under “experimental methods.” All clay minerals and clay mineral fractions employed were identified as to type by chemical analysis, electron microscopy, x-ray or electron diffraction, and cation exchange capacity methods. Thermal analysis data were also utilized in the identification of some materials. A total of 1534 different samples of clay material from 639 general source areas were involved. At least 5 fractions of each of these 1534 starting materials were employed in each type of identification method.

Samples studied included 388 kaolinites, 56 halloysites, 13 dickites, 390 montmorillonites, 6 hectorites, 9 nontronites, 37 potassium-saturated mont-

TABLE 1.—ANALYTICAL DATA ON REPRESENTATIVE CLAY MINERALS—KAOLINIC CLAY MINERALS

Material	Code No.	Total Samples	Total Fractions	Density (g/cm <sup>3</sup> )	C.M.C. <sup>3</sup>	Lattice Spacing (Å)	DTM <sup>4</sup> (°C)	Typical Chemical Analysis <sup>5</sup> (wt. %)											
								SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	ZnO	CaO	MnO	Ni <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	L.O.I. <sup>6</sup>	(+)-H <sub>2</sub> O
Kaolinites (Macon, Georgia)	1(a)	41	246	2.51-2.53	3.2-3.6	7.0, 3.54, 4.15-4.18	550-650 (-) 975-1000 (+)	45.24-45.32	36.96-37.00	0.24-0.26	0.04-0.06	0.41-0.43	0.48-0.56	0.0	0.34-0.35	0.47-0.49	1.18-1.24	14.78-14.84	13.31-13.37
								45.35-45.41	38.23-38.25	0.17-0.21	0.0	0.13-0.19	0.26-0.30	0.0	0.58-0.63	0.38-0.46	0.74-0.78	13.98-14.04	13.15-13.21
Kaolinites (Miss. Delta, New Mexico)	1(b)	37	259	2.55-2.58	3.3-3.6	7.1, 3.58, 4.12-4.17	585-660 (-) 950-1000 (+)	45.93-45.99	35.08-38.14	0.44-0.48	0.05, 0.06	0.00-0.01	0.40-0.42	0.0	0.23-0.28	0.36-0.40	0.47-0.48	13.86-15.92	13.40-13.46
								45.84-45.72	33.92-39.96	0.03-0.07	0.0	0.0	0.00-0.01	0.0	0.12-0.16	0.30-0.34	0.10-0.14	14.00-14.06	13.02-13.99
Kaolinites (Lewisidown, Montana)	1(d)	11	66	2.50-2.56	6.8-7.2	7.1, 4.45, 3.5-3.6	602-615 (-) 980-1000 (+)	47.10-47.20	37.62-37.76	0.34-0.42	0.0-0.1	0.17-0.25	0.06-0.10	0.0	0.00-0.02	1.35-1.47	0.01-0.02	13.76-13.88	13.20-13.32
								47.05-47.19	36.70-36.80	0.55-0.71	0.21-0.29	0.07-0.11	0.0	0.20-0.28	2.06-2.18	0.00-0.01	11.95-12.11	11.44-11.00	
Kaolinites (Schussens, France)	1(g)	4	21	2.48-2.55	3.2-3.5	7.1, 4.28-4.32, 3.5-3.6	590-600 (-) 975-990 (+)	47.50-47.71	36.01-36.12	0.0	0.0	0.22-0.25	0.02-0.07	0.0	0.08-0.14	2.10-2.20	0.14-0.16	12.50-13.62	11.88-12.00
								46.62-46.70	37.58-37.66	0.60-0.64	0.00	0.20-0.24	0.24-0.28	0.0	0.35-0.46	0.70-0.82	0.20-0.21	13.10-13.20	12.92-13.02
Kaolinites (Hirsch, Bavaria)	1(h)	6	30	2.61-2.65	2.6-3.4	7.15, 4.35-4.45, 3.5-3.6	590-600 (-) 925-975 (+)	46.70-46.80	37.64-37.72	0.36-0.46	0.00	0.38-0.44	0.16-0.20	0.0	0.36-0.45	0.64-0.72	0.10-0.20	13.70-13.80	13.19-13.29
								45.30-45.48	37.14-37.30	0.18-0.24	0.00	0.58-0.70	0.10-0.14	0.02	0.45-0.55	0.40-0.44	0.40-0.44	14.00-14.08	13.17-13.25
Kaolinites (Beaumont, Texas, Soil)	1(j)	28	140	2.45-2.55	4.2-5.5	7.1, 4.1-4.2, 3.5-3.6	575-600 (-) 950-1000 (+)	45.13-45.35	36.88-37.02	0.24-0.34	0.10-0.20	0.42-0.52	0.48-0.56	0.0	0.46-0.52	0.18-0.24	14.80-14.88	13.80-13.88	
								46.37-46.47	37.78-37.86	0.57-0.63	0.02-0.03	0.22-0.26	0.22-0.34	0.0	0.32-0.44	0.62-0.72	0.15-0.41	13.16-13.28	12.86-12.98
Kaolinites (College Station, Texas Soil)	1(l)	44	440	2.46-2.50	3.8-4.2	7.1, 4.10-4.15, 3.5-3.6	570-600 (-) 970-1000 (+)	44.61-44.82	37.72-37.92	0.51-1.42	0.00-0.12	0.25-0.40	0.35-0.45	0.03	0.10-0.15	0.08-0.16	0.12-0.32	15.00-15.16	13.94-14.08
								44.53-44.84	37.92-37.91	0.21-1.52	0.00-0.15	0.22-0.42	0.30-0.48	0.05	0.10-0.28	0.10-0.27	0.10-0.35	14.00-14.20	13.15-13.35
Kaolinites (San Saba, Texas, Soil)	1(m)	5	40	2.51-2.58	3.9-4.5	7.15, 4.1-4.3, 3.5-3.6	570-595 (-) 975-1000 (+)	43.92-44.00	38.30-38.34	0.17-0.25	0.01-0.09	0.07-0.09	0.36-0.40	0.01	0.15-0.21	0.45-0.57	0.10-0.14	17.14-17.34	14.50-14.70
								43.94-44.00	38.32-38.34	0.15-0.25	0.01-0.10	0.07-0.09	0.35-0.40	0.01	0.15-0.20	0.42-0.56	0.10-0.15	17.12-17.36	14.52-14.76
Kaolinites (Miss. Delta Region)	1(n)	40	320	2.40-2.61	3.0-3.6	7.1, 2.7-4.1-4.3, 3.5-3.6	No data	44.98-45.06	40.40-40.44	0.09-0.16	0.0	0.38-0.46	0.04-0.05	0.0	0.10-0.18	0.15-0.19	0.0	14.28-14.36	13.08-13.16
								4.0-4.1, 3.0-3.55											
Kaolinites (Gulf of Mexico)	1(o)	80	822	2.45-2.55	3.1-3.5	7.1, 2.4-4.1-4.2, 3.50-3.55	No data												
Halloysites (Pt. Chevreuil, La., Soil)	1(q) <sup>7</sup>	16 <sup>8</sup>	96	2.30-2.51	5.0-6.4	7.3-7.5, 4.35-4.45, 3.60-3.65	No data												
Halloysites (Miss. Delta Region)	1(r) <sup>9</sup>	22 <sup>9</sup>	176	2.31-2.51	5.0-6.4	7.3-7.5, 4.35-4.45, 3.60-3.65	No data												
Dioctites (Gulf of Mexico)	1(c) <sup>10</sup>	4 <sup>10</sup>	20	2.61-2.65	5.2-7.4	7.1, 2.7-4.3-4.4, 4.0-4.1, 3.0-3.55	No data												

<sup>1</sup> See text, "General Discussion, clay materials," for electron microscopy information, literature references, and additional marine sample source information.  
<sup>2</sup> Separate "crude" starting materials.  
<sup>3</sup> Cation exchange capacity in new exchangeable cations per 100 g of solid clay material.  
<sup>4</sup> Differential thermal analysis, (-) = dip, (+) = up, ± 5°C apply to all samples involved.  
<sup>5</sup> Ranges shown indicate minimum to maximum values found for series of samples from source cited.  
<sup>6</sup> Loss on ignition.  
<sup>7</sup> See text section "General Discussion, clay materials," for data source information on: kaolinites 1 (e) 5 samples; halloysites 1 (p) 18 samples; dioctites 1 (e) 9 samples.  
<sup>8</sup> Nine samples from starting materials that differ from 1(c); 7 samples from starting materials similar to materials cited in 1(c).  
<sup>9</sup> Fourteen samples from starting materials that differ from 1(n); 8 samples from starting materials similar to materials cited in 1(n).  
<sup>10</sup> These samples from starting materials similar to materials cited in 1(c).

morillonites, 317 illites, 7 "metabentonites", 44 illite-montmorillonites, and 116 chlorite-montmorillonites, 92 vermiculites, and 59 chlorites.

Complete analytical data for all the clay materials cited are not given herein but representative data for each clay mineral type of fraction employed are either presented or a source for such data is cited. Any significant differences in results for materials of the same clay type but of different chemical composition are mentioned, however, in the section on "Experimental Results". The following data apply to prepared clay fractions and do not necessarily agree with values reported for similar materials by other laboratories.

1. *Kaolinitic clay minerals.*—

(a) Kaolinites (Macon, Georgia), 41 samples, 246 fractions: See Table 1 and Whitehouse and McCarter (1958, p. 86).

(b) Kaolinites (Bath, So. Carolina), 37 samples, 246 fractions: See Table 1 and Whitehouse and McCarter (1958, p. 86).

(c) Kaolinites (Mesa Alta, New Mexico), 8 samples, 259 fractions: analytical data in Table 1; electron microscopic appearance (not shown), hexagonal and irregular thin plates and aggregates in 1–0.05 $\mu$  size range.

(d) Kaolinites (Lewistown, Montana), 11 samples, 66 fractions: analytical data in Table 1; electron microscopic appearance (not shown), euhedral and subhedral thin plates and dense aggregates in size range 0.12–1.50 $\mu$ .

(e) Kaolinites (Murfreesboro, Arkansas), 5 samples, 25 fractions: Data consistent with those reported in American Petroleum Institute Project 49, Preliminary Report No. 1 (1949).

(f) Kaolinites (Cornwall, England), 22 samples, 110 fractions: analytical data in Table 1; electron microscopic appearance (not shown), irregular and well defined euhedral thin plates and aggregates in 0.05–1.6 $\mu$  size range, quartz present.

(g) Kaolinites (Echassieres, France), 4 samples, 30 fractions: analytical data in Table 1; electron microscopic appearance (not shown), irregular and hexagonal thin plates and aggregates in the 0.1–0.8 $\mu$  size range, quartz present.

(h) Kaolinites (Hirshau, Bavaria), 6 samples, 30 fractions: analytical data in Table 1; electron microscopic appearance (not shown), euhedral hexagonal and elongated plates and aggregates in the 0.2–1.7 $\mu$  range.

(i) Kaolinites (Mexia, Texas, soil), 21 samples, 105 fractions: extracted from soil clay fractions containing 80–95 percent montmorillonites, 5–20 percent kaolinites, 0–5 percent illites, and 1–5 percent quartz; analytical data for kaolinites in Table 1; electron microscopic appearance (not shown), irregular and hexagonal thin plates and dense aggregates in the 0.1–1.2 $\mu$  size range, quartz present.

(j) Kaolinites (Beaumont, Texas, Prairie soil), 28 samples, 140 fractions: extracted from soil clay fractions, containing 80–98 percent montmorillonites, 0–15 percent kaolinites, 0–10 percent illites, 0.5–4 percent quartz;

analytical data for kaolinites in Table 1 ; electron microscopic appearance (not shown), irregular and hexagonal thin plates and aggregates in the 0.1–1.5 $\mu$  size range, quartz present.

(k) Kaolinites (Point Chevreuil, Louisiana, soil), 36 samples, 180 fractions : extracted from soil clay fractions containing 50–70 percent montmorillonites, 5–15 percent kaolinites, 2–7 percent halloysites, 5–15 percent illites, 0–15 percent chlorites, illite–montmorillonites, vermiculites and chlorite–montmorillonites, and 1–5 percent quartz ; analytical data for kaolinites in Table 1 ; electron microscopic appearance (not shown), well defined elongated hexagonal thin plates and aggregates in the 0.1–1.4 $\mu$  size range, quartz present.

(l) Kaolinites (College Station, Texas, soil), 44 samples, 440 fractions : extracted from soil clay fractions containing 60–90 percent montmorillonites, 5–30 percent illites, 2–8 percent kaolinites, and 1–8 percent quartz ; analytical data for kaolinites in Table 1 ; electron microscopic appearance (not shown), irregular and hexagonal thin plates and aggregates in the 0.08–1.4 $\mu$  size range, quartz present.

(m) Kaolinites (San Saba, Texas, soil), 5 samples, 40 fractions : extracted from soil clay fractions containing 80–95 percent montmorillonites, 0–15 percent kaolinites, 5–15 percent illites, and 0–6 percent quartz ; analytical data for kaolinites in Table 1 ; electron microscopic appearance, irregular to euhedral thin plates and dense aggregates (see clay mineral soil fraction, Fig. 1, and discussion in “ experimental results ”).

(n) Kaolinites (marine sediments in Mississippi Delta region of Gulf of Mexico ; average results from material collected at 40 locations defined by 29° 10' to 29° 30' N, 89° 00' to 89° 30' W, and north and east of Grand Bay, Main Pass and Pass Loutre), 40 samples, 320 fractions : extracted from sediment clay fractions containing 40–80 per cent montmorillonites, 0–20 percent illites, 0–30 percent chlorites, vermiculites, illite–montmorillonites, and chlorite–montmorillonites, 0–8 per cent kaolinites, 0–5 percent halloysites, and 1–5 percent quartz ; analytical data for kaolinites in Table 1 ; electron microscopic appearance (not shown), irregular to euhedral thin plates and dense aggregates in the 0.3–1.5 $\mu$  size range.

(o) Kaolinites (marine sediments in Gulf of Mexico ; average results from material collected at 80 locations defined by 28° 00' to 28° 40' N, 93° 40' to 95° 20' W), 80 samples, 822 fractions : extracted from sediment clay fractions containing 60–84 percent montmorillonites, 4–10 percent kaolinites, 0–5 percent halloysites, 4–12 percent illites, 0–2 percent dickites, 3–20 percent chlorites, vermiculites, illite–montmorillonites and chlorite–montmorillonites, and 3–7 percent quartz ; analytical data for kaolinites in Table 1 ; electron microscopic appearance, irregular to hexagonal thin plates and aggregates in the 0.1–2.0 $\mu$  size range (Figs. 2 and 3).

(p) Halloysites (Bedford, Indiana), 4 samples, 20 fractions ; (Eureka, Utah), 6 samples, 30 fractions ; (Wagon Wheel Gap, Colorado), 8 samples, 40 fractions : data consistent with those reported in American Petroleum Institute Project 49, Preliminary Report, No. 1 (1949).

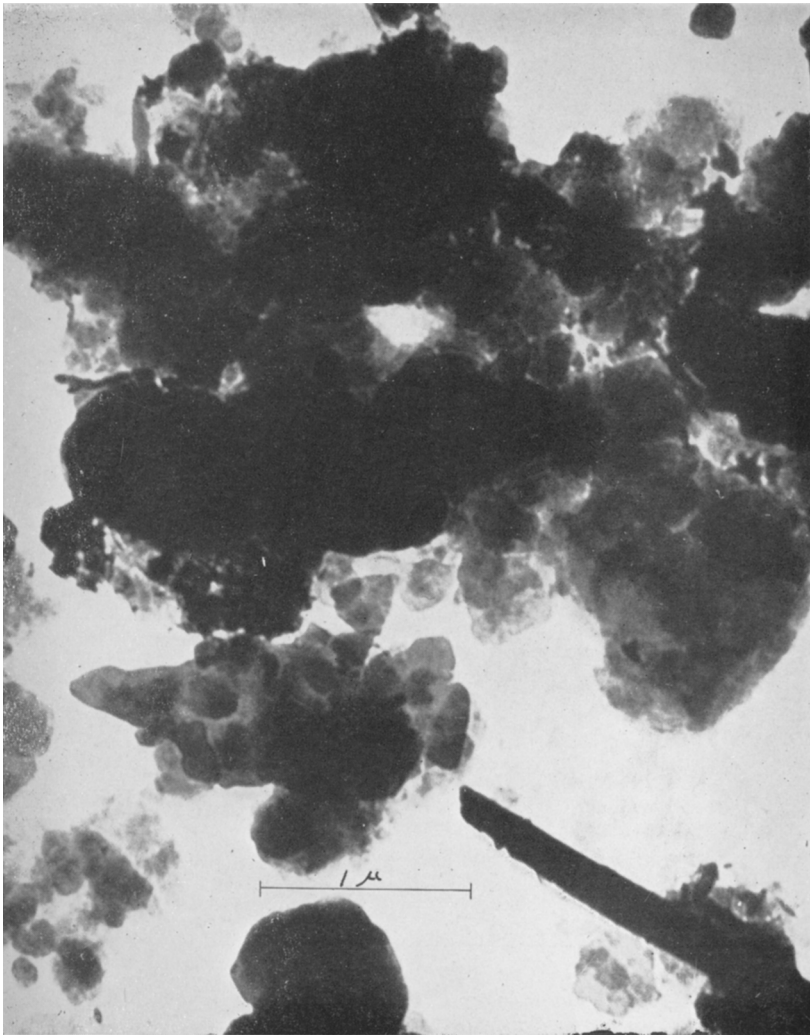


FIGURE 1.—Typical clay mineral fraction of a Texas soil clay (San Saba, Texas).

(To face p. 10)





FIGURE 2.—Typical clay mineral fraction of a Gulf of Mexico marine deposit (28°26.2' N, 94°23.3' W).

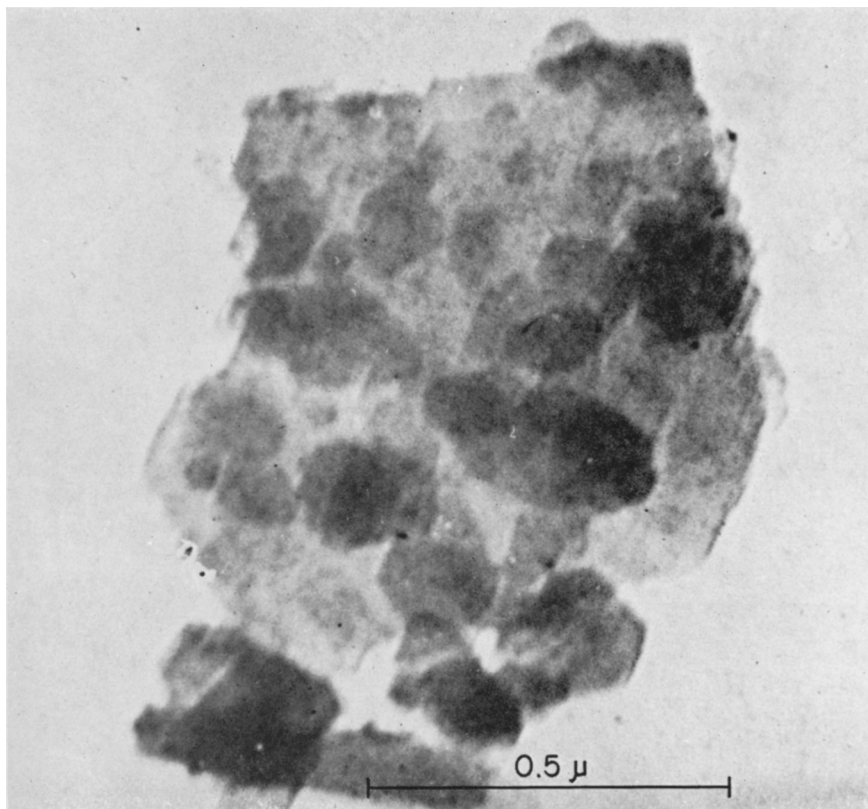


FIGURE 3.—Typical kaolinitic clay mineral from Gulf of Mexico marine deposit (28°30.9' N, 94°33.8' W).

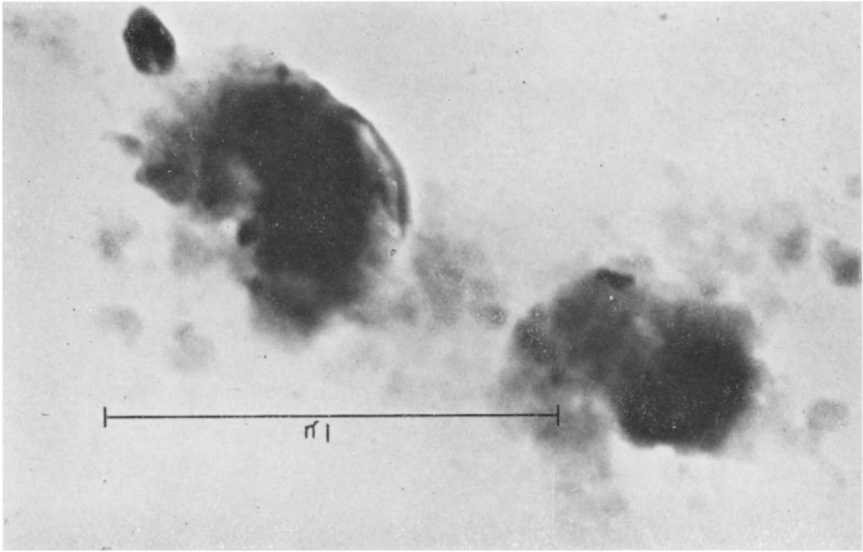


FIGURE 4.—Basic fibrous structure of montmorillonitic clays from which larger plate-like, lathlike and "fluffy" aggregates are woven or derived. (This field from dispersed marine deposit material)

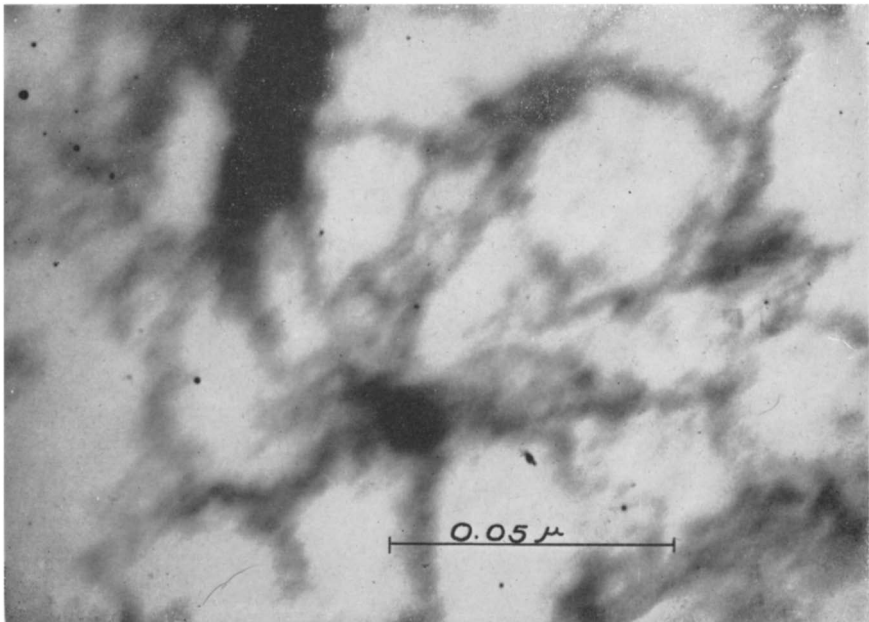


FIGURE 5.—Typical montmorillonitic clay states of aggregation in near-shore waters of Gulf of Mexico.

TABLE 2.—ANALYTICAL DATA OF REPRESENTATIVE CLAY MINERALS<sup>1</sup>—MONOMORPHIC AND LITIC CLAY MINERALS

Code No.	Material	Total Samples	Total Fractions	Density <sup>2</sup> (g/cm <sup>3</sup> )	C.E.C. <sup>3</sup>	Lattice spacings (Å)	DTA <sup>4</sup>	Typical Chemical Analysis <sup>5</sup> (wt. %)										L.O.I. <sup>6</sup> (+) H <sub>2</sub> O	
								SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	MnO	Li <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O		TiO <sub>2</sub>
2(a)	Monmorillonites (Utikon, Wyoming)	46	322	2.01-2.02	148-151	17.7 (glycol), 4.45-4.55 (1.49)	145-150 (-), 809-810 (-), 846-853 (+)	58.53-58.58	18.30-18.30	2.75-2.88	0.0-0.02	2.25-2.35	0.38-0.41	0.0	2.37-2.63	0.52-0.58	0.06-0.08	14.40-14.50	7.48-7.58
2(b)	Monmorillonites (Ponkille, Miss.)	38	225	2.58-2.65	132-141	16.8 (glycol), 5.16-4.44 (1.49)	180-250 (-), 650-700 (-), 1010-1050 (+)	50.97-50.15	16.38-16.52	1.38-1.44	0.25-0.29	4.02-4.28	2.10-2.31	0.03-0.01	0.12-0.18	0.44-0.54	0.27-0.31	23.20-23.30	7.87-7.97
2(c)	Monmorillonites (Clay Spur, Wyoming)	36	216	2.05-2.10	98-110	17.7 (glycol), 4.45-2.68 (1.49)	175-225 (-), 650-700 (-), 880-900 (+)	60.20-60.32	18.12-18.18	2.73-2.83	0.07-0.09	2.84-2.92	0.18-0.24	0.0	1.50-1.58	0.22-0.30	0.08-0.14	14.87-14.97	6.71-6.81
2(d)	Monmorillonites (Houston, Texas, Soil)	57	285	2.10-2.25	120-135	17.5 (glycol), 4.30-2.62 (1.49)	No data	59.52-59.61	18.29-18.41	2.71-2.81	0.05-0.17	3.69-3.87	0.15-0.29	0.0	2.15-2.25	1.02-1.08	0.10-0.14	14.12-14.28	7.34-7.50
2(e)	Monmorillonites (San Saba, Texas, Soil)	5	25	2.21-2.22	110-125	17.5 (glycol), 4.42-2.55 (1.49)	No data	49.79-50.01	19.05-19.30	2.18-2.30	0.0-0.01	3.16-3.28	0.38-0.56	0.0	1.28-1.40	0.10-0.14	0.17-0.25	23.37-23.45	7.69-7.76
2(f)	Monmorillonites (PA, Chevreuil, La., Soil)	68*	465	2.34-2.42	90-110	17.5 (glycol), 4.38-2.46 (1.50)	No data	59.63-59.84	18.57-18.69	2.81-2.89	0.02-0.08	3.22-3.62	0.20-0.28	0.02	1.21-1.27	0.61-0.89	0.08-0.12	13.56-13.72	7.24-7.40
2(g)	Monmorillonites (Isla, Delta Region)	40*	363	2.21-2.42	120-150	17.5 (glycol), 4.4-2.52 (2.60), 1.49-1.51	No data	55.02-57.13	18.92-19.00	2.57-2.74	0.00-0.42	1.51-1.64	0.22-0.54	0.00-0.02	0.21-0.20	0.40-1.01	0.10-0.20	19.40-19.00	7.10-8.00
2(h)	Monmorillonites (Gulf of Mexico)	86*	886	2.22-2.45	122-150	17.5 (glycol), 4.4-2.52 (2.60), 1.49-1.51	No data	55.48-57.16	18.87-19.03	2.51-2.71	0.00-0.44	1.51-1.68	0.20-0.52	0.00-0.02	0.23-0.18	0.37-1.60	0.10-0.21	18.45-14.04	7.08-8.04
2(i)	Restonites (Hector, Calif.)	6	30	2.83-2.48	18-35	17.6-17.7 (glycol), 4.4-2.52 (2.60), 1.51	175-225 (-), 770-810 (-), 880-915 (+)	53.91-53.97	0.08-0.19	0.00-0.04	0.00	25.88-25.92	0.18-0.18	0.00	1.15-1.27	0.16-0.26	0.00-0.02	14.85-14.93	5.57-5.65
2(j)	Xonotrites (Marion, Wash.)	9	45	2.15-2.64	140-160	16.5 (glycol), 4.3-4.2 (2.58, 1.51)	170-220 (-), 400-500 (-), 875-900 (+)	40.42-40.50	5.18-5.23	31.32-31.40	0.16-0.26	0.00-0.04	1.76-1.88	0.0	0.17-0.25	0.19-0.29	0.0	20.80-20.90	6.08-6.13
2(k)	Monmorillonites K-saturated (Erbahn, Illinois)	37	185	2.21-2.42	30-75	10.9-11.6, 4.51, 2.58, 1.49	No data	39.29-39.36	18.47-18.53	2.79-2.83	0.0-0.01	1.75-1.85	0.18-0.26	0.0	0.28-0.02	3.79-3.85	0.05-0.07	11.57-11.63	8.19-8.25
3(a)	Illite (Morris, Illinois)	25	150	2.68-2.74	20-36	10.0 (diffuse), 4.48, 3.31, 17-18 (glycol) absent	500-600 (-), 800-900 (-), 875-900 (+)	52.72-52.78	24.81-24.85	4.08-4.16	0.21-0.31	2.22-2.36	0.28-0.34	0.0	0.33-0.37	5.66-5.74	0.56-0.68	8.76-8.82	7.91-7.97
3(b)	Illite (Chevreuil, La.)	27	135	2.70-2.74	24-28	10.0 (slightly diffuse), 4.50, 3.31, 17-18 (glycol) absent	500-600 (-), 800-900 (-), 875-900 (+)	57.48-57.56	17.98-18.05	4.85-4.99	0.29-0.24	2.18-2.30	0.31-0.31	0.0	0.08-0.12	5.83-5.91	0.74-0.82	9.71-9.77	6.33-6.39
3(c)	Illite (Amarillo, Texas, Soil)	17	85	2.76-2.81	20-28	10.0 (4.47, 3.30, 1.88, 1.31, 17-18 (glycol) absent)	No data	40.82-41.06	26.20-26.44	6.76-6.86	0.15-0.26	6.70-6.78	0.68-0.86	0.0	1.89-2.02	3.68-3.72	0.37-0.45	11.71-11.79	10.10-10.18
3(d)	Illite (Chattanooga Bay, La.)	38	228	2.70-2.74	22-26	10.0 (diffuse), 4.46, 3.31, 2.56, 1.96, 1.31, 17-18 (glycol) absent	No data	49.11-49.30	28.42-29.00	2.37-2.35	0.00-0.04	3.27-3.39	0.20-0.28	0.00-0.02	0.12-0.20	7.17-7.25	0.47-0.55	9.20-9.28	7.98-8.06
3(e)	Illite (New Mexico, Soil)	42	297	2.70-2.78	24-28	10.0 (4.47, 3.30, 2.99, 2.56, 17-18 (glycol) absent)	No data	49.10-49.32	28.78-28.98	2.29-2.38	0.00-0.02	3.25-3.40	0.20-0.28	0.0	4.06-4.22	3.41-3.49	0.10-0.14	9.78-9.79	9.12-9.18
3(f)	Illite (Miss. Delta Region)	40*	321	2.71-2.75	22-26	10.0 (diffuse, slightly amorphous), 4.48, 3.30, 3.0, 17-18 (glycol) absent	No data	50.72-52.57	24.72-25.86	4.10-4.55	0.25-1.20	2.64-3.16	0.08-0.15	0.00-0.01	0.10-0.20	7.12-7.28	0.48-0.52	9.18-9.28	8.05-8.12
3(g)	Illite (Gulf of Mexico)	78*	841	2.66-2.72	33-35	10.0 (diffuse), 4.41, 3.31, 17-18 (glycol) absent	No data	50.72-52.57	24.72-25.86	4.10-4.55	0.25-1.20	2.64-3.16	0.08-0.15	0.0	0.17-0.21	6.15-6.48	0.27-0.62	7.86-8.14	7.56-7.89

<sup>1</sup> See text. <sup>2</sup> General Discussion, clay minerals<sup>7</sup> for electron microscopy information. Literature references, and additional matrix sample source information. <sup>3</sup> Cation exchange capacity in meq exchangeable cations per 100 g of solid clay material. <sup>4</sup> Differential thermal analysis, (-) = dip, (+) = peak, (-) = double dip, (-) = complex, a small endothermic dip followed by small exothermic peak. <sup>5</sup> Percentages are minimum to maximum values found for series of samples from each source. <sup>6</sup> Loss on ignition. <sup>7</sup> See text. <sup>8</sup> General Discussion, clay minerals<sup>7</sup> for data source information on: monmorillonites 2(c) 25 samples. <sup>9</sup> Occur in association with halloysites 1(c) and halloysites 1(c) but extracted from different batches of starting material. <sup>10</sup> Occur partly in association with kaolinites 1(c) but extracted from different batches of starting material. <sup>11</sup> Occur partly in association with kaolinites 1(c) and monmorillonites 2(g) but extracted from different batches of starting material. <sup>12</sup> Occur partly in association with kaolinites 1(c), halloysites 1(c), and monmorillonites 2(g) but extracted from different batches of starting material. <sup>13</sup> Occur partly in association with kaolinites 1(c) and monmorillonites 2(i) but extracted from different batches of starting material.

(q) Halloysites (Point Chevreuil, Louisiana, soil), 16 samples, 96 fractions : 7 samples extracted from soil clay fractions similar to those described in 1(k) ; 9 samples from soil clay fractions containing 60–90 percent montmorillonites, 2–15 percent halloysites, 10–20 percent illites, 0–5 percent chlorites, illite–montmorillonites, vermiculites and chlorite–montmorillonites, and 0–4 percent quartz ; analytical data for halloysites in Table 1 ; electron microscopic appearance (similar in appearance to the tubular form of halloysite present in Fig. 1, a Texas soil clay), elongate to tubular forms in the 0.2–2.5  $\mu$  size range, approximately 0.1–0.2  $\mu$  in diameter.

(r) Halloysites (marine sediments in Mississippi Delta region ; average results from region cited in 1(n), 22 samples, 176 fractions : 8 samples extracted from sediment clay fractions similar to those described in 1(n) ; 14 samples from fractions containing 80–90 percent montmorillonites, 0–15 percent illites, 0–10 percent vermiculites, illite–montmorillonites, and chlorite–montmorillonites, 1–15 percent halloysites, and 1–8 percent quartz ; analytical data for halloysites in Table 1 ; electron microscopic appearance (not shown), same as cited in 1(q).

(s) Dickites (Ouray, Colorado), 3 samples, 15 fractions ; (San Juanito, Chihuahua, Mexico), 3 samples, 15 fractions ; (St. George, Utah), 3 samples, 15 fractions : data consistent with those given in American Petroleum Institute Project 49, Preliminary Report No. 1 (1949).

(t) Dickites (marine sediments, Gulf of Mexico, 29° 27.5' N, 94° 28.5' W), 4 samples, 20 fractions : extracted from sediment clay fractions similar to those described in 1(n) ; analytical data for dickites in Table 1 ; electron microscopic appearance (not shown), euhedral and irregular thick plates and dense aggregates in the 1.6–2.5  $\mu$  size range.

## 2. *Montmorillonitic clay minerals.*—

(a) Montmorillonites (Upton, Wyoming), 46 samples, 322 fractions : See Table 2 and Whitehouse and McCarter (1958, p. 86).

(b) Montmorillonites (Polkville, Mississippi), 38 samples, 228 fractions : See Table 2 and Whitehouse and McCarter (1958, p. 86).

(c) Montmorillonites (Clay Spur, Wyoming), 36 samples, 216 fractions : analytical data in Table 2 ; electron microscopic appearance (not shown), fibrous, forms fluffy thin aggregates in the 20 Å–2.0  $\mu$  size range.

(d) Montmorillonites (Chambers, Arizona), 7 samples, 35 fractions ; (Otay, California), 7 samples, 35 fractions ; (Amory, Mississippi), 8 samples, 40 fractions : data consistent with those reported in American Petroleum Institute Project 49, Preliminary Report No. 1 (1949) except in electron microscopic appearance. The habit of these montmorillonites is thread- or strandlike, forming fluffy aggregates that are not plates (Whitehouse and McCarter, 1958).

(e) Montmorillonites (Houston, Texas, Black Prairie soil), 57 samples, 285 fractions : extracted from soil clay fractions containing 85–97 percent

montmorillonites, 1-2 percent kaolinites, 0-1 percent illites, and 1-3 percent quartz; analytical data for montmorillonites in Table 2; electron microscopic appearance (not shown), fibrous, forming dense aggregates with fluffy irregular edges.

(f) Montmorillonites (San Saba, Texas, soil), 5 samples, 25 fractions: extracted from soil clay fractions similar to those described in 1(m); analytical data for montmorillonites in Table 2; electron microscopic appearance, fibrous, forming fluffy dense aggregates (some aggregates are included in Fig. 1).

(g) Montmorillonites (Point Chevreuil, Louisiana, soil), 66 samples, 465 fractions: extracted from soil clay fractions similar to those described in 1(k) and 1(q); analytical data for montmorillonites in Table 2; electron microscopic appearance (not shown), fibrous, forming fluffy and irregular dense aggregates.

(h) Montmorillonites (marine sediments in Mississippi Delta region of Gulf of Mexico; average results from material collected at 40 locations as defined in 1(n)), 40 samples, 363 fractions: extracted from sediment clay fractions similar to those described in 1(n) and 1(r); analytical data for montmorillonites in Table 2; electron microscopic appearance (not shown), fibrous, forming fluffy thin to dense aggregates with fibrous edges.

(i) Montmorillonites (marine sediments in Gulf of Mexico; average results from material collected at 80 locations as defined in 1(o)), 80 samples, 886 fractions: 47 samples extracted from sediment clay fractions similar to those described in 1(o); 33 samples extracted from sediment clay fractions containing 82-94 percent montmorillonites, 0-6 percent illites, 0-12 percent chlorites, illite-montmorillonites, vermiculites and chlorite-montmorillonites, and 1-4 percent quartz; analytical data for montmorillonites in Table 2; electron microscopic appearance: basic fibrous structure of these montmorillonites is shown dispersed in Fig. 4. The general aggregate habits are shown in Fig. 5. States of aggregation have been preserved by critical point method (Whitehouse and McCarter, 1958).

(j) Hectorites (Hector, California), 6 samples, 30 fractions: See Table 2 and American Petroleum Institute Project 49, Preliminary Report No. 1 (1949).

(k) Nontronites (Manito, Washington), 9 samples, 45 fractions: analytical data in Table 2; electron microscopic appearance (not shown), fibrous to latlike aggregates with threadlike striations.

(l) Potassium montmorillonites (produced by saturating Upton, Wyoming and Polkville, Mississippi, montmorillonites, 2(a), (b), preceding, with potassium ion by settling the clay through a saturated potassium chloride solution and allowing the clay-potassium chloride solution system to age 6 months; mixed-layer clay minerals which are sometimes called "potassium montmorillonites" or "metabentonites" are described under "materials," 5(a), later in this report), 37 samples, 185 fractions: analytical data in Table 2; electron microscopic appearance (not shown), fluffy, thin to dense aggregates.

### 3. Illitic clay minerals.—

(a) Illites (Fithian, Illinois), 25 samples, 150 fractions : See Table 2 and Whitehouse and McCarter (1958, p. 86).

(b) Illites (Morris, Illinois), 27 samples, 135 fractions : analytical data in Table 2 ; electron microscopic appearance (not shown), irregular thin flakes, forming dense aggregates with diffuse to distinct irregular outlines in the 0.05–1.5 $\mu$  size range, flake minimum thickness of about 30 Å.

(c) Illites (Point Chevreuil, Louisiana), 52 samples, 326 fractions, 37 samples extracted from soil clay fractions similar to those described in 1(k), 1(q) and 2(g) ; 15 samples from fractions containing 40–50 percent montmorillonites, 20–30 percent illites, 10–15 percent kaolinites, 0–25 percent vermiculites and illite–montmorillonites, 0–5 percent halloysites, and 0–4 percent quartz ; analytical data for illites in Table 2 ; see also Fig. 6 and Whitehouse and McCarter (1958, pp. 86–87).

(d) Illites (Amarillo, Texas, soil), 17 samples, 85 fractions : extracted from soil clay fractions containing 60–70 percent illites, 10–35 percent kaolinites, 5–10 percent quartz, and 0–15 percent sepiolites (?) ; analytical data for illites in Table 2 ; electron microscopic appearance, irregular thin plates and aggregates, often poorly defined, in the 0.05–0.9 $\mu$  size range (Fig. 6 is typical).

(e) Illites (marine sediments, Atchafalaya Bay, Louisiana), 38 samples, 228 fractions from sediment clay fractions containing 60–70 percent montmorillonites, 4–12 percent illites, 10–20 percent chlorites, vermiculites, illite–montmorillonites, and chlorite–montmorillonites, 0–5 percent kaolinites, 0–2 percent halloysites, and 2–8 percent quartz ; analytical data for illites in Table 2 ; electron microscopic appearance, irregular to diffuse thin plates and aggregates in the 0.05–1.0 $\mu$  size range (Fig. 6 is typical).

(f) Illites (Gallup, New Mexico, soil), 42 samples, 297 fractions : extracted from soil clay fractions containing 78–84 percent montmorillonites and 16–22 percent illites ; analytical data in Table 2 ; electron microscopic appearance, irregular and diffuse thin plates and aggregates, slightly better defined than material shown in Fig. 6, in 0.1–1.2 $\mu$  size range.

(g) Illites (marine sediments in Mississippi Delta region of Gulf of Mexico ; average results from material collected at 40 locations defined by 28° 10' to 29° 10' N, 89° 00' to 89° 30' W, and north and east of Grand Bay, Main Pass, and Pass Loutre), 40 samples, 321 fractions : 18 samples extracted from sediment clay fractions similar to those described in 1(n) and 2(h) ; 22 samples extracted from fractions containing 30–60 percent montmorillonites, 30–40 percent illites, 5–15 percent kaolinites, 0–10 percent halloysites and 2–8 percent quartz ; analytical data for illites in Table 2 ; electron microscopic appearance similar to illites 1(e). See also Fig. 6.

(h) Illites (marine sediments in Gulf of Mexico ; average results from material collected at 76 locations defined by 28° 00' to 28° 40' N, 93° 40' to 95° 20' W), 76 samples, 841 fractions : 54 samples extracted from sediment clay fractions similar to those described in 1(o), 1(t), and 2(i) ; 22 samples

from fractions containing 40–60 percent montmorillonites, 5–15 percent kaolinites, 5–10 percent chlorites, vermiculites, chlorite–montmorillonites, and illite–montmorillonites, 15–50 percent illites, and 0–8 percent quartz; analytical data for illites in Table 2; electron microscopic appearance, irregular thin plates and aggregates, commonly poorly defined, in the 0.05–1.0 $\mu$  size range (Fig. 6 is typical).

4. *Vermiculitic or related mixed-layer clay minerals.*—

(a) Vermiculites (Libby, Montana), 25 samples, 204 fractions: analytical data in Table 3; electron microscopic appearance, very thin plates and sheets which stack to form dense aggregates and which fold readily upon rapid drying or flocculation (Fig. 7 is typical).

(b) Vermiculites (Greenville, South Carolina), 27 samples, 217 fractions: analytical data in Table 3; electron microscopic appearance, very thin plates and sheets, which stack to form dense aggregates (Fig. 7 is typical).

(c) Vermiculites (Raleigh, North Carolina, soil), 8 samples, 40 fractions: extracted from soil clay fractions containing 25–35 percent vermiculites, 25–30 percent chlorites, 25–35 percent illites, 4–8 percent kaolinites, and 2–6 percent quartz; analytical data for vermiculites in Table 3; electron microscopic appearance, very thin plates and sheets that readily fold upon rapid drying or flocculation (thin plates in Fig. 7 and folding illustrated in Fig. 8 are typical).

(d) Vermiculites (marine sediments, Atchafalaya Bay, Louisiana), 32 samples, 259 fractions: 22 samples extracted from sediment clay fractions similar to those described in 3(e); 10 samples extracted from fractions containing 30–40 percent montmorillonites, 30–40 percent illites, 30–40 percent vermiculites, 0–10 percent chlorites, and 0–12 percent quartz; electron microscopic appearance, very thin plates (estimated as 30 Å thick), which stack to form dense aggregates and fold readily upon rapid drying or flocculation (see Figs. 7, 8).

5. *Other mixed-layer clay minerals.*—

(a) Illite–montmorillonites (metabentonites) (Catawba, Virginia), 7 samples, 35 fractions: analytical data in Table 3; electron microscopic appearance (not shown), irregular thin plates dominant, euhedral six-sided plates, fluffy aggregates, kaolinite present.

(b) Illite–montmorillonites (Point Chevreuil, Louisiana, soil), 44 samples, 267 fractions: 27 samples extracted from soil clay fractions similar to those described in 1(k) and 1(q); 17 samples extracted from fractions containing 40–60 percent montmorillonites, 10–25 percent illites, 20–30 percent illite–montmorillonites, 5–10 percent vermiculites, and 2–10 percent quartz; analytical data for illite–montmorillonites in Table 3; electron microscopic appearance (not shown), dense aggregates with fluffy edges, some fine grained irregular plates.

(c) Chlorite–montmorillonites (marine sediments in Mississippi Delta





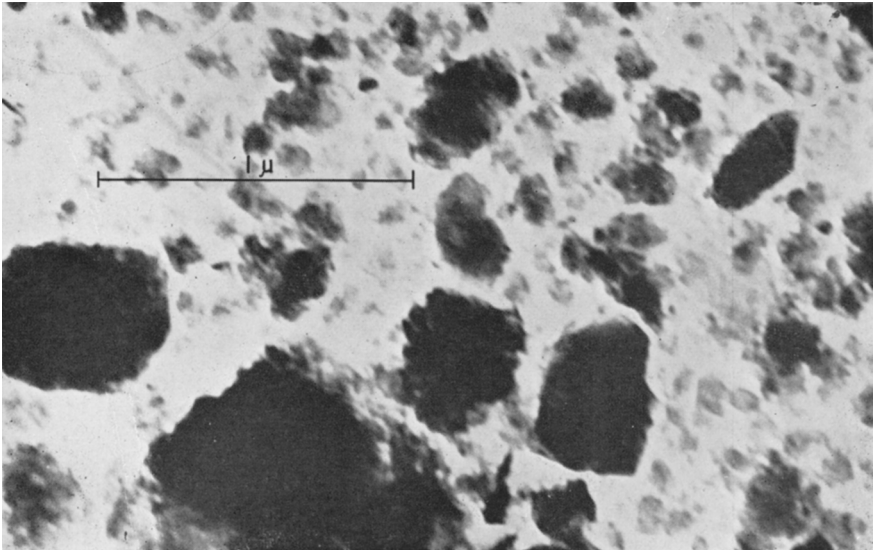


FIGURE 6.—Typical physical structure of illitic clays in soils and in near-shore waters of Gulf of Mexico.

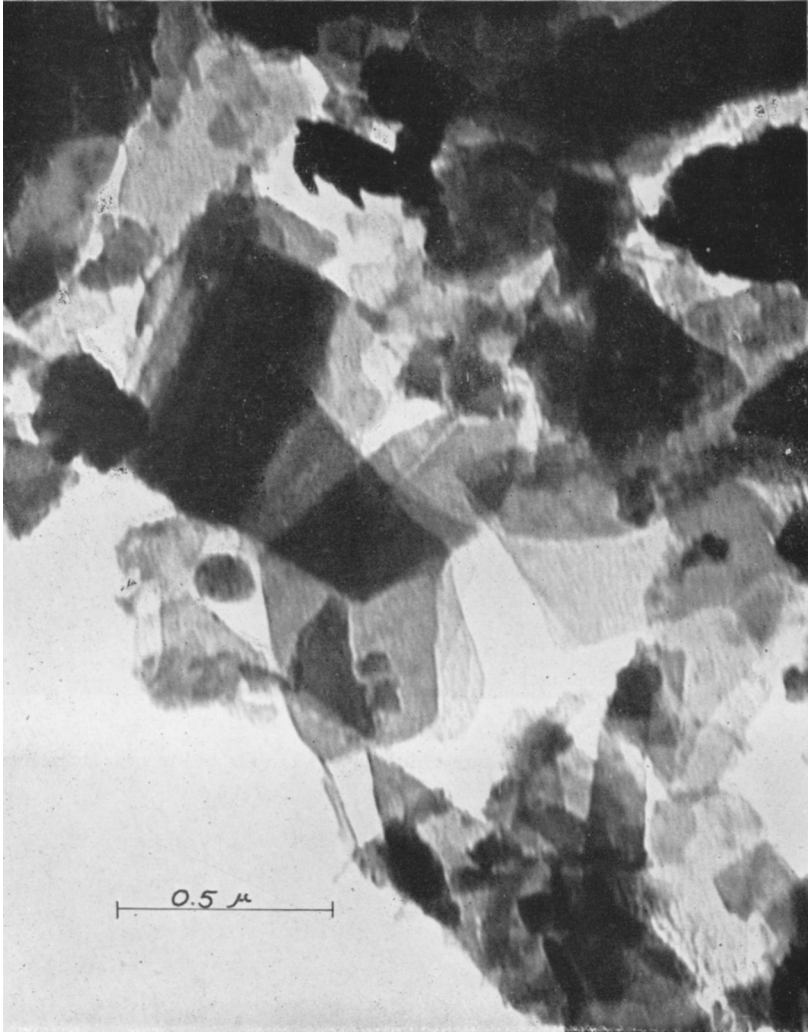


FIGURE 7.—Typical physical structure of vermiculitic clays in terrestrial deposits, soils, and marine sediments.

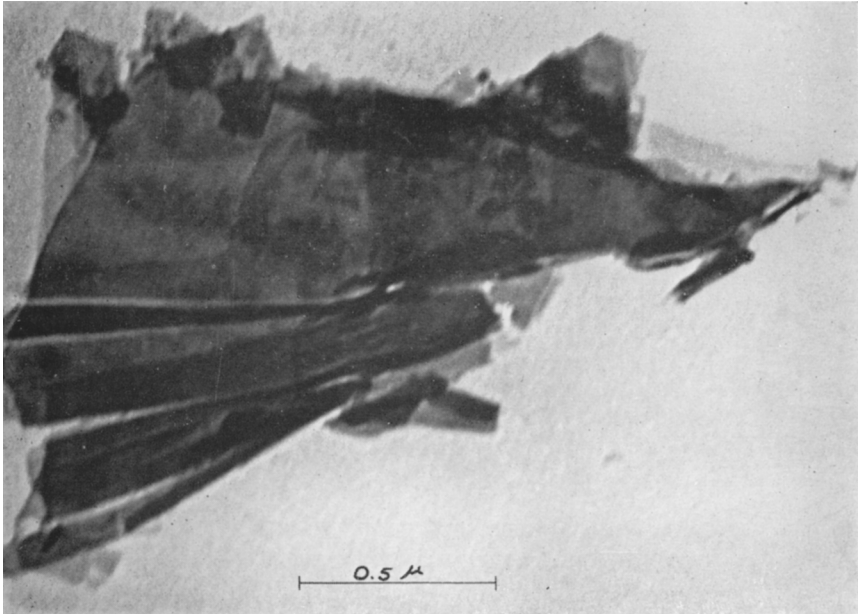


FIGURE 8.—Typical folding of vermiculitic clay "sheets" induced by flocculation or by rapid drying

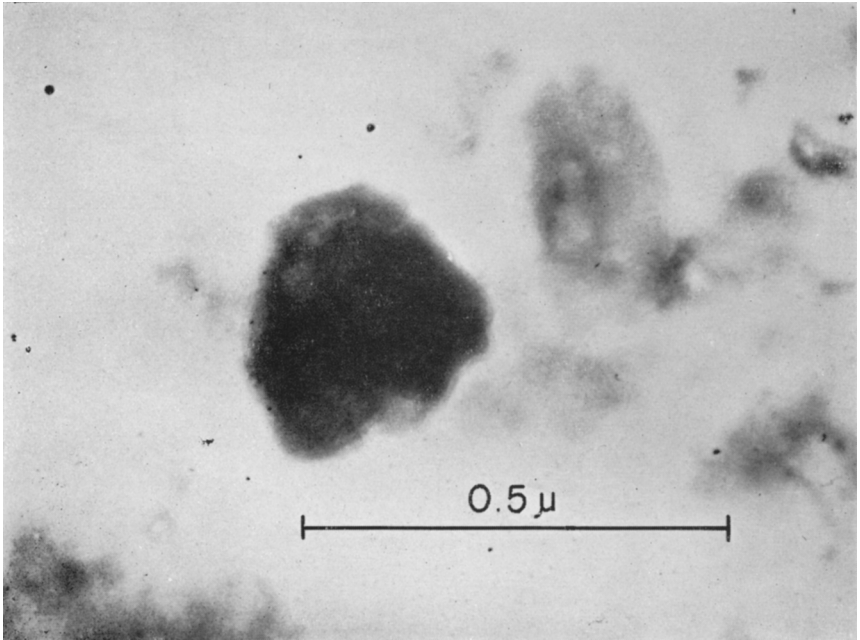


FIGURE 9.—Typical appearance of some types of chlorite in soils and marine sediments.

region of Gulf of Mexico ; average results from material collected at 40 locations as defined in 3(g), preceding), 40 samples, 767 fractions : 17 samples extracted from sediment clay fractions similar to those described in 1(n) and 1(r) ; 23 samples extracted from fractions containing 50–75 percent montmorillonites, 10–25 percent chlorite–montmorillonites, 2–15 percent chlorites, 5–25 percent illites, and 10–20 percent illite–montmorillonites and vermiculites, 0–8 percent kaolinites, 0–4 percent halloysites and 1–6 percent quartz ; analytical data for illite–montmorillonites in Table 3 ; electron microscopic appearance (see Whitehouse and McCarter, 1958), stiff thin strands and fluffy aggregates with threadlike striations.

(d) Chlorite–montmorillonites (marine sediments in Gulf of Mexico ; average results from material collected at 76 locations as defined in 3(h)), 76 samples, 767 fractions : 43 samples extracted from sediment clay fractions similar to those described in 2(i), 3(h), and 6(e) ; 33 samples extracted from fractions containing 35–60 percent montmorillonites, 10–20 percent illite–montmorillonites, 15–25 percent chlorite–montmorillonites, 5–10 percent chlorites, and 5–15 percent quartz ; analytical data for chlorite–montmorillonites in Table 3 ; electron microscopic appearance same as cited in 5(c).

#### 6. Chloritic clay minerals.—

(a) Chlorites (Clinochlore, Hiawassee, Georgia), 3 samples, 15 fractions : analytical data in Table 3, see also Martin, 1954) ; electron microscopic appearance (not shown), rounded thin plates and aggregated stacks of thin plates in the 0.5–3.5 $\mu$  size range.

(b) Chlorites (Atlanta, Texas, soil), 24 samples, 120 fractions : extracted from soil clay fractions containing 60–70 percent kaolinites, 10–30 percent chlorites, 5–20 percent illites, and 5–15 percent quartz ; analytical data for chlorites in Table 3 ; electron microscopic appearance, irregular to rounded thin plates (see Whitehouse and McCarter, 1958), commonly <0.4 $\mu$  in size, and often rendered dense by association with fibrous surface material (Fig. 9).

(c) Chlorites (Prochlorite, Chester, Vermont), 5 samples, 25 fractions : analytical data in Table 3 ; see also Martin (1954) ; electron microscopic appearance (not shown), euhedral flakes and aggregates in the 0.2–0.9 $\mu$  size range.

(d) Chlorites (Thuringite, Dona Ana County, New Mexico), 4 samples, 20 fractions : analytical data in Table 3 ; see also Martin (1954) ; electron microscopic appearance (not shown), euhedral thin plates and aggregates in the 0.2–2.2 $\mu$  size range.

(e) Chlorites (marine sediments of Gulf of Mexico ; average results from material collected at 23 locations defined by 29° 00' to 29° 40' N, 93° 40' to 94° 50' W), 23 samples, 234 fractions : extracted from sediment clay fractions similar to those described in 2(i), 3(h) and 5(d) ; analytical data for chlorites in Table 3 ; electron microscopic appearance, irregular and rounded thin plates and striated fibrous aggregates (see Fig. 9 and Whitehouse and McCarter, 1958, pp. 107, 108 and 110).

7. *Mixtures of clay mineral types.*—

(a) Prepared clay mineral mixtures : (i) 708 *binary* clay mineral mixtures prepared on a solid-weight percent basis by mixing weighed quantities ( $\pm 0.1$  mg) of following clay minerals : kaolinites and illites ; kaolinites and montmorillonites ; illites and montmorillonites ; chlorites and kaolinites ; chlorites and illites ; chlorites and montmorillonites ; kaolinites and illite-montmorillonites ; kaolinites and chlorite-montmorillonites ; kaolinites and dickites ; illites and chlorite-montmorillonites ; illites and illite-montmorillonites ; montmorillonites and illite-montmorillonites ; montmorillonites and chlorite-montmorillonites ; illites and halloysites ; montmorillonites and halloysites ; kaolinites and halloysites. Representative percentage compositions employed for either of the two components in such binary systems were : 1, 2, 3, 4, 5, 8, 10, 15, 20, 25, 40, 50, 60, 75, 80, 85, 90, 92, 95, 96, 97, 98, 99. Compositions intermediate to the representative compositions were employed in some cases to define settling rate alterations more specifically. (ii) 1312 ternary clay mineral mixtures and 1734 clay mineral mixtures of from 4 to 8 clay mineral components prepared on a similar dry solid-weight percent composition basis ; mixtures contained : equal amounts of all components ;  $>50$  percent of one component ;  $>40$  percent of each of two components ; etc. In alternate preparations, clay minerals extracted from marine deposits were remixed in association with the natural saline water originally collected with the crude deposit sample. (iii) 217 binary and ternary clay mineral mixtures, prepared on a similar dry-weight percent composition basis and aged in artificial sea-water for 3-5 years, including : montmorillonites and age-induced alteration products (Whitehouse and McCarter, 1958) ; illites and kaolinites ; illites and montmorillonites ; kaolinites and montmorillonites ; and illites, montmorillonites, and kaolinites. Representative percentage compositions were : 50, 50 ; 40, 60 ; 90, 10 ; 30, 30, 40 ; 80, 10, 10 ; 40, 40, 20.

(b) Natural clay mineral mixtures : (i) 939 natural clay mineral mixtures from soils and marine deposits, as described in 1(i)-(l), 1(n), 1(o), 1(q), 1(r), 2(e)-(i), etc. (512 mixtures from marine deposits ; 427 mixtures from soils). (ii) 637 natural clay mixture fractions containing two or more clay mineral components, from mixtures cited in (i) preceding (322 mixtures from soils and 315 mixtures from marine deposits). All separate fractions from soils and marine deposits, as well as the individual clay mineral types from such sources cited in "clay minerals," 1-6, were extracted by laborious repeated pipette analysis fractionation extending over many months and involving 500 to 1300 fractionation steps. Fractionation was carried out in distilled water, or in dilute sodium phosphate or sodium lignosulfonate solutions in accordance with the findings of Whitehouse and Jeffrey (1955). Ultracentrifugal and layer extraction methods did not prove satisfactory. Resubjection of the clay mineral mixture fractions from marine deposits to the natural saline water collected with the original crude deposit was involved in alternate preparations.

*Saline Waters*

Artificial sea-water, Gulf of Mexico water, Texas Bay water and saline waters of various ionic ratios and ionic strengths were employed in these studies. The artificial sea-water and other inorganic ionic media were prepared by the use of triple-distilled water and A.C.S. grade chemical materials that were further purified by recrystallization in the laboratory.

Three general formulae for artificial sea-water were employed. The compositions of the artificial sea-water are shown in Table 4. Formula (a) was

TABLE 4.—COMPOSITIONS OF ARTIFICIAL SEA-WATER

Chlorinity = 19.392‰		Chlorinity = 19.000‰		
Salt	Weight per litre Formula (a)	Salt	Weight per kilogram	
			Formula (b) <sup>3</sup> (g)	Formula (c) <sup>4</sup> (g)
NaCl	24.5336 g	NaCl	26.7260	23.4760
MgCl <sub>2</sub> ·6H <sub>2</sub> O	11.1120 g	MgCl <sub>2</sub> ·6H <sub>2</sub> O	4.8228	10.6290
Na <sub>2</sub> SO <sub>4</sub>	4.0944 g	MgSO <sub>4</sub> ·7H <sub>2</sub> O	6.6480	0.0000
KCl	0.6945 g	CaCl <sub>2</sub> ·6H <sub>2</sub> O	2.3786	2.2734
NaHCO <sub>3</sub>	0.2011 g	KCl	0.7210	0.6640
KBr	0.1005 g	NaHCO <sub>3</sub>	0.1980	0.1920
H <sub>3</sub> BO <sub>3</sub>	0.0272 g	NaBr	0.0580	0.0000
CaCl <sub>2</sub> ·6H <sub>2</sub> O	0.0348 g	KBr	0.0000	0.0960
SrCl <sub>2</sub> ·6H <sub>2</sub> O	0.0404 g	Na <sub>2</sub> SO <sub>4</sub>	0.0000	3.9170
NaF	0.0030 g	H <sub>3</sub> BO <sub>3</sub>	0.0580	0.0260
Ba(NO <sub>3</sub> ) <sub>2</sub> <sup>1</sup>	0.0994 mg	SrCl <sub>2</sub> ·6H <sub>2</sub> O	0.0000	0.0403
Mn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>1</sup>	0.0546 mg	Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	0.0056	0.0000
Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O <sup>1</sup>	0.0396 mg	Na <sub>2</sub> Si <sub>4</sub> O <sub>9</sub>	0.0015	0.0000
Zn(NO <sub>3</sub> ) <sub>2</sub> <sup>1</sup>	0.0151 mg	AlCl <sub>3</sub> ·6H <sub>2</sub> O	0.0235	0.0000
Pb(NO <sub>3</sub> ) <sub>2</sub> <sup>1</sup>	0.0066 mg	NH <sub>3</sub>	0.0020	0.0000
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O <sup>2</sup>	0.00028–0.0028 mg	LiNO <sub>3</sub>	0.0013	0.0000
pH = 6.5 – 9.8 (adjusted with 0.1 M Na <sub>2</sub> CO <sub>3</sub> and HCl and filtered if necessary)		pH = 7.5 – 8.5 (adjusted with 0.1 M Na <sub>2</sub> CO <sub>3</sub> and HCl)		

<sup>1</sup> Included only in alternate studies of each clay sample.

<sup>2</sup> Included only in special studies.

<sup>3</sup> McClendon, Gault and Mulholland (1917).

<sup>4</sup> Lyman and Fleming (1940).

prepared as described by Whitehouse and McCarter (1958, pp. 89–90). Formulae (b) and (c) were prepared in accordance with the procedures of McClendon, Gault and Mulholland (1907) and Lyman and Fleming (1940) except that crystalline reagents were employed instead of granular reagents in some cases. The total salt concentration of the artificial sea-water was varied over the chlorinity range 0.5–20.0‰ but the same ionic ratios were



maintained in the general studies. In addition, variations of the magnesium, calcium, strontium and heavy metal contents were utilized in some specific experiments. In many cases 1 ppm mercuric chloride or a drop of 15 percent formalin solution was added to the water to minimize any microbiological interferences that might develop as a result of the exposure of the media to air over long periods of time. Dilutions of the artificial sea-water compositions shown in Table 4 are indicated herein in terms of "chlorinity" (g/kg of solution). Chlorinity was checked in every case by the Mohr (1856) (Berry and Driver, 1939) method.

The actual sea-water samples employed were collected east of the Mississippi Delta in the vicinity of Grand Bay and from Gulf of Mexico waters in the region defined by 28° 10' to 29° 10' N, 93° 30' to 94° 50' W, south of the Galveston Bay and Sabine Lake areas of the Gulf Coast. Chlorinities of all samples were determined experimentally. The samples were filtered through a micropore filter to remove suspended matter but no dilution of the actual water was made.

The samples of Texas Bay saline waters cited were collected from Copano Bay, Aransas Bay, Mesquite Bay and San Antonio Bay near Rockport, Texas, and St. Joseph and Matagordo Islands. These samples were also

TABLE 5.—IONIC RATIOS FOR SALINE WATER SAMPLES

Ionic Ratio (major ions)	Cl—g Ratios <sup>1</sup>			
	Typical Ocean Waters <sup>2</sup>	Gulf of Mexico Waters	Miss. Delta Waters	Texas Bay Waters
Na/Cl	0.556	0.54–0.56	0.53–0.56	0.63–0.65 C <sup>3</sup> 0.42–0.67 A 0.61–0.65 M 0.51–0.81 S
Mg/Cl	0.0669	0.065–0.068	0.064–0.068	0.040–0.045 C <sup>3</sup> 0.041–0.067 A 0.038–0.045 M 0.032–0.065 S
Ca/Cl	0.021	0.020–0.021	0.020–0.021	0.010–0.012 C <sup>3</sup> 0.005–0.037 A 0.005–0.015 M 0.002–0.026 S
K/Cl	0.020	0.018–0.021	0.016–0.021	0.012–0.014 C <sup>3</sup> 0.006–0.024 A 0.005–0.024 M 0.005–0.024 S

<sup>1</sup> Grams per unit chlorinity.

<sup>2</sup> Sverdrup, Johnson and Fleming (1942).

<sup>3</sup> C, Copano Bay ; A, Aransas Bay ; M, Mesquite Bay ; S, San Antonio Bay.

filtered but not diluted. The ionic ratios of the major ionic components of these bay waters were found to vary, and some differed markedly from the ionic ratios common to ocean water (Sverdrup, Johnson and Fleming, 1942) and from such ratios for the Gulf of Mexico and Mississippi Delta region waters. The extent of these variations is indicated in Table 5. These ionic ratios were determined by the standard "wet" chemical techniques cited under "experimental methods," which follows later in this discussion.

Saline waters of variable ionic ratio at constant ionic strengths were also prepared from distilled water and A.C.S. grade reagents and employed in these investigations. A general comparison of chlorinity, molality, and ionic strength of all the saline waters employed is given in Table 6.

TABLE 6.—CHLORINITY, MOLALITY AND IONIC STRENGTH OF SALINE WATERS  
(general comparison only)

"Salinity" (ocean water only ; ‰)	Chlorinity (Cl ; ‰)	Molality ( $M_L$ ; moles/kg)	Ionic Strength (I.S. ; moles-charge <sup>2</sup> /kg)
36.1	20.0	0.543	0.722
34.3	19.0	0.516	0.686
32.5	18.0	0.489	0.650
30.7	17.0	0.462	0.614
28.9	16.0	0.435	0.578
27.1	15.0	0.408	0.542
25.3	14.0	0.380	0.505
23.5	13.0	0.353	0.469
21.7	12.0	0.326	0.433
19.9	11.0	0.299	0.397
18.1	10.0	0.272	0.361
16.3	9.0	0.245	0.325
14.5	8.0	0.217	0.289
12.7	7.0	0.190	0.253
10.9	6.0	0.163	0.217
9.1	5.0	0.136	0.181
7.3	4.0	0.109	0.144
5.4	3.0	0.082	0.108
3.6	2.0	0.054	0.072
1.8	1.0	0.027	0.036
0.9	0.5	0.014	0.018

### *Organic Materials*

The following organic materials were used in the study of the influence of the effects of organic compounds, dissolved or dispersed in saline waters, upon the settling tendencies of the clay minerals.

1. *Carbohydrates and related compounds*.—Reference source : E-DPI, Eastman, Distillation Products Industries ; NBC, Nutritional Biochemicals Corporation ; PL, prepared in laboratory.

(a) Monosaccharides : (i) Aldopentoses : lyxose, xylose, arabinose, ribose

(NBC). (ii) Aldohexoses : galactose, glucose, mannose (E-DPI) ;  $\beta$ -glucose, glucose penta-acetate,  $\beta$ -D-glucose penta-acetate (NBC). (iii) Keto-hexoses : fructose, sorbose (NBC). (iv) Deoxyhexoses : L-fucose, L-rhamnose hydrate (NBC). (v) Deoxypentoses : desoxyribose (NBC). (vi) Polyhydric alcohols : erythritol, arabitol, mannitol, inositol, xylitol, sorbitol (NBC).

(b) Disaccharides : (i)  $\beta$ -Lactose, lactose hydrate, sucrose, cellibiose hydrate, trehalose hydrate, melibiose hydrate (NBC).

(c) Trisaccharides : Raffinose hydrate (NBC).

(d) Polysaccharides : Soluble starch, dextrin, pectin, agar (NBC) ; fucoidin (PL) ; cellulose (NBC), cellulose acetate (E-DPI) ; heparin, inulin, glycogen, hyaluronic acid (NBC).

(e) Other compounds : Acetyl glucosamine, galactosamine hydrochloride, glucuronate-sodium, quercetin, ascorbic acid, dehydroascorbic acid (NBC) ; glucose-6-phosphate-barium, fructose-6-phosphate-barium, galactose-6-phosphate-barium (NBC).

2. *Proteins and related compounds.*—Reference source : E-DPI, Eastman, Distillation Products Industries ; NBC, Nutritional Biochemicals Corporation ; PL, prepared in laboratory.

(a) Amino acids : Arginine, histidine, lysine hydrochloride, valine, D-alanine, isoleucine, tryptophan, leucine, methionine, phenylalanine, threonine, cystine, D-L-tyrosine (NBC).

(b) Soluble, simple proteins : Ovalbumen, lactalbumen (NBC), laboratory peptone (NBC).

(c) Phosphoproteins : Casein (NBC) ; vitellin (PL).

(d) Protamines : Protamine nucleinate ; protamine sulfate (NBC).

(e) Globulins : Ovalglobulin (PL) ; edestin (NBC) ; gluten (NBC).

(f) Histones : Histone (from calf thymus nuclei) (NBC).

(g) Insoluble proteins (scleroproteins) : Keratin, fibroin, zein (NBC).

(h) Other compounds : Gelatin, ribonucleic acid, sodium desoxyribonucleate (NBC) ; lecithin (phospholipid) (NBC) ; "humic acid" from quinone (PL) ; "humic acid" soil fraction (PL).

Seventy compounds are listed herein but only 57 different basic structures are involved. Saline-water solutions or dispersions of all compounds listed were prepared and used in the following concentrations (in grams of organic compound per liter of saline water) : 0.0005 ; 0.0010 ; 0.0020 ; 0.0040 ; 0.0080 ; 0.0160 ; 0.0320 ; 0.0640 ; 0.01280 ; 0.020 ; 0.040 ; 0.080 ; 0.100 ; 0.200 ; 0.300 ; 0.400 ; 0.500 ; 0.600 ; 0.700 ; 0.800 ; 0.900 ; 1.000. Artificial sea-water and saline waters of varied ionic ratio composition and varied ionic strength were employed as the solution or dispersion media. All dispersion systems were agitated thoroughly for 20 min in a Hamilton Beach dispersion apparatus at 14,000 rev/min.

### *Experimental Methods*

*Mineralogical examination and identification of clay materials.*—Techniques of mineralogical examination included chemical analysis, x-ray diffraction,

electron diffraction, thermal analysis, cation exchange capacity, density determinations and electron microscopy. A description or citation for most of the methods employed is given in Whitehouse and McCarter (1958, p. 92). However, cation exchange capacities were determined by the methods of Lewis (1950) as well as by the method of Coffman (1946). The critical point electron microscopy technique is described in Whitehouse and McCarter (1958, p. 93).

*Saline water analysis.*—The major ionic component concentrations of Gulf of Mexico water, Mississippi Delta region water and Texas Bay waters were determined by "wet" chemical methods described by Hillebrand, Lundell, Bright and Hoffman (1953). The chlorinity of all solutions was determined by the Mohr method (Berry and Driver, 1939).

*Organic compound concentration determinations.*—The concentration of carbohydrates in saline water, before and after exposure to settling clays, was determined on the macro scale by the Dische (1949) colorimetric method employing cysteine hydrochloride, and on the semimicro scale by anthrone test, the tetrazolium test and the Feulgen test, where applicable (Cheronis, 1954). Beckman Model DU spectrophotometric equipment was employed, and calibration curves for carbohydrate concentrations in the absence of clay material were prepared for every determination. An alternate approach, utilized when necessary, was a modification of the Robertson and Ward (1951) method that has been employed to measure the cation exchange capacity of clay minerals. This procedure utilizes the change in color of a methylene blue solution produced by the adsorption of this reagent by the clay. When the clay material has been exposed previously to other organic matter and adsorption has occurred, less methylene blue will be adsorbed subsequently. The extent of adsorption can then be expressed in terms of a "methylene blue equivalent." This method has relative merit but is not necessarily a measure of the total weight of the original organic material adsorbed.

The concentrations of soluble amino acids and proteins, before and after exposure to settling clays, were estimated by the triketohydrindene (ninhydrin), the phosphotungstate and the phosphomolybdate tests (Cheronis, 1954). Insoluble proteins and other similar compounds were estimated by nephelometric methods based on spectrophotometric calibration curve for the concentration range involved (Rona and Kleinman, 1923). Similar procedures were utilized in the estimation of concentrations of "humic acid,"  $H_1$ , derived from quinone via oxidation by an alkaline solution of hydrogen peroxide. The "humic acid" soil fraction (Gillam, 1949), extracted from Brazos County, Texas, soil, was studied by both nephelometric and carbohydrate-spectrophotometric methods.

*Determination of the freezing point of saline water.*—In order to evaluate the influence of organic materials upon the effective ionic strength of saline water, some determinations of the freezing point elevations were made via the Beckman method (Daniels, Matthews and Williams, 1941, pp. 76-77). Preliminary work in this regard, upon other inorganic-organic ionic media is described by Cohn and Edsall (1943, pp. 257-275).

*Methods for determination of settling rates of clay minerals in quiet saline water.*—The experimental methods employed to measure the settling rates of clay minerals were: (a) the Andreason (1935) pipette analysis method, modified for sampling 10 cm or 5 cm below the liquid surface in accordance with the manual pipette method described by Krumbein and Pettijohn (1938); (b) the Kelley–Wiegner densitometric method (Kelley, 1924); (c) the Oden balance method (Oden, 1915); (d) a nephelometric–spectrometric procedure.

The first three methods were utilized for settling rate studies only, while the spectrophotometric method was utilized primarily in studies of the coacervation states of the clay minerals in saline water. The pipette analysis method and the densitometric method are in general use for “particle size” distribution determinations, and utilize gravitational settling of solid material suspended in a liquid as the fundamental principle for fractionation of a solid sample. “Size” is computed on the basis of Stokes’ (1851) law or Wadell’s (1936) law. Rubey’s (1933) formula, Oseen’s (1910) law and Goldstein’s (1929) law are more generally applicable but the simpler equations of Stokes and Wadell may be employed when settling velocities do not exceed 30 cm/min (Arnold, 1911). Velocities measured by these methods are usually interpreted in terms of “equivalent diameters,” i.e. the “size” the falling particles would have if they were spherical or equivalent in shape. “Size” ranges determined in this way are usually selected on the basis of the Wentworth (1922)–Udden (1914) grade scale, a logarithmic transformation of the Wentworth scale ( $\phi$ -scale, Krumbein, 1934), the Atterberg (1905) grade scale, or a logarithmic transformation of the Atterberg scale (zeta scale, Krumbein, 1937). A  $\phi$ -value of 9 corresponds to an “equivalent diameter” of  $1.95\ \mu$ , the upper limit of “size” of the clay fractions studied. The pipette extraction of clay material at a 10 cm depth from a 5–20 g/l. suspension of clay in 0.01 N ammonia solution after a time interval greater than 12 hr 37 min at 20°C yields a “size” fraction less than  $1.95\ \mu$  on the basis of Wadell’s law. Clay samples used were subjected to this procedure or to similar methods, using either Calgon or “sodium lignosulfonate” as the dispersing agent (Whitehouse and Jeffrey, 1955).

Since these methods determine the weight of solid material that accumulates at a given depth in the suspension within selected time intervals, weight–settling rate histograms and cumulative curves may be obtained by sampling after selected time intervals. At a time  $t$  and at a given depth  $h$  solid particles with settling velocities greater than  $h/t$  will have settled below the depth  $h$ . In addition, particles with settling velocities smaller than  $h/t$ , but falling through a shorter distance, will have settled below the depth  $h$ . The total weight of particles reaching the depth  $h$  at the end of time  $t$  is equal to the weight of that fraction, with a settling velocity of or greater than  $h/t$  plus a portion of the material with a settling velocity less than  $h/t$ . The actual increase in weight,  $dw/dt$ , at time  $t$  is due to this latter group of particles since they have been falling at constant rate since the beginning of the observations. The actual weight of these smaller particles is  $tdw/dt$ .

The pipette method of analysis depends upon the pipette removal of a portion of the suspension at a selected depth  $h$  at selected times after the liquid-solid mixture is agitated to obtain a uniform suspension. According to Weyssenhoff (1920), only about 0.003 sec is required for constant settling velocity to be obtained in a suspension of this type provided "equivalent diameters" do not exceed  $30\mu$  and the solid concentration does not exceed 25 g/l. in a 1 l. vessel of diameter greater than 5 cm. With the suspension at rest, a calibrated pipette extraction of 20 ml is made after a time  $t$  at a depth of 5 or 10 cm. The pipette taps a spherical zone rather than a horizontal stratum but Köhn (1928), Keen (1931, p. 82), and Gessner (1931, p. 79) have shown that the net error is practically negligible. The suspension sample is evaporated to dryness at  $50^{\circ}\text{C}$  and weighed. Since artificial sea-water introduces salt residue upon evaporation of the extract, the solid is washed, filtered or dialysed, and dried until constant weight is obtained. The weight of the residue, multiplied by a proportionality factor representing the ratio of pipette volume to total suspension volume, gives the total amount of clay material having settling velocities less than  $h/t$ . After the first pipette sample is withdrawn, the suspension is again agitated and a longer period of time is allowed to elapse before a second sampling. After this second time interval particles with smaller settling velocities will settle below  $h$ . The second pipette sample contains a weight of solid clay material that differs from that of the first sample by an amount equal to the weight of material with settling velocities intermediate to the velocities that correspond to the selected time intervals. This process is repeated for time intervals that measure settling velocities to a lower limit of  $2.0 \times 10^{-5}$  cm/sec. The time intervals selected limit the specific velocity measurements obtained but are altered as necessary to detect differentiation within a settling range. The sum of the weight of solid obtained by pipette extraction times the proportionality factor is compared with the known total weight of solid in the suspension as a guide to reliable determination. The results herein presented by this method are based upon the settling of suspensions of 3.6 g or less of clay mineral per liter in columns of 32.2 cm height and 6.3 cm diameter, in troughs  $2 \times 2 \times 2$  ft, and in tanks  $4 \times 4 \times 4$  ft.

The Kelley-Wiegner tube method measures the change in density of the suspension at the given depth  $h$  by means of a micromanometer filled with the clear settling medium. The rate of settling is determined by observation of the rate at which the level in the micromanometer changes. The weight at a depth of 25.2 cm is calculated on the basis of the equation

$$w = \frac{dVSL \sin \alpha}{h(S - d)}$$

where  $w$  is the weight of material settling past the manometer contact after time  $t$ ,  $d$  is the density of the liquid medium,  $V$  is the volume of the suspension above the manometer contact,  $S$  is the density of the clay,  $L$  is the length of liquid column in the almost horizontal section of the manometer,  $\alpha$  is the small angle made by this section with the true horizontal,  $h$  is the height

of the suspension above the manometer contact. The successive time interval approach previously described was employed to determine settling rate ranges. The equipment employed in these clay studies had values of  $V = 100$  ml,  $L = 0-50$  cm calibrated in millimeter divisions,  $\sin \alpha = 0.030-0.050$ ;  $d$  was evaluated from Knudsen's (1901) *Hydrographic Tables* for sea-water, or by pycnometer method;  $S$  was determined by pycnometer method. Maintenance of constant temperature within  $\pm 0.2^\circ\text{C}$  or close observation of temperature changes with corrections applied to data obtained was a part of all experimental runs. As a possible guide to concentration gradient effects down the column, experimental runs both with and without agitation of the suspension between successive time intervals were made.

The clay material was prepared for settling rate analysis by pretreatment with 0.01 N ammonia solution, 0.12 g/l. "sodium lignosulphonate", or 1.2 g/l. "Calgon", with subsequent fractionation to obtain the  $< 2\mu$  fractions by gravitational settling as previously described or by centrifugal extraction (Baver, 1948) from a suspension at 2500-3000 rpm using a rotor of 30 cm diameter and 100 ml centrifuge tubes. It was then dried, weighed, and wetted with sodium carbonate solution (pH = 8), triple-distilled water, or filtered Brazos River, Texas, water before exposure to sea-water. Clay suspensions in sea-water covering the concentration range 0.01-3.6 g/l. were investigated extensively. Selected clay mixtures also were studied. Clay mineral concentrations in the range 3.6-15 g/l. were utilized in some special studies.

The Oden balance method was utilized primarily as a calibrating device in developing the pipette method technique to a high degree of precision.

The influence of temperature upon settling rate determinations by the pipette analysis method was measured by use of a refrigerated air bath with a temperature variation of  $\pm 0.2^\circ\text{C}$  and in a water bath through which pre-cooled water was circulated with a temperature variation of  $\pm 0.5^\circ\text{C}$ .

A nephelometric-spectrometric method was used for comparison studies of the rates of clearing of the clay mineral suspensions in saline waters and for relative evaluation of the influence of clay mineral concentration gradients upon the settling velocities as depth within the suspension increased. The suspensions of clay were placed in silica cells (12 mm square and 48 mm high, with a 10 mm light path) and subjected to spectrophotometric measurement of light transmission at  $\lambda = 400 \text{ m}\mu$  over specific time intervals in a Beckman Model DU spectrophotometer under temperature conditions of  $26 \pm 0.5^\circ\text{C}$ . Studies of the influence of such concentration gradients in saline water-clay mineral settling systems with total water depths of 4 ft and 6 ft were also made via a pipette analysis method in which the pipette, attached to appropriate lengths of pressure tubings, was lowered to varied depth and filled via controlled suction procedures.

*Methods for study of the coacervation of settling clay minerals.*—The coacervation of clay minerals in saline waters of varied chlorinity and ionic ratio composition was recognized and relatively measured by the following techniques: (a) a nephelometric-spectrophotometric method, based upon light transmission through thoroughly flocculated suspensions of clay

minerals in saline water, over the range,  $\lambda = 400\text{--}900$  m $\mu$ ; (b) an ultramicropipette sampling method, based upon the assumption that different degrees of coacervation should introduce random mass per unit volume at some ultramicrovolume level; (c) the electron microscopy critical point technique for preserving states of aggregation (Whitehouse and McCarter, 1958, pp. 93, 114).

In the nephelometric-spectrophotometric work, saline water suspensions of clay minerals were placed in molded methacrylate plastic cells of 1 cm<sup>2</sup> cross-section and light transmission data over the range  $\lambda = 400\text{--}900$  m $\mu$  were obtained by the use of a Beckman Model B spectrophotometer.

Measurements were made as rapidly as possible to minimize effects of settling of the clay materials. Cells were rotated to give measurements in four different cell positions for each sample. Results reported represent the average of thirty such measurements per sample. Light transmission is expressed on the basis of reference adjustment of the instrument to 100 percent transmission for distilled water or for saline water at each  $\lambda$  cited. The temperature variation of the suspensions during all experimental runs was  $\pm 1.50$ .

The ultramicropipette method utilized volumetric extractions of 1 ml, 0.1 ml, 0.01 ml and 0.001 ml from thoroughly agitated and flocculated clay mineral-saline water suspensions at the chlorinities cited. Extension to the ultramicrovolume level of  $1 \times 10^{-6}$  ml was accomplished by aliquot dilution of the first extracts followed by subsequent pipette removal of required volumes from the aliquot media.

The electron microscopy critical point technique is based upon the fact that a liquid may be changed completely and imperceptibly into a gas without the formation of liquid-gas phase boundaries if the liquid under pressure is heated to its critical temperature (Whitehouse and McCarter, 1958). This method is superior to freeze drying techniques in the preservation of clay mineral states of aggregation since any movement of a liquid or ice phase through the material is minimized.

*Methods for study of turbulent transport of clay minerals in saline water.*—The differential transport of clay minerals by turbulent saline water was subjected to preliminary investigation by the following methods: Thoroughly agitated and flocculated clay mineral suspensions in a 4 ft  $\times$  4 ft  $\times$  4 ft tank were pumped from the tank through 1 in. diameter plastic or iron pipes of 100 ft total length. The pipes were primed with the uniform suspension and the clay mineral concentration of the affluent and effluent waters checked at the beginning of each run. The pipe was kept as level as possible and no curvature was introduced into the pipe at any point beyond the affluent sampling valve. The pump employed was a Vanton pump, with Teflon lining, capable of 40 g/min at 0 lb/in<sup>2</sup>, coupled to a 1½ h.p., rheostat controlled, motor-driven mechanism. Rate of flow of the suspension was measured with a Penn Linameter type, self cleaning flowmeter and by actual volumetric collection of the effluent for specific time intervals. The temperature of the flowing suspensions was  $25 \pm 1.0^\circ\text{C}$ . The velocities of flow required



to maintain constant composition of individual clay mineral types were measured. By repeated recirculation of effluent saline water-clay mixture suspension fractions of 1200, 800, 400 and 200 l. the tendency for relative clay mineral enrichment of the effluent suspension was studied. The clay mixtures were prepared from known quantities of selected clay mineral types and the relative clay mineral contents of the effluent estimated by a combination of pipette analysis, chemical analysis, electron microscopy and electron diffraction procedures, described or cited earlier in this report.

## EXPERIMENTAL RESULTS

### *Differential Settling of Clay Minerals in Artificial Sea-water*

Representative settling velocities for three clay mineral types in quiet artificial sea water (formulae (a), (b) and (c) (Table 4)) at 26°C are shown in histogram form in Fig. 10 and as cumulative curves in Fig. 11. Heavy metal ions were not present. These results are based upon 120 experimental runs per sample by the pipette analysis method and 20 experimental runs by the Kelley-Wiegner manometer method. These results apply within  $\pm 1.0$  percent to kaolinites 1(a)-(f), montmorillonites 2(a)-(d) and illites 3(a)-(h) (see "General Discussion, clay materials"). Within experimental limits the systems tend to approach monodispersivity (a narrow velocity range) at any specific chlorinity. This observation has unique transport significance and also facilitated the selection of representative settling rates for comparison herein.

The reproducibility of the experimental results is given in Table 7. For clay materials with lyophilic character, particularly montmorillonites, the pipette analysis method gave more consistent results than the manometer

TABLE 7.—GENERAL REPRODUCIBILITY OF EXPERIMENTAL RESULTS FOR SETTLING VELOCITIES IN QUIET SALINE WATER

Method	Velocity Range (cm/min)	Velocity (%)		
		Kaolinites	Montmorillonites	Illites
Pipette	0.002-0.08	$\pm 0.5$	$\pm 1.0$	$\pm 0.5$
Oden balance	0.002-0.08	$\pm 0.5$	$\pm 3.2$	$\pm 0.6$
Manometer	0.002-0.08	$\pm 0.8$	$\pm 5.5$	$\pm 0.5$
Pipette	0.10-0.50	$\pm 1.0$	—	$\pm 1.0$
Oden balance	0.10-0.50	$\pm 0.9$	—	$\pm 1.2$
Manometer	0.10-0.50	$\pm 1.8$	—	$\pm 1.5$
Pipette	0.60-1.10	$\pm 1.0$	—	$\pm 1.0$
Oden balance	0.60-1.10	$\pm 1.0$	—	$\pm 1.0$
Manometer	0.60-1.10	$\pm 2.0$	—	$\pm 2.0$

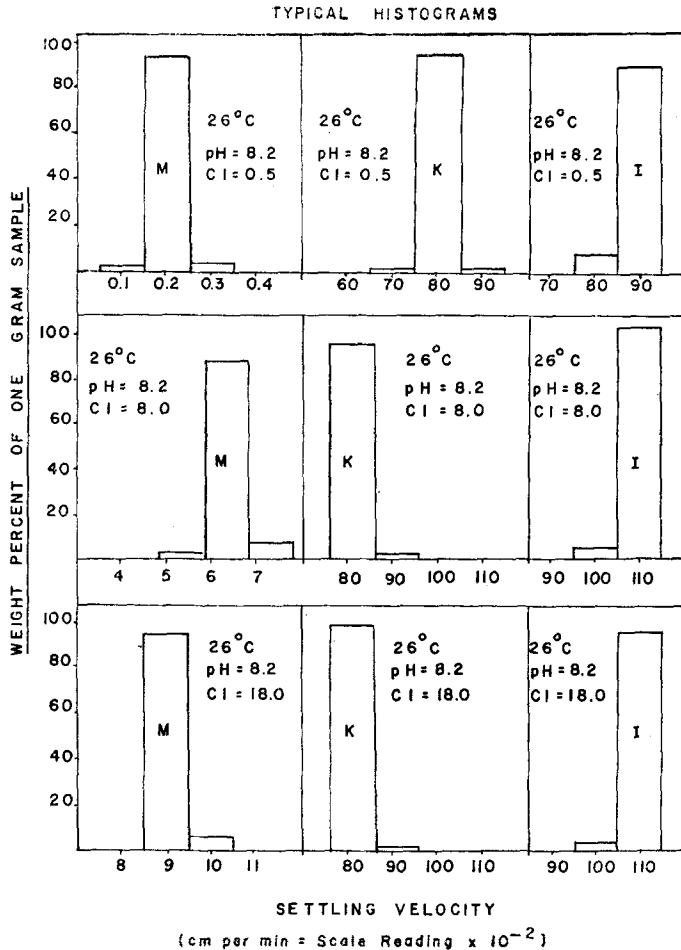


FIGURE 10.—Typical histograms for montmorillonitic (M), kaolinitic (K), and illitic (I), clay minerals in quiet artificial sea water and ocean water settling media (Cl = chlorinity of water).

method. The Oden balance method served as a guide and preliminary check on the precision of the methods but was found to be inferior to the pipette method in studies of montmorillonites. A summary of representative settling velocities found for the three clay mineral types in all three artificial sea-water compositions is listed in Table 8. No significance was assigned to the minor differences in settling rates in the three media, although formula (b) exhibited a slight tendency to induce faster settling at lower chlorinity values in accordance with the discussion of the effect of higher ionic strengths, at specific chlorinities, described later herein.

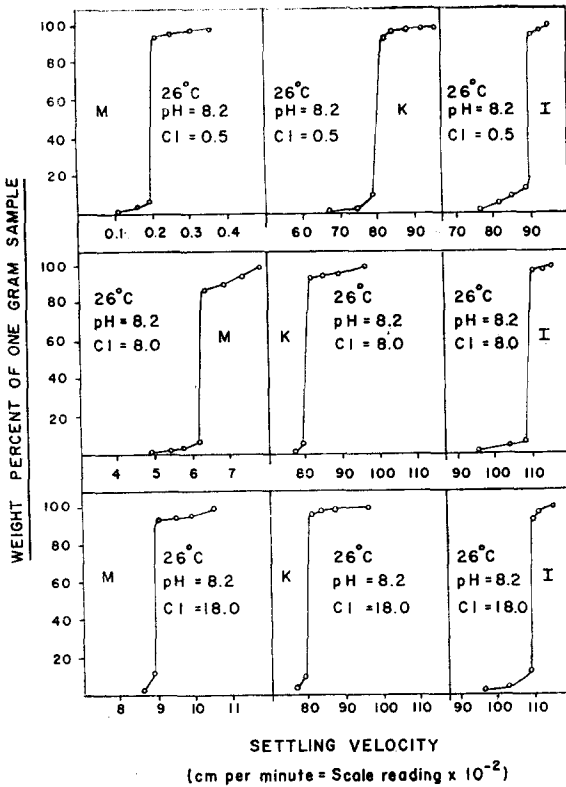


FIGURE 11.—Typical cumulative curves for montmorillonitic (M), kaolinitic (K) and illitic (I), clay minerals in quiet artificial sea water and ocean water settling media (Cl = chlorinity of water).

The general effect of pH variations of artificial sea-water upon settling rates is shown in Table 9. Negligible variation in settling velocities for all three clay mineral types over the pH range 6.5–8.5 was noted. Slight increases in settling velocities characterize the pH range 8.5–9.8. It should be noted that the saline media involved in these studies contain potassium ion and constant ionic ratio composition at all chlorinities cited.

The pH influence on calcium montmorillonite settlings differs to some extent from these general results (Table 10). High pH increases settling rates significantly at chlorinities below 6‰. This can be attributed to less loss of calcium by ion exchange at high pH and less coacervation.

All settling rate values herein reported as representative for specific clay mineral types or specific samples apply to “thoroughly agitated and flocculated” clay minerals. No time dependence for flocculation is involved, except in the preparation of the suspensions prior to the start of the settling

TABLE 8.—REPRESENTATIVE SETTLING VELOCITIES OF THREE CLAY MINERAL TYPES IN ARTIFICIAL SEA-WATER  
(26°C; cm/min = value listed  $\times 10^{-2}$ ; pH = 8.2)

Experimental Method	Clay Mineral	Artificial Sea-water Formula <sup>1</sup>	Chlorinity (%)					
			0.5	1.0	2.0	6.0	12.0	18.0
Pipette	Kaolinites	A	80.1	80.5	81.0	81.2	81.2	81.2
		B	80.2	80.5	81.2	81.2	81.2	81.2
		C	80.1	80.4	81.1	81.2	81.2	81.2
Manometer <sup>2</sup>	Kaolinites	A	80.0	80.5	81.2	81.1	81.2	81.2
		B	80.0	80.5	81.2	81.0	81.2	81.2
		C	80.2	80.5	81.2	81.1	81.2	81.2
Pipette	Montmorillonites	A	0.21	0.35	0.77	4.02	7.52	8.75
		B	0.24	0.37	0.79	4.11	7.58	8.79
		C	0.22	0.35	0.78	4.06	7.55	8.77
Pipette	Illites	A	89.1	90.1	105.0	110.0	110.0	110.0
		B	89.2	90.1	106.0	110.0	110.0	110.0
		C	89.1	90.1	105.0	110.0	110.0	110.0
Manometer	Illites	A	88.5	89.5	100.0	105.0	110.0	110.0
		B	88.9	89.8	100.0	106.0	110.0	110.0
		C	88.4	89.2	100.0	105.0	110.0	110.0

<sup>1</sup> Heavy metal ions not present.

<sup>2</sup> Manometer method not applicable for montmorillonites (see Table 7).

rate experimental runs. The effect of time of agitation and flocculation in the formation of "thoroughly flocculated" suspensions was studied in considerable detail before a method for determination of settling rates was adopted (Table 11).

As much as 20 min of agitation of the montmorillonite suspension (0.01–3.6 g clay mineral per l.) in a Hamilton Beach dispersion apparatus at 14,000 rpm was found essential to obtain consistent results. From 5 to 10 min agitation periods were adequate for kaolinites and illites.

During experimental runs utilizing agitation times less than 20 min for montmorillonite, random fall of gelatinous lumps was noted. Coacervation is influential in montmorillonite flocculation (Hauser and leBeau, 1938) and uniform dispersal is essential to minimize local occlusion of solvents by groups of particles, i.e. "lumps." Such extreme coacervation effects render settling values higher than should occur in moving turbulent water as a consequence of insufficient experimental agitation of the sample. Another probable indication of the influence of coacervation upon the settling rate of montmorillonite is the increase in settling rate as chlorinity increases. A detailed

TABLE 9.—GENERAL EFFECT OF pH VARIATION UPON SETTLING VELOCITIES  
(26°C, artificial sea-waters A, B and C<sup>1</sup>)

pH	Clay Mineral	Settling Velocities (cm/min = value listed $\times 10^{-2}$ )					
		Chlorinity (‰)					
		0.5	1.0	2.0	6.0	12.0	18.0
6.5	K <sup>2</sup>	80.2	80.4	81.2	81.3	81.3	81.3
6.8	K	80.2	80.5	81.1	81.2	81.2	81.2
7.1	K	80.1	80.5	81.1	81.2	81.2	81.2
7.5	K	80.1	80.5	81.1	81.2	81.2	81.2
7.8	K	80.1	80.5	81.1	81.2	81.2	81.2
8.5	K	80.1	80.4	81.1	81.2	81.2	81.2
9.2	K	80.0	80.3	80.8	81.0	81.0	81.0
9.8	K	79.9	80.1	80.8	80.9	80.9	80.9
6.5	M <sup>2</sup>	0.21	0.35	0.76	4.00	7.51	8.75
6.8	M	0.21	0.35	0.77	4.01	7.50	8.75
7.1	M	0.21	0.35	0.77	4.01	7.51	8.75
7.5	M	0.21	0.35	0.77	4.01	7.51	8.75
7.8	M	0.21	0.35	0.77	4.02	7.51	8.75
8.5	M	0.21	0.35	0.76	4.02	7.52	8.75
9.2	M	0.23	0.37	0.78	4.08	7.54	8.79
9.8	M	0.24	0.38	0.78	4.12	7.61	8.95
6.5	I <sup>2</sup>	89.0	90.0	105.0	110.0	110.0	110.0
6.8	I	89.1	90.0	105.0	110.0	110.0	110.0
7.1	I	89.1	90.0	105.0	110.0	110.0	110.0
7.5	I	89.1	90.0	105.0	110.0	110.0	110.0
7.8	I	89.0	90.1	105.0	110.0	110.0	110.0
8.5	I	89.1	89.9	105.0	110.0	110.0	110.0
9.2	I	89.2	90.2	106.0	113.0	114.0	114.0
9.8	I	89.3	90.4	108.0	116.0	116.0	116.0

<sup>1</sup> See Tables 4 and 5.<sup>2</sup> K = kaolinites, 1(a)-(h); M = montmorillonites, 2(a), (c)-(g); I = illites, 3(a)-(h).

discussion of this phenomenon is given later in this report, but it should be noted that settling velocities of montmorillonite increase gradually as chlorinity increases over the Cl range 0-18‰, while kaolinitic and illitic settling velocities are relatively constant above a chlorinity of 2‰. The random fall of "liquid-solid" lumps in quiet, montmorillonitic settling systems was not eliminated by this prior agitation procedure, when the montmorillonite concentration exceeded 3.65 g/l. The procedure was applicable to illitic and kaolinitic systems over the concentration range 0.01-15.8 g/l.

It was also observed that restirring of the suspension between successive

TABLE 10.—SPECIAL EFFECT OF pH VARIATION ON SETTLING VELOCITIES  
OF CALCIUM MONTMORILLONITES<sup>1</sup>  
(26°C, artificial sea-waters, A, B and C<sup>2</sup>)

pH	Settling Velocities (cm/min = value listed $\times 10^{-2}$ )						Calcium Content of Flocculate (as CaO, %)
	Chlorinity (‰)						
	0.5	1.0	2.0	6.0	12.0	18.0	
6.5	0.17	0.31	0.65	3.92	7.46	8.71	0.24
7.1	0.21	0.35	0.77	4.01	7.51	8.75	0.24
7.5	0.21	0.35	0.77	4.01	7.51	8.75	0.24
8.2	0.21	0.35	0.76	4.02	7.51	8.75	0.29
8.8	0.26	0.39	0.81	4.24	7.54	8.82	0.42
9.4	0.34	0.51	1.02	4.88	7.57	8.91	1.75
9.8	0.38	0.61	1.21	5.20	7.62	8.97	2.04

<sup>1</sup> See "General Discussion, clay materials," 1(b).

<sup>2</sup> See Table 4.

TABLE 11.—EFFECT OF INITIAL AGITATION TIME UPON SETTLING VELOCITIES  
OF CLAY MINERALS  
(0.01–3.6 g clay mineral per litre saline water)  
Settling velocities (26°C, pH = 7.5–8.5)  
(cm/min = value listed  $\times 10^{-2}$ )

Clay	Chlorinity	Clay Conc. (g/l.)	Agitation Time <sup>1</sup> (min)				
			5	10	15	20	25
K	2.0	0.80–3.6	81.0	81.0	81.0	81.0	81.0
		0.01–0.8	81.0	81.0	81.0	81.0	81.0
M	2.0	0.80–3.6	0.7–7.5	0.7–5.0	0.7–1.1	0.77	0.77
		0.01–0.8	0.7–2.1	0.7–1.8	0.7–0.8	0.77	0.77
I	2.0	0.80–3.6	105.0	105.0	105.0	105.0	105.0
		0.01–0.8	105.0	105.0	105.0	105.0	105.0
K	18.0	0.80–3.6	81.2	81.2	81.2	81.2	81.2
		0.01–0.8	81.2	81.2	81.2	81.2	81.2
M	18.0	0.80–3.6	7–22	8–14	8–10	8.75	8.75
		0.01–0.8	7–12	7–10	8–9.2	8.75	8.75
I	18.0	0.80–3.6	110.0	110.0	110.0	110.0	110.0
		0.01–0.8	110.0	110.0	110.0	110.0	110.0

<sup>1</sup> In a Hamilton Beach dispersion apparatus at 14,000 rev/min.

readings of the manometer of the Kelley-Wiegner tube led to results 10-25 percent higher than those obtained when the suspension was not stirred (Table 12). The fact that concentration gradients apparently play a significant part in the settling of these lyophilic clays at concentrations below the limits cited by Rubey (1930) is supported by these results and by a comparison of the rates of clearing by the spectrophotometric method with the results obtained by pipette extraction during successive restirring of the suspension, i.e. by the experimental method adopted.

TABLE 12.—EFFECT OF CONCENTRATION GRADIENTS UPON MEASURED SETTLING VELOCITIES OF CLAY MINERALS  
Settling velocities (26°C, pH = 7.5-8.5)  
(cm/min = value listed  $\times 10^{-2}$ )

Clay	Clay Conc. (g/l.)	Chlorinity	Pipette Method	Manometer Method		Rate of Clearing
				Stirred	Not Stirred	
K	2-3.6	18	81.2	81.2	62.4	70.5
I	2-3.6	18	110.0	110.0	81.5	87.2
M	2-3.6	18	8.75	—	—	7.6
K	1-1.5	18	81.2	81.2	65.2	45.2
I	1-1.5	18	110.2	110.0	89.1	93.2
M	1-1.5	18	8.75	—	—	7.9
K	0.1-0.9	18	81.3	81.2	70.4	78.5
I	0.1-0.9	18	110.2	110.2	95.5	102.5
M	0.1-0.9	18	8.80	—	—	8.4
K	0.05-0.08	18	81.3	81.2	79.2	80.5
I	0.05-0.08	18	110.2	110.2	110.0	110.2
M	0.05-0.08	18	8.80	—	—	8.6
K	0.01-0.04	18	81.3	81.2	78.4	80.5
I	0.01-0.04	18	110.2	110.2	109.8	110.0
M	0.01-0.04	18	8.80	—	—	8.6

<sup>1</sup> K = Kaolinites; I = Illites; M = Montmorillonites.

Consequently, the results of Dreveskracht and Thiel (1941) are subject to misinterpretation in evaluation of the settling rates of clay minerals. Table 12 supports this argument.

Table 12 also introduces the factor of clay concentration and indicates that settling velocities determined by the pipette method are relatively the same over the concentration range 0.01-3.6 g of clay l. of artificial sea-water.

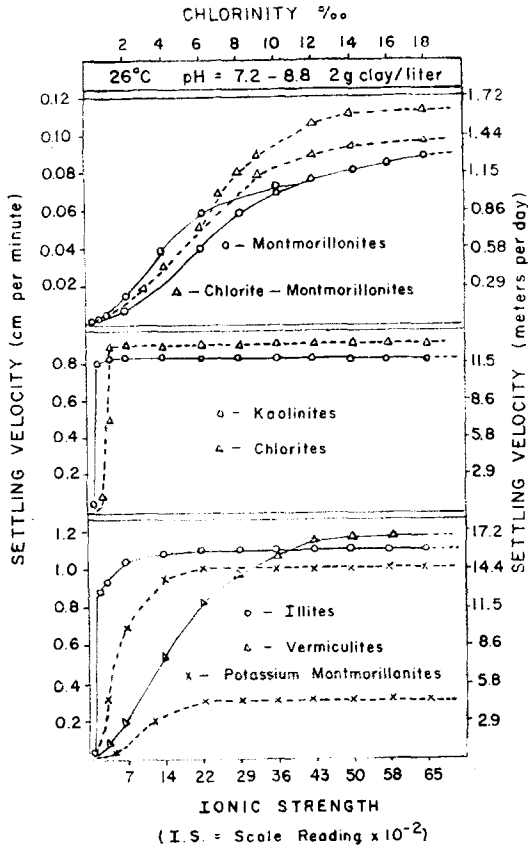


FIGURE 12.—Settling velocities of clay minerals in quiet artificial sea-water and filtered ocean water.

Fig. 12 summarizes the settling velocities obtained over the chlorinity range 0–18‰ at 26°C for all clay minerals cited in the preceding section “General Discussion.” Variations shown are discussed later under “settling of clay minerals in ocean water.” Results for three clay types are listed in m/24 hr day in Table 13 for convenience in application to geological oceanography considerations. Montmorillonites, as previously noted, increase in settling velocity quite gradually as the chlorinity increases and have much lower settling velocities than illites or kaolinites, even at a chlorinity of 18. Among the factors that may be influential in producing this difference, as well as causing the slightly greater rate for illite over kaolinite, are relative particle size prior to flocculation, surface solvation, cation exchange capacity and degree of coacervation. Concentration of clay apparently is not a significant factor over the range 0.01–3.6 g/l. (Table 12). At higher concentrations



TABLE 13.—CHARACTERISTIC INITIAL SETTLING RATES OF CLAY MINERALS IN SALINE WATER

(pH 7.5-8.5, fresh-water size less than 2 μ, vel. in m/day)

Temp. (°C)	Clay	Chlorinity (‰)								
		0.5	1	2	4	6	8	12	16	18
26	K	11.5	11.7	11.8	11.8	11.8	11.8	11.8	11.8	11.8
	I	12.9	14.3	15.1	15.8	15.8	15.8	15.8	15.8	15.8
	M	0.03	0.05	0.11	0.36	0.58	0.86	1.1	1.2	1.3
22	K	10.7	10.9	11.0	11.0	11.0	11.0	11.0	11.0	11.0
	I	12.0	13.3	14.0	14.7	14.7	14.7	14.7	14.7	14.7
	M	0.03	0.05	0.10	0.33	0.54	0.81	1.03	1.1	1.2
18	K	10.0	10.1	10.2	10.2	10.2	10.2	10.2	10.2	10.2
	I	11.1	12.2	12.9	12.9	12.9	12.9	12.9	12.9	12.9
	M	0.03	0.04	0.09	0.31	0.50	0.75	0.96	1.05	1.1
14	K	9.2	9.2	9.3	9.3	9.3	9.3	9.3	9.3	9.3
	I	10.2	11.2	11.8	11.8	11.8	11.8	11.8	11.8	11.8
	M	0.02	0.03	0.08	0.29	0.45	0.69	0.87	0.95	1.0
10	K	7.6	7.6	7.8	7.8	7.8	7.8	7.8	7.8	7.8
	I	8.5	9.6	10.3	10.3	10.3	10.3	10.3	10.3	10.3
	M	0.02	0.03	0.07	0.24	0.38	0.59	0.71	0.79	0.85
8	K	7.3	7.4	7.5	7.5	7.5	7.5	7.5	7.5	7.5
	I	8.2	9.1	9.6	10.0	10.0	10.0	10.0	10.0	10.0
	M	0.02	0.03	0.07	0.23	0.37	0.55	0.70	0.76	0.83
6	K	6.8	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.9
	I	7.6	8.4	8.9	9.2	9.2	9.2	9.2	9.2	9.2
	M	0.02	0.03	0.06	0.21	0.34	0.51	0.65	0.71	0.76

TABLE 14.—FLOCCULATION CONSIDERATIONS OF RELATIVE SETTLING VELOCITIES (Cl = 18, pH = 8.2)

Clay	Cation Exchange Capacity	Relative Initial "Size"	Settling Velocity at 50% of Samp' (cm/min) 26°C			
			(a) Before Flocculation	(b) After Flocculation	Ratio (b)/(a)	Relative Final "Size"
M	148.0	1	1 × 10 <sup>-3</sup>	9 × 10 <sup>-2</sup>	90	1.0
K	3.4	7	7 × 10 <sup>-3</sup>	80 × 10 <sup>-2</sup>	114	8.9
I	32.0	6	6 × 10 <sup>-3</sup>	110 × 10 <sup>-2</sup>	183	12.2

coacervation of montmorillonite is a very significant factor toward random accelerated fall in quiet sea-water.

Figs. 13 and 14 show the settling velocity distributions of the  $<2\ \mu$  fraction of the samples in distilled water, in dilute sodium carbonate solution and in water from the Brazos River, Texas. These results are based on actual, slightly different samples and small differences between action of different media should not be considered real. An idea as to the extent of flocculation of the three clay species may be obtained from the cumulative curves of Figs. 11 and 14. If the settling velocities corresponding to 50 percent by weight of sample are compared the results in Table 14 are obtained.

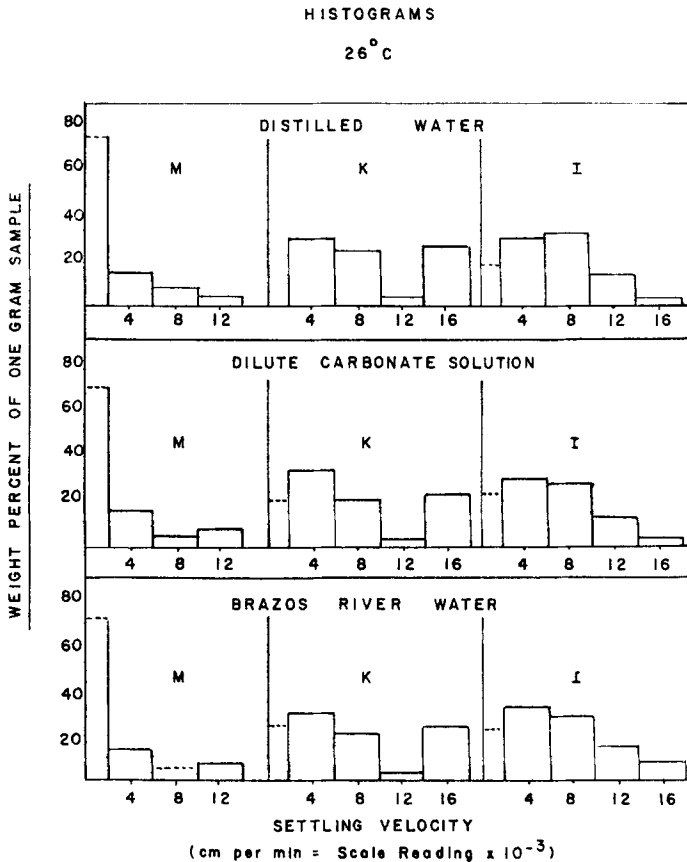


FIGURE 13.—Typical histograms for montmorillonitic (M), kaolinitic (K), and illitic (I), clay minerals in reference settling media (small differences between actions of different liquid media are not necessarily real since slight differences in samples of each clay type were involved).

The ratios (b)/(a) (Table 14) give an approximate relative measure of the increase in settling velocity brought about by the flocculating effect of the sea-water. The magnitudes obtained indicate that initial particle size distribution may be a quite significant factor as mentioned by Dreveskracht and Thiel (1941) (See "Introduction"). The relative initial and final "sizes" shown also indicate this but imply that other factors must also be considered. Initially kaolinite is slightly more coarse than illite, yet it settles more slowly. This may be caused by more solvation that slows the kaolin down but the initial particle size distributions were determined by gravitational settling in liquid media also. The extent of flocculation may be a function of the relative cation exchange capacities and associated coacervation. Since the cation exchange capacity of illite is greater than that of kaolinite (Table 14), this may be a partial explanation. However, illite is more dense than kaolinite and may be less solvated and coacervated in sea-water than in fresh-water because of ionic dehydration and coulombic force effects. Upon flocculation in sea-water this density factor may become more dominant. However, the cation exchange capacity of montmorillonite is far

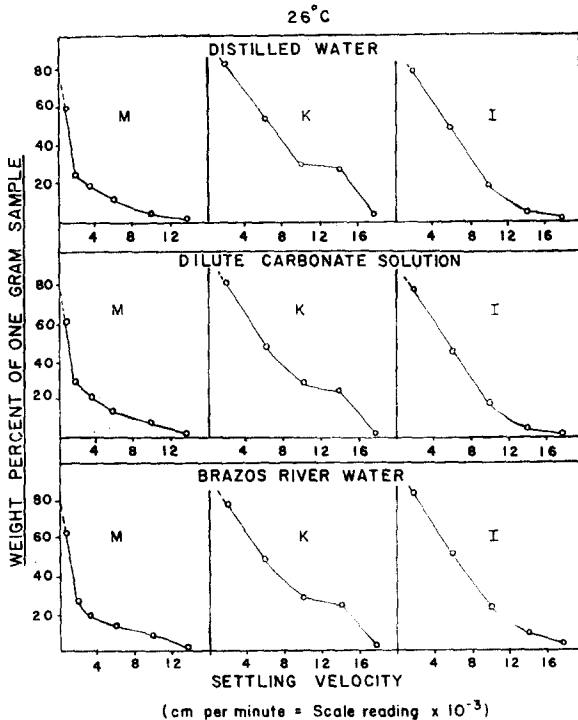


FIGURE 14.—Typical cumulative curves for montmorillonitic (M), kaolinitic (K), and illitic (I), clay minerals in reference settling media (small differences between action of different liquid media are not necessarily real since slight differences in samples of each clay type were involved).

greater than the cation exchange capacity of illite, and even though it is less dense, it falls much less rapidly than its relative particle size distribution would indicate until high chlorinities are reached. High cation exchange capacity is, however, associated with high coacervation (Hauser and leBeau, 1938), which would tend to decrease settling velocity except under conditions that permit occlusion of solvent between settling entities to form "lumps." Such coacervation, as previously mentioned, may be reduced slowly within limits by increasing the ionic strength of the suspension medium with associated increase in settling velocity as shown herein for montmorillonite.

A modified form of the Gompertz (1825) equation approximately fits the curves shown for montmorillonites in Fig. 12.

$$(r_x)_t = (r_0)_t + A_t B_m^{C_m} \left(\frac{x}{2} - 1\right) \quad (1)$$

where  $r_x$  = settling rate of clay mineral in saline water at a given temperature,  $t$ ;

$r_0$  = fresh-water settling rate of clay mineral before entry into saline water;

$A_t = f(t)$ ,  $t$  = centigrade temperature;

$B_m, C_m$  = constants for the specific clay material,  $m$ , involved;

$x$  = chlorinity of saline water in parts per thousand ( $\text{‰}$ ) or parts per million (ppm).

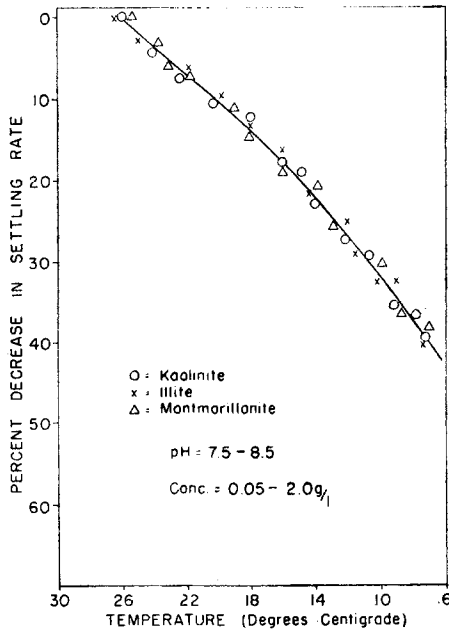


FIGURE 15.—Influence of water temperature variations upon the settling rates of clay minerals in quiet saline waters.

The numeral, 2, in  $(x/2 - 1)$  is an arbitrary selection designed to facilitate calculation of  $A_t$ ,  $B_m$ ,  $C_m$ . Other numerical constants could be used instead.

The variation in settling rate of the clays over the temperature range 6–26°C is shown in Fig. 15. All clay minerals at the concentrations employed follow a similar pattern of settling rate change with temperature. Such pattern is relatively the same as that to be expected from changes in viscosity and density of the water medium or (viscosity suspension–viscosity solvent)/viscosity solvent seems linear with temperature in this range (Huggins, 1939; Einstein, 1906, 1911). Based upon a 26°C reference the change may be represented in the following binomial form :

$$\Delta = 36.22 - 1.302t - 9.17 \times 10^{-3}t^2 + 3.12 \times 10^{-4}t^3 \quad (2)$$

where  $t$  = temperature (°C),  $\Delta_{26}^{\circ} = 0$ .

This information enables equation (1) to be written in more specific form for the temperature range 6–26°C, and for  $(r_x)_t$  in m/24 hr day.

$$r_x = r_0 + (45.46 - 1.64t - 1.15 \times 10^{-2}t^2 + 3.92 \times 10^{-4}t^3)B_m^{C_m} \left(\frac{x}{2} - 1\right) \quad (3)$$

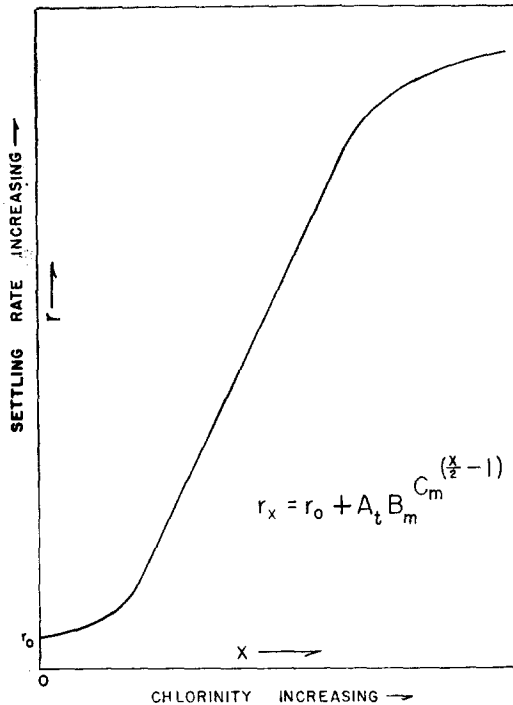


FIGURE 16.—Typical cumulative curve form for the settling velocities of a clay mineral in quiet saline water.

For most of montmorillonitic materials examined in this study

$$\left. \begin{aligned} r_0 &= 0.52 - 1.87 \times 10^{-2}t - 1.32 \times 10^{-4}t^2 + 5.64 \times 10^{-6}t^3 \\ (r_0)_{26^\circ} &= 1.44 \times 10^{-2} \text{ m/day} \\ B_m &= 0.0821; C_m = 0.554; x = \text{‰} \end{aligned} \right\} (4)$$

Fig. 16 shows the typical form of this settling rate or flocculation curve for clay minerals in saline water at constant temperature. Such settling rate and flocculation processes extend over narrow or wide (‰) chlorinity ranges in attaining maximum settling rates (Figs. 17 and 12). The settling rate curves for illitic and kaolinitic clays approach a maximum near a chlorinity of 2‰ while similar curves for montmorillonites extend to a chlorinity of about 18‰ before a maximum is realized. The constants  $A_t$  ( $A$  at any selected reference temperature),  $B_m$  and  $C_m$  may be derived in the following way: From a selected set of settling data, values of  $x$  (chlorinity) at equal intervals are chosen and substituted into the logarithmic form of equation (1). In order to avoid the logarithm of zero, corresponding to  $r_x = r_0$ , the value of  $x$  may be taken as zero at chlorinity equal to 2‰ or 2 ppm and chlorinity

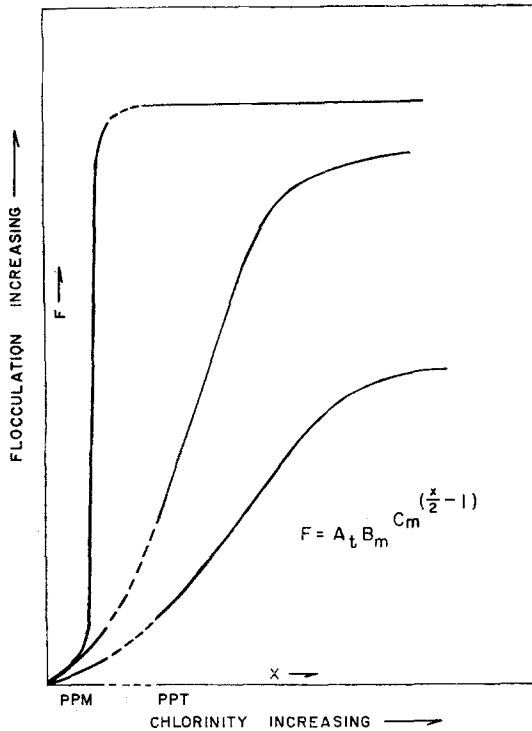


FIGURE 17.—Typical cumulative curve forms for the extent and range of flocculation of clay minerals in quiet saline water (ppm = parts per million; ppt = parts per thousand).

intervals of 2 parts per unit weight employed, rendering  $x_1$  (equation (5))

$$= \frac{x}{2} - 1$$

$$\log r_x = \log A_t + C_m^{x_1} \log B_m \tag{5}$$

A series of equations (equation (5)), into which the actual data, at equal chlorinity intervals, are substituted, are subsequently divided into three groups,  $G_1$ ,  $G_2$  and  $G_3$ , of  $n$  equations each, the members of each group added, and a ratio of the differences in the group sums prepared. For convenience, let  $r_x = r$ , then

$$\left. \begin{aligned} G_1 &= \sum_{r_0}^{r_{n-1}} \log r = n \log A_t + \sum_0^{n-1} C_m^{x_1} \log B_m \\ G_2 &= \sum_{r_n}^{r_{2n-1}} \log r = n \log A_t + \sum_n^{2n-1} C_m^{x_1} \log B_m \\ G_3 &= \sum_{r_{2n}}^{r_{3n-1}} \log r = n \log A_t + \sum_{2n}^{3n-1} C_m^{x_1} \log B_m \end{aligned} \right\} \tag{6}$$

$$\left. \begin{aligned} G_1 - G_2 &= \left( \sum_0^{n-1} C_m^{x_1} - \sum_n^{2n-1} C_m^{x_1} \right) \log B_m \\ G_2 - G_3 &= \left( \sum_n^{2n-1} C_m^{x_1} - \sum_{2n}^{3n-1} C_m^{x_1} \right) \log B_m \end{aligned} \right\} \tag{7}$$

$$\frac{G_1 - G_2}{G_2 - G_3} = \frac{\sum_0^{n-1} C_m^{x_1} - \sum_n^{2n-1} C_m^{x_1}}{\sum_n^{2n-1} C_m^{x_1} - \sum_{2n}^{3n-1} C_m^{x_1}} \tag{8}$$

$$\frac{G_1 - G_2}{G_2 - G_3} = \frac{\sum_0^{n-1} C_m^{x_1} - \sum_n^{2n-1} C_m^{x_1}}{C_m^n \left( \sum_0^{n-1} C_m^{x_1} - \sum_n^{2n-1} C_m^{x_1} \right)} = 1/C_m^n \tag{9}$$

Consequently,

$$C_m = \left( \frac{G_2 - G_3}{G_1 - G_2} \right)^{1/n} \tag{10}$$

and from equation (7), it follows that

$$\log B_m = \frac{G_1 - G_2}{\sum_0^{n-1} C_m^{x_1} (1 - C_m^n)} \tag{11}$$

since

$$\sum_0^{n-1} C_m^{x_1} = 1 + C_m + C_m^2 \dots C_m^{n-1}$$

and

$$\sum_0^{n-1} C_m^{x_1} C_m = C_m + C_m^2 + \dots + C_m^{n-1} + C_m^n$$

then, by subtraction,

$$\begin{aligned} \sum_0^{n-1} C_m^{x_1} - \left( \sum_0^{n-1} C_m^{x_1} \right) C_m &= 1 - C_m^n \\ \sum_0^{n-1} C_m^{x_1} &= \frac{1 - C_m^n}{1 - C_m} \end{aligned} \quad (12)$$

Substitution into equation (11) yields

$$\log B_m = \frac{(G_1 - G_2)(1 - C_m)}{(1 - C_m^n)^2} \quad (13)$$

Log  $A_t$  can then be derived from equation (6), as follows :

$$\log A_t = 1/n \left[ G_1 - \left( \sum_0^{n-1} C_m^{x_1} \right) \log B_m \right] \quad (14)$$

or

$$\log A_t = 1/n \left[ G_1 - \frac{(G_1 - G_2)}{1 - C_m^n} \right] \quad (15)$$

Equation (3) and similar expressions are particularly useful for the prediction of settling rates of individual clay mineral types at any chlorinity value and temperature level within the ranges 0-20‰, and 6°-30°C. Such prediction also lends itself well to the settling studies of clay mineral mixtures in quiet saline water.

For montmorillonites, this empirical equation (equation (3)) approaches a settling velocity of 1.3 m/day as an upper limit at 26°C. Consequently, it was of interest to measure the settling rate of such clay at a chlorinity higher than is common to sea-water. At a chlorinity of 25, a settling rate of 1.27 m/day at 26°C was found by the pipette method for montmorillonites 2(a)-(k). It should be noted that this value applies to montmorillonites obtained not only from terrestrial deposits, but also from soils and marine deposits, and includes hectorites and nontronites. Potassium-saturated montmorillonitic settling rates (Fig. 12) differ markedly, however, reaching a near maximum of 4.37 m/day at a chlorinity of 6‰. The use of an empirical expression, similar to equation (3) but based upon a reference chlorinity of 2 ppm, facilitated the prediction of the settling rates of clay type 2(l) (see "General Discussion, clay materials") in later work.

Since the settling rate for most montmorillonites does not exhibit a settling rate "size" increase (Table 14) comparable with that for illites, it is apparent that initial settling "size" (fresh-water) does not dominantly govern settling "size" even at high chlorinities. Therefore, equation (3) probably represents changing coacervation of montmorillonite and such coacervation is never eliminated completely by ionic dehydration and coulombic effects in sea-



TABLE 15.—VELOCITY DISTRIBUTIONS OF CLAY MIXTURES

No.	Initial Percent (wt.) (±0.2)			Wt. (%) of Sample	Settling Velocities of Mixtures (26°C) (cm/min = value listed × 10 <sup>-2</sup> )										Slow Fraction		
	M	K	I		Chlorinity = 0.50, pH = 8.2										SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (rel. %)	Estimated Composition (% wt.)	
					0.1	0.2	0.3	0.7	72.3	26.1	0.9						
					0	0	0	0.6	71.9	26.4	1.1						
S-1	0	75	25	Predict. Exper.												1.18	100 K
S-2	0	25	75	Predict. Exper.	0	0	0	0.2	28.1	70.4	1.3						
S-3	75	0	25	Predict. Exper.	0	0	0	0.2	28.7	70.2	0.9						
					1.5	72.0	1.5	0.0	1.0	23.0	1.0						
					1.8	77.0	2.5	0.0	0.5	17.5	0.8						
S-4	25	0	75	Predict. Exper.	0.5	24.0	0.5	0.0	3.0	69	3.0						
					0.5	25.4	1.0	0.0	2.6	68	2.5						
S-5	50	25	25	Predict. Exper.	1.0	48.0	1.0	0.5	24.8	23.5	1.2						
					1.5	52.5	1.5	0.5	24.3	18.7	1.0						
S-6	40	30	30	Predict. Exper.	0.8	38.4	0.8	0.6	29.8	28.2	1.4						
					1.2	40.8	1.1	0.6	29.6	25.7	1.0						
S-7	20	40	40	Predict. Exper.	0.4	19.2	0.8	0.8	39.7	37.6	1.5						
					0.5	20.2	1.0	0.8	39.5	36.6	1.4						
S-8	50	0	50	Predict. Exper.	1.0	48.0	1.0	0.0	2.0	46	2.0						
					1.2	50.5	1.5	0.0	1.8	43	2.0						
S-9	50	50	0	Predict. Exper.	1.0	48.0	1.0	1.0	47.5	1.0	0.5						
					1.2	48.0	0.8	1.0	47.5	1.0	0.5						
S-10	0	50	50	Predict. Exper.	0	0	0	1.0	49.5	47.0	2.5						
					0	0	0	1.0	49.8	48.0	1.2						

	Chlorinity = 8.0, pH = 8.2											
	5.0	6.5	8.0	70	80	90	100	110	115			
S-1	0	0	0	0	72	0.8	2.7	23.5	1.0	100 K	1.18	
	Predict. Exper.	0	0	0	71.6	1.0	2.9	23.2	1.3			
S-2	0	0	0	0	24	0.3	1.6	71.1	3.0	100 K	1.18	
	Predict. Exper.	0	0	0	24	0.3	1.6	71.1	3.0			
S-3	75	0	25	0	0	0	0.5	23.5	1.0	95 M. 5 I	3.33	
	Predict. Exper.	0.7	64.5	9.8	0	0	0	17.0	0.5			
S-4	25	0	75	0	0	0	0.9	71.1	3.0	96 M. 4 I	3.33	
	Predict. Exper.	0.2	21.5	3.3	0	0	0	70.0	2.5			
S-5	50	25	25	0	24.0	0.3	1.2	23.5	1.0	94 M. 6 I	3.32	
	Predict. Exper.	0.5	43.0	6.5	0	24.0	0.3	0.7	18.5			0.5
S-6	40	30	30	0	28.8	0.4	1.4	28.2	1.2	96 M. 4 I	3.33	
	Predict. Exper.	0.4	34.4	5.2	0	28.9	0.5	1.4	25.5			0.8
S-7	20	40	40	0	38.4	0.5	1.9	37.6	1.6	97 M. 3 I	3.33	
	Predict. Exper.	0.2	17.2	2.6	0	39.0	1.0	0.8	37.0			1.0
S-8	50	0	50	0	0	0	1.0	47.0	2.0	97 M. 3 I	3.33	
	Predict. Exper.	0.5	43.0	6.5	0	0	0	0.5	44.6			1.5
S-9	50	50	0	0	48.0	0.6	1.4	0	0	100 M	3.34	
	Predict. Exper.	0.5	43.0	6.5	0	47.8	0.8	1.4	0			0
S-10	0	50	50	0	48.0	0.6	2.4	47.0	2.0	100 K	1.18	
	Predict. Exper.	0	0	0	48.0	0.6	2.4	47.0	2.0			

TABLE 15.—VELOCITY DISTRIBUTIONS OF CLAY MIXTURES—*contd.*

No.	Initial Percent (wt.) ( $\pm 0.2$ )			Wt. (%) of Sample	Settling Velocities of Mixtures (26°C) (cm/min = value listed $\times 10^{-2}$ )											Slow Fraction	
	M	K	I		9.0	10.0	10.5	70	80	90	100	110	115	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (rel. %)	Estimated Composition (% wt.)		
S-1	0	75	25	Predict.	0	0	0	0	72.0	1.5	2.1	24.0	0.4	1.18	100 K		
				Exper.	0	0	0	72.0	1.3	2.0	24.2	0.5					
S-2	0	25	75	Predict.	0	0	0	0	24.0	0.5	2.3	72.0	1.2	1.18	100 K		
				Exper.	0	0	0	24.0	0.5	2.3	72.2	1.0					
S-3	75	0	25	Predict.	71.4	0.4	3.2	0	0	0	0.6	24.0	0.4	3.34	100 M		
				Exper.	66.5	0.2	1.2	5.2	9.0	0	0.2	17.5	0.2				
S-4	25	0	75	Predict.	23.8	0.1	1.1	0	0	0	1.8	72.0	1.2	3.34	100 M		
				Exper.	22.5	0.0	0.5	2.2	2.0	0	1.5	70.4	0.9				
S-5	50	25	25	Predict.	47.6	0.2	2.2	0	24.0	0.5	1.1	24.0	0.4	3.34	100 M		
				Exper.	42.4	0.0	1.7	5.2	30.6	0.5	1.1	18.3	0.3				
S-6	40	30	30	Predict.	38.1	0.15	1.75	0	28.8	0.6	1.3	28.8	0.5	3.35	100 M		
				Exper.	35.5	0.10	1.30	3.0	32.0	0.6	1.3	26.0	0.2				
S-7	20	40	40	Predict.	19.0	0.1	0.9	0	38.4	0.8	1.7	38.4	0.7	3.34	100 M		
				Exper.	17.0	0.0	0.6	2.3	40.8	0.8	1.4	36.6	0.5				
S-8	50	0	50	Predict.	47.6	0.2	2.2	0	0	0	1.2	48.0	0.8	3.34	100 M		
				Exper.	45.5	0.2	1.0	3.2	3.4	0	1.2	45.0	0.5				
S-9	50	50	0	Predict.	47.6	0.2	2.2	0	48.0	1.0	1.0	0	0	3.34	100 M		
				Exper.	47.8	0.2	2.4	0	48.0	0.7	1.3	0	0				
S-10	0	50	50	Predict.	0	0	0	0	48.0	1.0	2.2	48.0	0.8	1.18	100 K		
				Exper.	0	0	0	48.0	0.5	2.6	48.1	0.8					

water of normal or usual composition. High concentrations of metallic ions, e.g.  $\text{Fe}^{3+}$ , would be expected, however, to decrease further the degree of coagervation and induce faster settling rates.

In order to ascertain the degree to which the relative individual rates of settling of the clay types apply when clay mixtures are exposed to saline water, selected mixtures of all clay minerals cited above were studied. Some mixtures examined are listed in Table 15 to illustrate the methods employed in detection of clay mineral interactions that alter the individual settling tendencies of the clay minerals involved. A comparison was made between a predicted velocity distribution based upon the individual cumulative curves (Fig. 11) and the experimental velocity distribution for each mixture. These tables list results for chlorinities of 0.5, 8.0 and 18.0. Table 15 indicates that the experimental results for binary clay mixtures of kaolinite and illite, or kaolinite and montmorillonite agree closely with the predicted values for the mixtures concerned (see mixtures S-1, S-2, S-9, S-10). On the other hand binary mixtures of montmorillonite and illite, S-3, S-4, S-8, do not exhibit such agreement. The slower settling ranges, characteristic of the montmorillonite, seem to gain material at the expense of the characteristic illitic settling ranges. In order to interpret this apparent transfer of material, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  percent ratio was determined for the fractions less than  $0.35 \times 10^{-2}$  cm/min and compared with a similar ratio for the individual montmorillonitic component. The combined results of chemical analysis and velocity distribution comparison indicate that this slow fraction contains 6-7 percent illitic material. The reference  $\text{SiO}_2/\text{Al}_2\text{O}_3$  percent ratios are 3.338 (montmorillonites), 3.081 (illites), 1.182 (kaolinites). The M/I ratio for the slow fraction is calculated from the expression

$$M/I = \frac{R_e - 3.081}{3.338 - R_e}$$

where  $R_e$  = experimental ratio for the slow fraction. The montmorillonite restrains the settling of a small quantity of the illite in an 18.3 : 1 weight ratio. This same phenomenon is exhibited within the three-component mixtures S-5, S-6, S-7. The montmorillonitic velocity ranges again gained at the expense of the illitic velocity ranges while the kaolinitic velocity ranges remained relatively undisturbed. Mixture S-5, however, restrained slightly more illite.

These interpretations became more involved at high chlorinities (Table 15). At chlorinity of 8 the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  percent ratio indicated that slightly less illite was restrained within the slow fraction less than  $8.5 \times 10^{-2}$  cm/min. However, examination of data for mixtures S-3, S-4, S-5 indicated that material had entered velocity ranges between the montmorillonite ranges and the illitic ranges. On the basis of the percentage changes involved and analysis this was material of composition close to 50-50 montmorillonite-illite. This effect was also apparent in mixtures of the three components S-5, S-6, S-7 (Table 15). At a chlorinity of 18 material was gained by intermediate velocity ranges at the expense of both the illitic and montmorillonitic ranges. In this

case (Table 15) the analysis ratio for the fraction slower than  $8.5 \times 10^{-2}$  cm/min corresponded to that of the individual montmorillonitic component. The apparent losses in weight by the illitic range and the montmorillonitic range to the intermediate ranges were of the same order of magnitude. Again a 50-50 illitic-montmorillonite complex was indicated for the intermediate ranges. In the three-component mixtures at chlorinity 18 this increase in the intermediate ranges overlapped, in part, the kaolinitic range. However, the increase in this overlap region plus the material increase in other ranges intermediate to montmorillonite and illite was of the same order of magnitude as the sum of the decreases in the montmorillonite and illite ranges relative to the predicted distribution. This was not considered conclusive evidence, however, that kaolinite does not influence the alteration in settling rate distribution.

Nevertheless, binary mixtures containing a kaolinitic component S-1, S-2, S-3, S-10 did not exhibit any interaction that was detected by the methods employed for these mixtures. Settling range fractions less than  $85 \times 10^{-2}$  cm/min of such binary mixtures gave  $\text{SiO}_2/\text{Al}_2\text{O}_3$  values characteristic of the individual kaolinitic component and the predicted and experimental distributions closely agreed as previously indicated.

Some interaction of kaolinites with chloritic-montmorillonitic mixes, prepared by aging of montmorillonite that has settled through artificial sea-water via the method of Whitehouse and McCarter (1958), and with chlorite-montmorillonites extracted from marine sediments, 5(c) and (d) above, was noted. The degree of this interaction, which is approximately 20 percent kaolinite by weight, is shown in histogram form in Fig. 18.

The approximate clay mineral compositions and corresponding settling rates of all clay mineral settling entities, detected as active in clay mineral mixtures in artificial sea-water and ocean water, are shown in Table 16. Some of the compositions indicated depend on pH and temperature. The chlorinity conditions and initial clay mineral mixture and clay concentration requirements for the development of each settling entity are also listed. Each such settling phase was also tested for persistence in turbulent saline water, pumped and recirculated through a coiled 80 ft length of  $\frac{1}{2}$  in. diameter plastic pipe. The effluent clay mineral-saline water was sampled at periodic intervals and subjected to chemical, electron diffraction and electron microscopy analysis. Subsequent pipette analysis of the extracted samples in quiet gravitational systems also provided indicative evidence for lack of persistence of some entities. On the other hand, possible reassociation of separates *negates* this latter method as an indicator of persistence of the entities in turbulent flow.

Flow velocities in the range of 0.5-6 miles/hr were employed and the concept of turbulent flow was based upon a Reynolds' number criterion of 2300 or greater (Reynolds, 1883).

The basic clay mineral entities were extracted from prepared clay mineral mixtures, actual marine sediments and soils by multiple settling and repeated pipette extraction. The clay materials were first washed and reagitated in

some of the supernatant sea-water in an effort to remove free carbonates. Separations of materials with different gravitational settling rates often involved 500 to 1100 pipette extraction, or fractionation, steps on the same sample during periods as long as 3 months. Ultracentrifugal separation does not work when montmorillonitic materials are involved. Such separation both destroys and creates settling entities that are not characteristic of ordinary gravitational settling processes. The centrifugally induced random occlusion of water by montmorillonite leads to "trapping" of other clay minerals that would separate via ordinary gravitational settling. The materials extracted via pipette fractionation from quiet settling systems were

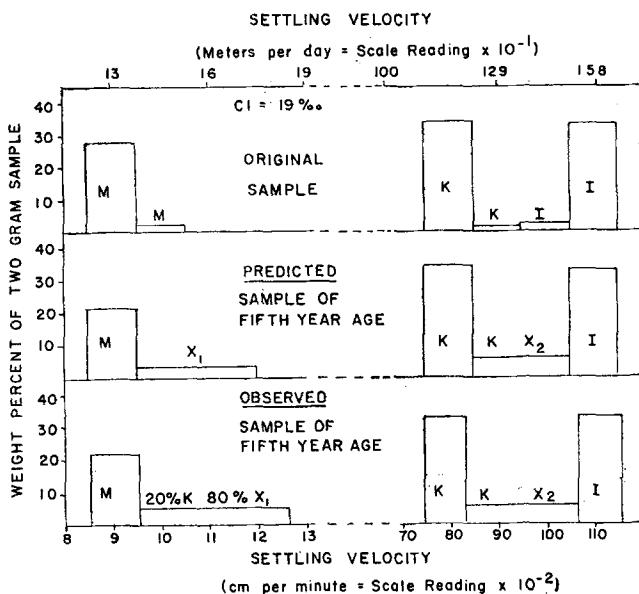


FIGURE 18.—Histogram illustrating partial transport of kaolinitic clay by an experimentally developed chloritic-illitic mix of fifth year age.

washed with 0.01 N sodium carbonate solution to remove soluble salts and to minimize loss of calcium from the clay before chemical analysis. States of aggregation in the settling entities were preserved for electron microscopy and electron diffraction examination by the critical point method (Whitehouse and McCarter, 1958).

*Differential Settling of Clay Minerals in Quiet Ocean Waters,  
Texas Bay Waters, and Saline Waters of Varied  
Ionic Ratio Composition*

In order to evaluate the possible application of the settling velocity results obtained in artificial sea-water to the prediction of relative settling of such material in actual marine waters, experimental measurements were made

TABLE 16.—CLAY MINERAL COMPOSITIONS AND DIFFERENTIAL SETTLING VELOCITIES FOR SETTLING ENTITIES WITHIN CLAY MINERAL MIXTURES IN ARTIFICIAL SEA-WATER AND IN FILTERED OCEAN WATER

Settling Entity <sup>1</sup>	Existence Temp. Range <sup>2</sup> (within 6–30°C)	Settling Velocity (m/day) (26°C) <sup>3</sup>	Initial Clay Mixture Composition Requirements <sup>4</sup>	Existence Chlorinity Range <sup>2</sup> (‰)	Existence pH Range <sup>2</sup>	Existence Clay Conc. Range <sup>2</sup> (g/l.)	Active in Turbulent Water
Kaolinites, K 1(a)–(n)	6–30	11.5–11.8	> 1.2% K if M present	0.5–20.0	6.5–9.8	0.01–15.6	yes
		0.2–11.5	> 1.2% K if M present	0.2–0.5	6.5–9.8		yes
Halloysites, H 1(o), (q), (r)	6–30	11.5–11.8	> 1.2% H if M present	1.2–20.0	6.5–9.8	0.01–15.6	yes
		0.2–11.5	> 1.2% H if M present	0.2–1.2	6.5–9.8		yes
Dickites, D 1(s), (t)	6–30	11.6–11.8	> 0.5% D if M present	0.3–20.0	6.5–9.8	0.01–15.6	yes
		0.2–11.6	> 0.5% D if M present	0.2–0.3	6.5–9.8		yes
Montmorillonites, M 2(a); (c)–(l)	9–30	0.02–0.58	M present	0.2–6.0	6.5–9.8	0.01–3.6	yes
		0.58–1.30	M present	6.0–20.0	6.5–9.8		yes
Montmorillonites, M 2(b)	9–30	0.05–0.74	M present	0.2–6.0	9.2–9.8	0.01–3.6	yes
		0.58–1.30	M present	6.0–20.0	6.5–9.8		yes
		0.02–0.58	M present	0.2–6.0	6.5–9.1		yes
Hectorites, HM 2(d)	9–30	0.02–0.58	HM present	0.2–6.0	6.5–9.8	0.01–3.6	yes
		0.58–1.30	HM present	6.0–20.0	6.5–9.8		yes
Nonttronites, NM 2(k)	6–30	0.02–0.86	NM present	0.2–6.0	6.5–9.8	0.01–8.4	yes
		0.86–1.30	NM present	6.0–20.0	6.5–9.8		yes
Potassium montmorillonites, PM 2(l)	6–30	0.02–4.2	PM present	0.2–6.0	6.5–9.8	0.01–6.5	yes
		4.2–4.4	PM present	6.0–20.0	6.5–9.8		yes

Illites, I 1(a)-(h)	6-30	0.2-4.3 14.3-15.8	>	3.1% I if M present 3.1% I if M present	0.2-1.0 1.0-20.0	6.5-9.8 6.5-9.8	0.01-15.8	yes yes	
	Vermiculites, V 4(a)-(d)	6-30	0.2-14.3 14.3-16.9	>	1.4% V if M present V present	0.2-8.8 8.8-20.0	6.5-9.2 6.5-9.8	0.01-4.5 0.01-15.8	yes yes
Illite— montmorillonites, IM 5(a)		6-30	0.02-9.6 9.6-12.1		IM present IM present	0.2-1.0 1.0-20.0	6.5-9.8 6.5-9.8	0.01-4.2	no (I separates) no (I separates)
	Illite— montmorillonites, IM 5(b)	9-30	0.02-7.2 7.2-8.1		IM present IM present	0.2-1.0 1.0-20.0	6.5-9.8 6.5-9.8	0.01-3.6	yes yes
Chlorite— montmorillonites, CM 5(d)		9-30	0.02-0.9 0.9-1.4 0.9-1.6		CM present CM present CM present	0.2-6.0 6.0-20.0 6.0-20.0	6.5-9.8 6.5-9.2 6.5-9.8	0.01-3.6	yes yes yes
	6-30	0.2-7.3 7.3-12.8	>	0.6% C if M present 0.6% C if M present	0.2-0.8 0.8-20.0	6.5-9.8 6.5-9.8	0.01-15.6	yes yes	
		6-30	0.2-1.7 1.7-11.9	>	1.8% C if M present 0.8% C if M present	0.2-0.8 0.8-20.0	6.5-9.2 6.5-9.8	0.01-15.6	yes yes
Chlorites, C (a)-(c), (e) 6(d)	9-30	12.4-15.8		5-20% I, 40-60% M	0.5-12.0	7.2-9.2	0.01-3.6	yes	
	9-30	12.4-15.8		5-20% I, 40-60% M	0.5-14.0	7.2-9.8	0.01-3.6	yes	
	9-30	12.9-15.6		10-50% I, 20-50% M	0.5-12.0	7.2-9.8	0.01-3.6	no	
	9-30	12.8-15.5		10-50% I, 20-50% M	0.5-15.0	7.2-9.8	0.01-3.6	no	
	9-30	12.6-15.4		10-50% I, 20-50% M	0.5-20.0	7.2-9.2	0.01-3.6	no	
	9-30	7.0-7.9		60-80% M, 20-40% I	1.0-20.0	7.2-9.2	0.01-4.2	yes	
	9-30	7.2-8.1		40-90% M, 10-60% I	1.0-20.0	7.2-9.2	0.01-4.5	yes	
	9-30	7.6-8.8		40-80% M, 20-60% I	1.0-20.0	7.2-9.2	0.01-4.5	no	
	100% M	9-30	0.8-25.2 (random fall)	>	40% M	0.2-20.0	6.8-9.5	3.6-10.2	no



TABLE 16.—CLAY MINERAL COMPOSITIONS AND DIFFERENTIAL SETTLING VELOCITIES FOR SETTLING ENTITIES WITHIN CLAY MINERAL MIXTURES IN ARTIFICIAL SEA-WATER AND IN FILTERED OCEAN WATER—cont'd.

Settling Entity <sup>1</sup>	Existence Temp. Range <sup>2</sup> (within 6-30°C)	Settling Velocity (m/day) (26°C) <sup>3</sup>	Initial Clay Mixture Composition Requirements <sup>4</sup>	Existence Chlorinity Range <sup>2</sup> (‰)	Existence pH Range <sup>2</sup>	Existence Clay Conc. Range <sup>2</sup> (g/l.)	Active in Turbulent Water
100% M	6-9	0.2-2.8 (8°C) (random fall)	> 20% M	0.2-20.0	6.8-9.5	2.6-3.6	yes
99% M, 1% K	9-30	0.02-1.3	60% M, K present	0.2-20.0	6.5-9.8	0.12-3.6	no
99% M, 1% H	9-30	0.05-1.3	60% M, H present	0.2-20.0	6.5-9.8	0.16-3.6	no
99.5% M, 0.5% D	9-30	0.15-1.3	52% M, D present	0.2-20.0	6.5-9.8	0.22-3.6	no
99.4% M, 0.6% C	9-30	0.03-1.3	62% M, C present	0.2-20.0	6.5-9.8	0.15-3.6	no
99% M, 1% C	9-30	0.03-1.3	60% M, C present	0.2-20.0	6.5-9.8	0.20-3.6	no
98% M, 2% C	9-30	0.05-1.4	45% M, C present	0.2-20.0	6.5-9.8	0.18-3.6	no
92% IM, 8% K	6-30	0.02-8.5	80-90% IM, 10-20% K	0.2-20.0	7.5-8.8	0.6-4.7	no
81% CM, 19% K	9-30	1.3-1.6	70-90% CM, 10-30% K	12.0-20.0	7.2-8.9	0.2-3.6	yes
60% M, 40% V	9-30	0.02-2.5	20-90% M, 10-80% V	0.2-1.5	7.5-9.6	0.3-4.5	no
72% M, 28% V	9-30	0.05-0.42	40-90% M, 10-60% V	0.2-1.0	7.2-9.2	0.5-3.6	yes
50% M, 50% V	9-30	0.05-0.51	40-82% M, 18-60% V	0.2-1.4	7.2-9.2	0.8-3.6	yes
93% IM, 7% V	9-30	0.07-7.6	60-95% IM, 5-40% V	0.2-2.6	7.5-8.8	1.2-4.8	yes
86% CM, 14% V	9-30	0.03-0.83	52-98% CM, 2-48% V	0.2-1.5	7.2-9.2	1.2-3.6	no
32% CM, 68% V	9-30	0.10-0.92	20-85% CM, 15-80% V	0.2-2.6	7.5-8.8	0.5-3.8	no
92% M, 4% I, 4% K	9-30	0.03-1.2	20-80% M, 2-40% I, K	0.2-14.0	6.5-9.8	0.3-3.6	no
98% M, 1% I, 1% K	9-30	0.03-1.2	40-96% M, 1-30% I, K	0.2-20.0	6.5-9.8	0.5-3.6	no

<sup>1</sup> K = kaolinites, H = halloysites, D = dickites, M = montmorillonites, HM = hecterites, NM = nontronites, PM = potassium montmorillonites, I = illites, V = vermiculites, CM = chlorite-montmorillonites, IM = illite-montmorillonites, C = chlorites.

<sup>2</sup> Range in which settling unit is active.

<sup>3</sup> Settling velocity at 26°C unless otherwise specified.

<sup>4</sup> Other clay minerals also can be present.

TABLE 17.—REPRESENTATIVE EXPERIMENTAL AND PREDICTED SETTLING VELOCITIES OF CLAY MINERALS IN QUIET OCEAN WATERS AND QUIET BAY WATERS

Clay Mineral <sup>1</sup>	Saline Water <sup>2</sup>	Chlorinity (‰)	Ionic Strength	Settling Velocity (26°C) (m/day)		
				Experimental	Predicted	Difference
K	TB	1.25	0.045 <sup>3</sup> S	10.5	11.7	-1.2
K	MD	1.28	0.046	11.7	11.7	0.0
M	TB	1.25	0.045 S	0.03	0.06	-0.03
M	MD	1.28	0.046	0.06	0.06	0.0
I	TB	1.25	0.045 S	12.2	14.1	-1.9
I	MD	1.28	0.046	14.0	14.1	-0.1
C	TB	1.25	0.045 S	12.8	12.8	0.0
C	MD	1.25	0.046	12.8	12.8	0.0
K	TB	3.86	0.139 <sup>3</sup> S	10.5	11.8	-1.3
K	MD	4.67	0.168	12.0	11.8	0.2
M	TB	3.86	0.139 S	0.21	0.36	-0.15
M	MD	4.67	0.168	0.42	0.40	0.02
I	TB	3.86	0.139 S	14.1	15.8	-1.7
I	MD	4.67	0.168	15.4	15.8	-0.4
C	TB	3.86	0.139 S	12.8	12.8	0.0
C	MD	4.67	0.168	12.8	12.7	0.01
K	TB	12.74	0.460 <sup>3</sup> A	11.0	11.8	-0.8
K	MD	13.01	0.469	12.1	11.8	0.3
M	TB	12.74	0.460 A	0.5	1.1	-0.6
M	MD	13.01	0.469	1.1	1.1	0.0
I	TB	12.74	0.460 A	13.6	15.8	-2.2
I	MD	13.01	0.469	15.3	15.8	-0.5
C	TB	12.74	0.460 A	12.8	12.8	0.0
C	MD	13.01	0.469	12.8	12.8	0.0
K	TB	22.24	0.844 <sup>3</sup> M	11.6	11.8	-0.2
K	MD	17.21	0.621	12.1	11.8	0.3
K	GM	17.19	0.620	12.1	11.8	0.3
M	TB	22.24	0.844 M	0.73	1.27	-0.54
M	MD	17.21	0.621	1.25	1.26	-0.01
M	GM	17.19	0.620	1.21	1.25	-0.04
I	TB	22.24	0.844 M	14.5	15.8	-1.2
I	MD	17.21	0.621	15.5	15.8	-0.3
I	GM	17.19	0.620	15.4	15.8	-0.4
C	TB	22.14	0.844 M	12.8	12.8	0.0
C	MD	17.21	0.621	12.8	12.8	0.0
C	GM	17.19	0.620	12.8	12.8	0.0

<sup>1</sup> K = kaolinites, M = montmorillonites, I = illites, C = chlorites.

<sup>2</sup> TB = Texas Bay water, MD = Miss. Delta region water, GM = Gulf of Mexico water.

<sup>3</sup> See Table 5, footnote (3).

using water samples collected from the Gulf of Mexico, from the Mississippi Delta Region in the vicinity of Grand Bay, Louisiana, and from Copano Bay, Aransas Bay, Mesquite Bay, and San Antonio Bay, Texas (see Table 5 and "General Discussion, saline waters," above). The actual chlorinity values for the water samples were determined by the Mohr (1856) method. The sea-water was not diluted in the laboratory, but it was filtered to remove suspended matter and was subjected to chemical analysis to determine the ionic ratios of major ionic components (Table 5).

Agreement of the settling velocity results obtained with that predicted via equation (3), in this section for artificial sea-water were better than

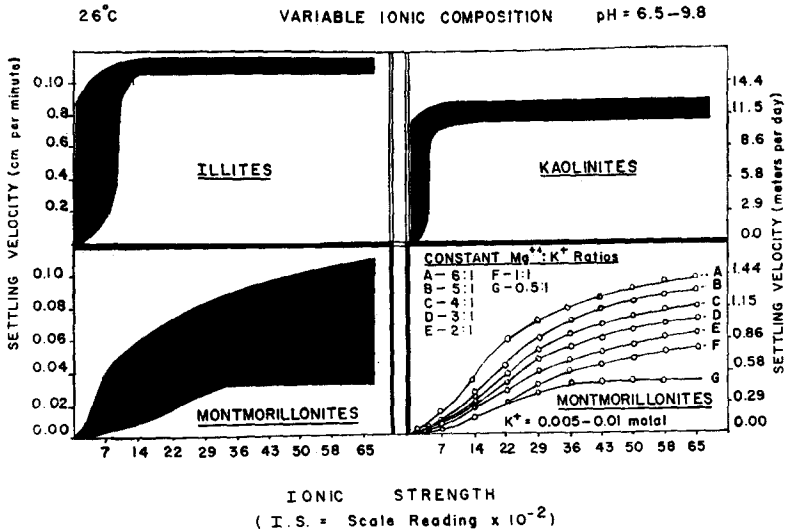


FIGURE 19.—Settling velocity variations of clay minerals in quiet saline waters of variable inorganic ionic ratio composition.

anticipated for both the Gulf of Mexico and the Mississippi Delta Region waters (see Table 17). Deviations from the predicted results for Texas Bay waters are explained readily on the basis of the ionic ratios listed in Table 3 and the influence of variable ionic compositions shown in Fig. 19.

Fig. 19 summarizes the settling rate results obtained for ionic solutions similar to ocean water in types of inorganic ionic components but different from ocean water in ionic ratio composition. In order to determine the extent to which particular interrelations of the ionic constituents of sea-water control the flocculation and settling of clay minerals, investigations of related ionic systems of fewer components were first studied. The calculated ionic strengths of such systems were adjusted over the ocean water ionic strength range from  $1 \times 10^{-10}$  to 0.686 moles-charge<sup>2</sup>/kg. The general approach was to increase the number, type and concentration of ionic components in many selected relative directions until the average composition of ocean waters (Table 4) was reached.

Ocean water contains the following approximate molal concentrations of major ionic constituents:  $\text{Na}^+$ , 0.46;  $\text{Ca}^{2+}$ , 0.01;  $\text{Mg}^{2+}$ , 0.05;  $\text{K}^+$ , 0.01;  $\text{Cl}^-$ , 0.54. The lowest molal concentrations of the major cations that were observed to initiate flocculation of the clay minerals, in the presence of chloride ion over the pH range 6.5–9.8, are shown in Table 18. Magnesium

TABLE 18.—MINIMUM MOLALITIES<sup>1</sup> OF OCEAN WATER MAJOR CATIONS REQUIRED FOR EXPERIMENTAL DETECTION OF FLOCCULATION OF CLAY MINERALS

Cation	Clay Conc. (g/l.)	Minimum Molalities (moles/kg) <sup>2</sup>				Ionic Potential (Z/R) <sup>3</sup>
		K	C	I	M	
$\text{Na}^+$	0.01–0.36	$10^{-2}$	$10^{-2}$	$5 \times 10^{-2}$	$10^{-1}$	1.00
$\text{Mg}^{+2}$	0.01–3.6	$10^{-9}$	$10^{-9}$	$10^{-3}$	$10^{-2}$	2.56
$\text{Ca}^{+2}$	0.01–3.6	$10^{-3}$	$10^{-3}$	$10^{-3}$	$10^{-2}$	1.89
$\text{K}^+$	0.01–3.6	$10^{-2}$	$10^{-2}$	$10^{-2}$	$10^{-2}$	0.75
$^{4}\text{Sr}^{+2}$	0.01–3.6	$10^{-3}$	$10^{-3}$	$10^{-3}$	$5 \times 10^{-3}$	1.74

<sup>1</sup> Sometimes called "flocculation values."

<sup>2</sup> K = kaolinites, C = chlorites, I = illites, M = montmorillonites.

<sup>3</sup> Ionic charge divided by ionic radius.

<sup>4</sup> Not necessarily a major component.

and calcium induced flocculation at concentrations lower than those observed for monovalent sodium or potassium. This is in accord with the Schulze-Hardy Rule (Hardy, 1899). Equivalent potassium concentrations were required for initiation of flocculation of all four clay types, and on the basis of relative ionic charge potassium is more effective in inducing flocculation of montmorillonites than are the other major cations. The minor cation,  $\text{Sr}^{2+}$ , which is also listed in Table 18, parallels  $\text{K}^+$  in initiating flocculation on the basis of unit ionic charge. In the overall general sense the order of decreasing effectiveness of the cations is  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$ . This differs in the order of magnesium and calcium cited by Wiegner (1925). Further, in relation to ionic potential, sodium and potassium are reversed. However, it is in montmorillonite that the "flocculation values" obtained for sodium and potassium differ to greatest extent.

Intramolecular positions of the montmorillonites apparently are more receptive to the effective radius of a hydrated potassium ion than to such radius of a hydrated sodium ion. Such concept has previously been advanced by Jackson (1939) and others, as an explanation for fixation of potassium in soil clays. On the other hand, Page and Bayer (1939) have stressed the importance of the relative, unhydrated, ionic radii in this connection.

Whitehouse and McCarter (1958) previously have emphasized that the ionic molal ratio of magnesium to potassium in saline waters controls the flocculation and subsequent settling of montmorillonites and dominantly influences any possible transformation of montmorillonites to chlorites and illites in ocean water. The pronounced effects of such ratio upon montmoril-

Ionic settling rates are shown in Fig. 19. Such control of these settling rates was absent when the potassium concentration was below 0.005 molal.

The settling of chlorites was independent of the ionic ratio composition of the saline water at any constant ionic strength. Illitic settling velocities exhibited considerable dependence on ionic ratios at ionic strengths below  $7 \times 10^{-2}$ , while kaolinitic rates showed only narrow dependence on ionic ratios at all ionic strengths or chlorinities concerned. Illitic rates were relatively independent of ionic ratios when the potassium concentration exceeded 0.007 molal.

A special influence of strontium on montmorillonitic settling rates was observed. When the strontium concentration exceeded 0.001 molal in the absence of potassium, the settling of montmorillonites was found to be a function of the magnesium-strontium ratio at any selected ionic strength. The resultant settling velocities were always less, however, than the rates found for montmorillonites in systems having a 3 : 1 magnesium-potassium ratio (Table 19 and Fig. 19). The theoretical equivalence of the univalent

TABLE 19.—INFLUENCE OF MAGNESIUM-STRONTIUM, MOLAL, IONIC RATIOS UPON THE SETTLING VELOCITIES OF MONTMORILLONITES IN SALINE WATERS OF EQUIVALENT IONIC STRENGTH

Mg/Sr Sr (0.001 molal)	Settling Rates (m/day) (26°C, pH = 6.5-9.8)					
	Ionic Strength					
	7	14	22	36	50	65
1 : 1	0.02	0.04	0.06	0.15	0.18	0.18
2 : 1	0.02	0.04	0.06	0.16	0.21	0.22
3 : 1	0.06	0.09	0.15	0.27	0.33	0.34
4 : 1	0.07	0.12	0.21	0.34	0.42	0.43
5 : 1	0.11	0.17	0.30	0.44	0.54	0.56
6 : 1	0.11	0.18	0.33	0.49	0.60	0.63
7 : 1	0.12	0.22	0.39	0.58	0.72	0.74
8 : 1	0.14	0.25	0.46	0.65	0.83	0.84
9 : 1	0.15	0.27	0.52	0.72	0.92	0.95

crystal radii of strontium and potassium (i.e. 1.32 Å v. 1.33 Å) may be influential in this apparent similarity of action by strontium and potassium, even though the divalent crystal radius of strontium is 1.13 Å. No dependence of settling rates of any clay mineral upon  $\text{Na}^+ : \text{Mg}^{2+}$ ,  $\text{Na}^+ : \text{Ca}^{2+}$ ,  $\text{Na}^+ : \text{K}^+$ ,  $\text{Mg}^{2+} : \text{Ca}^{2+}$ ,  $\text{Ca}^{2+} : \text{K}^+$  ratios at any constant ionic strength was noted.

The dominant cation exchange tendencies for the various clay minerals in ocean water were evaluated qualitatively on the basis of chemical analysis of the flocculates formed during the settling processes. The dominant tendencies may be summarized on an equilibrium basis as follows :

- |  |   |
|--|---|
| (1) Kaolinites<br>and<br>halloysites                   | $\text{Na}^+$ for $\text{K}^+$ , $\text{Na}^+$ or $\text{Mg}^{2+}$ for $\text{Ca}^{2+}$ , $\text{K}^+$ for $\text{Ca}^+$ ,<br>$\text{Mg}^{2+}$ for $\text{Na}^+$ , $\text{Mg}^{2+}$ for $\text{H}_3^+\text{O}$ .                      |
| (2) Illites<br>and<br>vermiculites                     | $\text{K}^+$ for $\text{H}_3^+\text{O}$ and $\text{H}_2\text{O}$ , $\text{Na}^+$ for $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ for<br>$\text{Na}^+$ , $\text{Ca}^{2+}$ for $\text{Mg}^{2+}$ , $\text{Mg}^{2+}$ for $\text{H}_3^+\text{O}$ . |
| (3) Montmorillonites<br>and<br>mixed-layer<br>minerals | $\text{K}^+$ for $\text{H}_3^+\text{O}$ and $\text{H}_2\text{O}$ , $\text{Mg}^{2+}$ for $\text{H}_3^+\text{O}$ , $\text{Mg}^{2+}$ for<br>$\text{Na}^+$ , $\text{Na}^+$ for $\text{Ca}^{2+}$ .   |
| (4) Chlorites  | $\text{Na}^+$ for $\text{K}^+$ , $\text{Na}^+$ for $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ for $\text{Mg}^{2+}$ , $\text{Mg}^{2+}$<br>for $\text{H}_3^+\text{O}$ and $\text{H}_2\text{O}$ .   |

These cation exchange tendencies apply during the settling of the clay minerals in ocean water of usual ionic ratio composition and to some extent within the settled clay deposit. However, the interstitial waters of actual marine deposits commonly develop a high  $\text{Ca}^{2+}$  content from nonclay mineral sources, and sodium-calcium exchange equilibria are altered to favor calcium replacement of sodium in illites and sodium or calcium replacement of any exchangeable magnesium in montmorillonitic clays. Considerable magnesium is, however, fixed by montmorillonites upon aging (Whitehouse and McCarter, 1958) and is not subject to replacement via ordinary ion exchange equilibria processes.

*The "Coacervate," or the Nature of Clay Mineral Settling Units or "Particles" in Ocean Water and Artificial Sea-water*

On the basis of evidence collected it is concluded herein that clay minerals do not settle as single solid unit phases, grains or solid aggregates in ocean water. The settling velocities of clay minerals in saline water are controlled by ion exchange and ion fixation mechanisms, by the coacervation tendencies of the clay minerals, and by the coulombic forces of the ionic components of the water. An idealized representation of a settling clay mineral coacervate is shown in Fig. 20. The circular form shown for the coacervation states was selected for convenience only and flake-like solid particles are not always involved. In fact, the coacervation states of montmorillonites have been shown by Whitehouse and McCarter (1958, pp. 88, 114) to contain interlocking, or interweaving, strands or threads of clay in association with occluded water.

Despite ionic replacements that occur, kaolinitic clay mineral "floculates" may be redispersed by decreasing the ionic strength of the saline water settling media and the settling velocity at the lower chlorinity reclaimed in the chlorinity range 2.2-20‰. A similar redispersal of illitic settling units can be effected in the chlorinity range 3.8-20‰. Montmorillonitic settling rates can be reclaimed by proper dilution down to a chlorinity of

about 8.1‰ and chlorites redisperse in the range 0.5–20‰. Complete, exact reclamation of the distilled water settling rates can not be effected by distilled water washing procedures, or by peptization procedures that utilize Calgon (sodium “hexametaphosphate”), ammonia solution, sodium hydroxide, sodium carbonate, “sodium lignosulfonate” (Marasperse N), or sodium pyrophosphate. Clay materials that have been exposed to ocean water exhibit a dispersal resistance to ultimate deflocculation that is distinctly different from the resistance displayed by similar materials not so exposed (see Whitehouse and Jeffrey, 1955). Nevertheless, it is apparent that the clay mineral settling unit is not a single, permanently formed, solid entity.

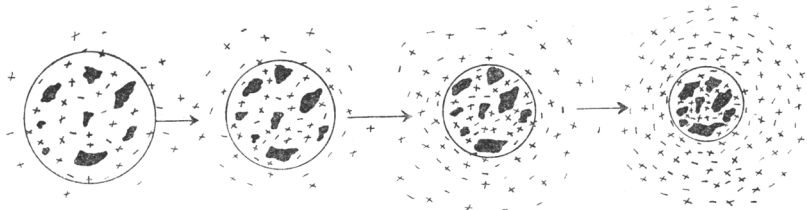


FIGURE 20.—Idealized representation of the effective settling entity (coacervate) of a clay mineral in saline water; increase in effective density, by ionic dehydration and coulombic force-induced deocclusion of water, without change in solid mass content. Solid black areas, clay with residual negative charge; plus and minus signs, ionic constituents in water; circles, settling coacervates (liquid–solid phases); arrows, direction of increasing ionic concentration of sea-water.

Further support to the concept of a settling coacervate has been given by the previous discussion of the use of the Gompertz type settling rate equation (see “Experimental Results, differential settling of clay minerals in artificial sea-water”). Even more striking in this connection is the correlation of the data acquired for light transmission of agitated clay mineral–saline water systems at  $\lambda = 400 \text{ m}\mu$  with the settling velocity data at specific chlorinities. These transmission data are shown in Table 20 for clay mineral concentrations of 0.2 g/l. over the chlorinity range 0.2–18‰ for four clay mineral types. The electron microscopic particle size ranges for solid clay are also given.

The change in chlorinity over the range 2.0–18‰ had little, if any, measurable effect on the transmission of 400 m $\mu$  radiation by kaolinitic, chloritic and illitic clay mineral suspensions, but was quite significant toward such transmission by montmorillonitic suspensions. These data fit well with the data previously cited for changes in the settling velocities of the clays as the chlorinity varies and imply that the effective settling “size” of the “floculates” does not change if transmission remains constant. Further, levels of maximum transmission at high chlorinities are inversely related to the solid particle sizes determined by electron microscopy, i.e.  $M = I > C > K$ . At the lower chlorinities (0.2‰) the smaller the solid size, the less the transmission. Chlorites are in a more advanced state of flocculation at 0.2‰

TABLE 20.—LIGHT TRANSMISSION<sup>1</sup> OF AGITATED, NONSETTLING CLAY MINERAL-OCEAN WATER SYSTEMS AS CHLORINITY INCREASES (26–27°C, 0.2 g clay mineral per l.;  $\lambda = 400 \text{ m}\mu$ )

Clay Mineral	Transmission (%)									E.M. Solid Particle Size <sup>2</sup> (m $\mu$ )
	Chlorinity (‰)									
	0.2	0.4	0.8	1.0	2.0	4.0	8.0	12.0	18.0	
Montmorillonites	3.7	5.4	7.4	9.0	20.0	26.0	38.5	43.0	45.0	2–40
Kaolinites	12.1	15.7	23.3	26.0	27.2	27.2	28.0	28.0	28.0	120–200
Illites	11.0	13.4	29.8	38.8	43.3	45.0	45.0	45.0	45.0	50–80
Chlorites	9.6	21.4	27.9	31.2	31.5	31.5	31.5	31.5	31.5	150–400

<sup>1</sup> Transmission of saline water involved is reference 100 percent transmission.

<sup>2</sup> Redispersed in distilled water.

than are kaolinites. Vermiculites are not listed but the transmission characteristics are similar to illitic suspensions above a chlorinity of 6‰. The general folding of vermiculite sheets during flocculation at lower chlorinities is shown in Fig. 8.

As an example of the correlation between transmission studies and settling rate studies, the expression for the transmission of montmorillonitic suspensions can be written as follows:

$$(T_x)_t = (T_0)_t + A_t B_m^{C_m} \left(\frac{x}{2} - 1\right)$$

where  $T_x$  = transmission at chlorinity  $x$  and temperature  $t$ ;

$T_0$  = transmission at distilled water-clay suspension at temperature  $t$ ;

$A_t, B_m, C_m$  = constants;  $A_t$  is  $t$  dependent;

$x$  = chlorinity of ocean water in ‰;

At 26.5°C, the constants,  $A_t, B_m, C_m$ , have the values 28.49, 0.0922, and 0.4606, respectively. The parallelism of this equation and the expression,

$$(r_x)_t = (r_0)_t + A_t B_m^{C_m} \left(\frac{x}{2} - 1\right)$$

previously given for settling rates is shown clearly in Table 21. Fractional increases in transmission and settling velocity relative to total increases over the chlorinity range 2–18‰ are compared. Such agreement supports the argument that the same dominant mechanism controls both effects. Similar action is characteristic of illitic, kaolinitic, and chloritic systems below chlorinities of 4‰, 2‰ and 1‰, respectively.



TABLE 21.—COMPARISON OF LIGHT TRANSMISSION AND SETTLING VELOCITY EQUATIONS FOR MONTMORILLONITIC CLAY MINERALS

Chlorinity	$\frac{T_x - T_0}{T_{18} - T_0}$	Interval Increase	$\frac{r_x - r_0}{r_{18} - r_0}$	Interval Increase
2	0.107	0.183	0.089	0.171
4	0.30	0.47	0.25	0.43
8	0.77	0.21	0.68	0.19
12	0.92	0.08	0.88	0.12
18	1.00		1.00	

The data given in Table 20, of course, apply to only one concentration level of clay mineral, and space does not permit complete tabulation of results at other concentrations. The same general phenomena are exhibited, however, over the clay mineral concentration range 0.01–3.6 g/l. except that over-all transmission decreases with increasing concentration provided the solid particulate and mineralogical nature of the solid does not change significantly. As solid particle size decreases, however, light transmission becomes dominantly a function of the wave length of the light employed rather than a function of the mass of the solid clay. In distilled-water suspensions of the individual clay types, transmission increases with increasing wave lengths in the range 400–900  $m\mu$ . Such increase exhibits some correspondence with the Rayleigh (1899) law despite the nonsphericity of the clay solid particles. As solid particle size increases the light transmitted is no longer critically determined by wave length and becomes a function of the opacity and reflection characteristics of the clay material and the refractive index of the suspension. Flocculation of clay minerals by sea-water increases transmission at shorter wave lengths (400  $m\mu$ ) and decreases transmission at the longer wave lengths (900  $m\mu$ ). These phenomena imply that the solid particles form closely associated groups of particles, upon flocculation, with greater separation between groups and closer association within each group as the chlorinity increases. No change in solid mass per group is necessary. Such a phenomenon is "coacervation."

Further, if such association of solid particles forms the settling entity, ultramicro-extractions of the suspensions should give random, rather than uniform, mass per unit volume at some ultramicro-level. This level, if detectable, should vary for different clay types and different chlorinities if the states of association of the solid particles differ. This variation is shown in Table 22, which lists results based on the ultramicropipette method described in "General Discussion, experimental methods," in this report. The total solid of 2 g/l. was recovered in every case and the consistent results obtained at  $1 \times 10^{-9}$  ml argue against the possibility of experimental error effects.

TABLE 22.—STATISTICAL STUDY OF ULTRAMICRO FRACTIONS OF CLAY MINERAL-OCEAN WATER AGITATED SUSPENSIONS  
(2 g clay mineral per l.)

Chlorinity (%)	Clay Mineral	Wt. of Solid per Microfraction <sup>1</sup> (value listed $\times 10^n =$ g per fraction)							E.M. Solid Particle Size <sup>2</sup> (m $\mu$ )
		Microfraction (ml)							
		$10^n$	1 $10^{-3}$	$1 \times 10^{-1}$ $10^{-4}$	$1 \times 10^{-2}$ $10^{-5}$	$1 \times 10^{-3}$ $10^{-6}$	$1 \times 10^{-6}$ $10^{-9}$	$1 \times 10^{-9}$ $10^{-12}$	
2	K	2.00	2.00	2.00	(2.9-1.1)	2.00	2.00	120-200	
	M	2.00	2.00	2.00	2.00	2.00	2.00	2-40	
	I	2.00	2.00	2.00	(2.8-1.2)	2.00	2.00	50-80	
4	K	2.00	2.00	2.00	(3.9-0.1)	2.00	2.00	120-200	
	M	2.00	2.00	2.00	2.00	(2.47-1.53)	2.00	2-40	
	I	2.00	2.00	2.00	(3.7-0.3)	2.00	2.00	50-80	
8	K	2.00	2.00	2.00	(3.93-0.07)	2.00	2.00	120-200	
	M	2.00	2.00	2.00	2.00	(3.44-0.56)	2.00	2-40	
	I	2.00	2.00	2.00	(3.8-0.2)	2.00	2.00	50-80	
12	K	2.00	2.00	2.00	(3.92-0.08)	2.00	2.00	120-200	
	M	2.00	2.00	2.00	2.00	(3.79-0.21)	2.00	2-40	
	I	2.00	2.00	2.00	(3.8-0.02)	2.00	2.00	50-80	
18	K	2.00	2.00	2.00	(3.93-0.07)	2.00	2.00	120-200	
	M	2.00	2.00	2.00	2.00	(3.95-0.05)	2.00	2-40	
	I	2.00	2.00	2.00	(3.8-0.02)	2.00	2.00	50-80	

<sup>1</sup> Average wt. per fraction based on 100 random extractions.

<sup>2</sup> Redispersed in distilled water.

The concept of a coacervated state, reversible or modified by saline water dilution, as the settling clay mineral entity, requires a revision of ideas relative to "particle" and "floculate" if such state persists in turbulent flows of saline water. Material "particulate" to one environment may be "flocular" to another environment, and material "particulate" to the second environment may be "flocular" to a third environment or to the first environment. In chemical ionic systems such as saline water, the "flocular bonds" must be considered of different "flocular bond strengths" and "bond orientation" as the chemical nature of the water system and the "floculate" varies. Such "floculates" will rarely be destroyed by mechanical dispersion alone, but can be modified by heat of dilution. To this extent the "coacervate" is a thermodynamically reversible entity.

The settling velocities of the coacervates of the clay minerals do not always represent, however, completely monodisperse settling systems (Fig.

11), particularly when a significant range of initial solid particle sizes (determined by electron microscopy) is involved. In general, the larger solid particles are found in any slower-settling coacervates and the smaller particles in any faster-settling coacervates. For example, the larger particles or crystals of kaolinite were found in the 0.65–0.80 cm/min settling fraction of kaolinite at a chlorinity of 0.5‰ (Fig. 11) and the smallest solid size range occurred in the 0.82–0.95 cm/min settling fraction. The bulk of the material, consisting of large to small solid units, was confined to the essentially mono-disperse coacervate settling fraction of 0.80 cm/min. This phenomenon is exhibited during the flocculation and settling of lyophobic suspended matter (Hartman, 1939) but its occurrence in settling coacervates has not been previously emphasized. The slower settling rates for the settling units containing the larger solid particles may be a consequence of horizontal orientation of the larger particles to produce maximum resistance of the coacervate to fall through the liquid settling medium. The general results for three clay types are shown in Table 23. These results offer one possible explanation for the observation of Powers (1954) that the solid crystal size of some clay minerals may show a slight increase in a downstream direction in some environments.

TABLE 23.—ELECTRON MICROSCOPIC STUDY OF SOLID PARTICLE SIZES WITHIN CLAY MINERAL SETTLING FRACTIONS (26°C; pH = 8.2)

Clay Mineral	Chlorinity (‰)	Settling Fraction (cm/min)	E.M. Solid Particle Sizes <sup>1</sup> (m $\mu$ )
Kaolinites	0.5	0.65–0.80	120–205
	0.5	0.80–0.82	120–160
	0.5	0.82–0.95	120–130
	18.0	0.78–0.81	120–205
	18.0	0.81–0.82	120–165
	18.0	0.82–0.98	120–125
Montmorillonites	0.5	0.0010–0.0020	2–40
	0.5	0.0020–0.0021	2–32
	0.5	0.0021–0.0036	2–20
	18.0	0.085–0.088	2–40
	18.0	0.088–0.090	2–30
	18.0	0.090–0.105	2–24
Illites	0.5	0.76–0.89	50–80
	0.5	0.89–0.91	50–72
	0.5	0.91–0.95	50–55
	18.0	0.96–1.10	50–80
	18.0	1.10–1.12	50–70
	18.0	1.12–1.15	50–58

<sup>1</sup> After redispersal in distilled water.

Heavy metal cations such as  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{4+}$  (Table 4) increase settling rates, or decrease the extent of coacervation, of the clay minerals in sea water. The higher settling velocities shown in Fig. 19 reflect the influences of the concentrations of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{4+}$  given in Table 4. The presence of  $4 \times 10^{-4}$  molal  $\text{Fe}^{3+}$  in sea-water (chlorinity = 19.392‰) induces the following increases in settling rates: kaolinites, from 11.8 to 13.4 m/day; montmorillonites, from 1.25 to 2.32 m/day; illites, from 15.8 to 16.4 m/day.

*The Differential Transport of Clay Minerals by the  
Turbulent Flow of Sea-water Through a Pipe*

The differential transport of clay minerals by turbulent saline water was investigated as described under "General Discussion, experimental methods", preceding. The persistence of clay mineral settling entities in such water has been shown in Table 16 and discussed previously.

The flow velocities required to sustain constant concentrations of four individual clay mineral types are shown in Table 24. The actual values

TABLE 24.—TRANSPORT OF CLAY MINERALS BY THE TURBULENT FLOW OF OCEAN  
WATER THROUGH 1 IN. I.D. PIPE  
( $25 \pm 1^\circ\text{C}$ ;  $\text{pH} = 8.2$ )

Clay Type <sup>1</sup>	Clay Conc. (g/l.)	Chlorinity (‰)	Suspension Sustaining Velocity (cm/sec)	Sustaining Velocity (miles/hr)
M	2	19.3	80.5	1.8
M	10	19.3	105.0	2.1
K	2	19.3	215.0	4.8
K	10	19.3	241.0	5.4
I	2	19.3	277.0	6.2
I	10	19.3	295.0	6.6
C	2	19.3	240.0	5.4
C	10	19.3	266.0	5.9

<sup>1</sup> M = montmorillonites, K = kaolinites, I = illites, C = chlorites.

obtained can not be applied realistically to turbulent flow of water through a river channel or in oceanic waters but the relative values indicate that turbulent flowing water transports clay minerals differentially with respect to mineral type. This is further emphasized by the data in Table 25 for the relative clay mineral enrichment of effluent induced by repeated recirculation of sea-water-clay mixture suspension fractions through 100 ft of pipe having an inner diameter (i.d.) of 1 in.

These results imply that clay mineral mixtures possibly can be transported short geographic distances by rapidly moving turbulent sea-water without

TABLE 25.—RELATIVE CLAY MINERAL ENRICHMENT OF EFFLUENT VIA REPEATED RECIRCULATION OF SEA-WATER-CLAY MIXTURE SUSPENSION FRACTIONS THROUGH 100 FT OF 1 IN. I.D. PIPE  
( $25 \pm 1^\circ\text{C}$ , chlorinity = 19.3‰, pH = 8.2)

Clay Mixture <sup>1</sup> (2 g/l.)	Flow Rate (cm/sec)	Affluent <sup>2</sup> (4 passes)
30 M, 35 K, 35 I	80.5	91.3 M, 1.2 K, 7.5 I
30 M, 35 K, 35 I	215.0	44.8 M, 44.9 K, 12.3 I
30 M, 35 K, 35 I	277.0	33.1 M, 35.5 K, 28.4 I

<sup>1</sup> M = montmorillonites, K = kaolinites, I = illites.

<sup>2</sup> 1200, 800, 400, 200 l.

differential transport being involved, but that transport is selective of clay mineral type in many cases. Transport without differentiation does not mean that differential settling is eliminated. If settling occurs at all, clay mineral types exhibit different rates of fall.

*The Influence of Clay Mineral Concentration Gradients Upon the Settling Velocities of Clay Minerals in Sea-water*

The relative effect of concentration gradients upon the measured settling velocities of three clay mineral types has been shown in Table 12. The data for the rate of clearing (spectrophotometric method) and for the not-stirred, manometer method are pertinent in this regard. As concentration of clay mineral increases, the rate of clearing (at a specific level within the settling system) decreases. The results obtained, when the clay suspensions used in the manometer method were not restirred in the manometer, also show such decrease in settling rate as the clay concentration increases.

Other results were obtained from studies of concentration gradients in tanks providing total water depths of 4 ft and 6 ft. Concentrations of four clay mineral types were varied over the range 0.05–20 g/l. The significant data obtained may be summarized as follows: kaolinites and chlorites exhibited settling rates comparable to those shown in Fig. 12 until a depth of 2.35 ft was reached in the clay concentration range 10.5–20.0 g/l. A decrease of 22.4 percent in settling rate occurred in the depth range 2.35–3.92 ft in 6 ft of water. For chlorite and kaolinite concentrations below 10.5 g/l., the settling rates shown in Fig. 12 were maintained to a depth of 3.85 ft in water of 6 ft depth. Illitic settling rates (Fig. 12) were maintained to a depth of 3.6 ft in water of 6 ft depth over the clay concentration range 0.05–15.8 g/l. In the 15.8–20.0 g/l. concentration range, illitic settling rates decreased 25.2 percent in the water depth range 2.16–3.8 ft. Typical montmorillonitic settling rates persisted to a depth of 4.52 ft in 6 ft of water over the concentration range 0.05–3.6 g/l. In the range 3.6–4.5 g/l. the random fall of gelatinous “lumps” of montmorillonite–water associations occurred, and

above 4.5 g/l. the montmorillonite suspensions cleared in a time-dependent stepwise fashion at a rate as slow as 0.005 cm/min at chlorinities less than 2‰.

The results obtained could not be explained on the basis of any hypso-metric decrease expression as depth increased, and the influence of clay mineral concentration gradients upon settling rates needs more extensive study for proper evaluation of the tendencies in some quiet water estuarine and marine environments. However, all clay minerals cited (except montmorillonites) eventually settled to the bottom of the columns. In clay mixtures a thixotropic suspension of montmorillonites persisted in the first 6 in. to 1 ft of water overlying the bottom deposits containing all clay minerals involved. Further, the bottom deposits exhibited no stratification with respect to clay mineral type after 3 days of aging. Reagitation, by a stirring rod, within the top 2 ft of water at 1 hr intervals over a period of 3 days kept the bottom deposits essentially free of montmorillonite if the original montmorillonite concentration did not exceed 2 g/l. Aging, without such agitation, produced a bottom deposit containing montmorillonite from which illites, kaolinites and chlorites were more easily removed than montmorillonite by agitation of the overlying thixotropic montmorillonitic suspension. Differential settling reoccurred, however, in the resuspended clay mineral mixtures.

*The General Influence of Selected Organic Materials  
Upon the Settling Rates of Clay Minerals  
in Quiet Artificial Sea-water*

Clay minerals that pass from terrestrial to marine environments encounter detrital organic matter during differential settling and after deposition. Such organic matter is derived from the decomposing bodies and dead gametes of innumerable marine plants and animals, from the largest to the most minute, and in certain regions from sewage, industrial wastes and other materials of terrestrial origin. Such detritus exists in relatively large masses in coarsely particulate form, in various degrees of colloidal dispersion, and in solution. ZoBell (1946) estimated that the amount of "dissolved" organic matter in near-shore sea-water averaged at least 5 mg/l. Fox (1950) considered this a conservative estimate and describes this organic matter as colloidal rather than "dissolved". Collier, Ray and Magnitzsky (1950) reported carbohydrates in sea-water. Concentrations as high as 0.1 g/l. were cited by the last-named investigators who considered such carbohydrate content largely in the form of dehydroascorbic acid and an unidentified "rhamnoside". Hood and Jeffrey (1953) studied the carbohydrate content of sea-water and gave a preliminary estimate of 0.1 mg/l. for the concentration of dehydroascorbic acid in sea-water. The presence of organic matter in sea-water and in marine sediments may have great influence on many natural processes that occur along the transport path of sedimentary matter and within marine deposits. Our attention herein is confined, however, to the influence of such matter upon differential settling rates of clay minerals.

Interaction of pure organic compounds with clay materials, particularly montmorillonite, has been studied by Hendricks (1941), Nikkilä and Oker-Blom (1952), Demolin and Barbier (1929), Ensminger and Gieseck (1942), Jordan (1949), Stevenson *et al.* (1952), Pinck and Allison (1951), MacEwan (1948), Myers (1937), Hansen (1944), Hauser (1950), Grim, Allaway and Cuthbert (1947), Bradley and Grim (1948), Whitehouse and Jeffrey (1953a), Whitehouse and McCarter (1958), and others. However, many of these investigators employed heat and considerable agitation, or both, in order to effect formation of the clay-mineral complex, although Pinck and Allison (1951) suggested that considerable interaction between montmorillonite and gelatin occurs in a simple mixture of clay and gelatin. Ensminger and Gieseck (1942) previously studied gelatin-clay complexes in acidic media. Meyers (1937) also indicated that adsorption of organic colloids to montmorillonite is most readily realized at low pH. Hendricks (1941) implied that large organic cations are retained by the clay micelle via van der Waals forces as well as by electrostatic forces. Hauser (1950) described to some extent the effect of adsorbed organic materials upon the physical properties of clay minerals. MacEwan (1948) demonstrated the affinity of polar organic molecules for montmorillonites and halloysites. Whitehouse and Jeffrey (1953a) described the adsorption tendencies of illitic, kaolinitic and montmorillonitic clay minerals for four selected carbohydrates dissolved in sea-water. Walker (1950) and Barshad (1950) have studied some types of vermiculite-organic complexes.

The interaction of organic matter with settling clays under conditions common to sea-water has been reported only by Whitehouse and Jeffrey (1953a) and Whitehouse and McCarter (1958), although Rivière (1953) has described some indirectly related work in this connection.

The general, over-all, influences of 57 different organic materials upon the settling rates of clay minerals in artificial sea-water are shown herein in Fig. 21. All effects indicated are not necessarily a consequence of actual adsorption of the organic materials by the clay minerals. In many cases, the influence is more properly considered a consequence of decreased inorganic ionic strength of the sea-water due to the formation of inorganic-organic ionic complexes. The specific results for 57 different organic structures, selected from the organic materials listed in "General Discussion, organic materials," are shown in Tables 26 and 27. An estimate of the nature of the active influence on settling rate is given therein in terms of extent of adsorption or degree of decreased inorganic ionic activity. The methods employed for adsorption measure and the freezing point lowering method used to estimate effective ionic strength have been described briefly in "General Discussion, experimental methods." The reader is referred to Cheronis (1954) for additional information. The concentrations of organic material listed are representative only. The phenomena of "salting in" and "salting out" of the various organic compounds are not discussed here. The use of relatively high concentrations of organic material in some cases parallels the condition of clay material falling through a column of sea-water and

subsequently being subject to more and more organic influences as it falls. This was confirmed experimentally.

A full evaluation of all results tabulated in Tables 26 and 27 is beyond the scope or emphasis of this paper. However, some specific observations with regard to the apparent nature, type and extent of the adsorption tendencies abets the understanding of the relative effects of the organic materials upon clay mineral settling rates. Sea-water of usual composition is an alkaline

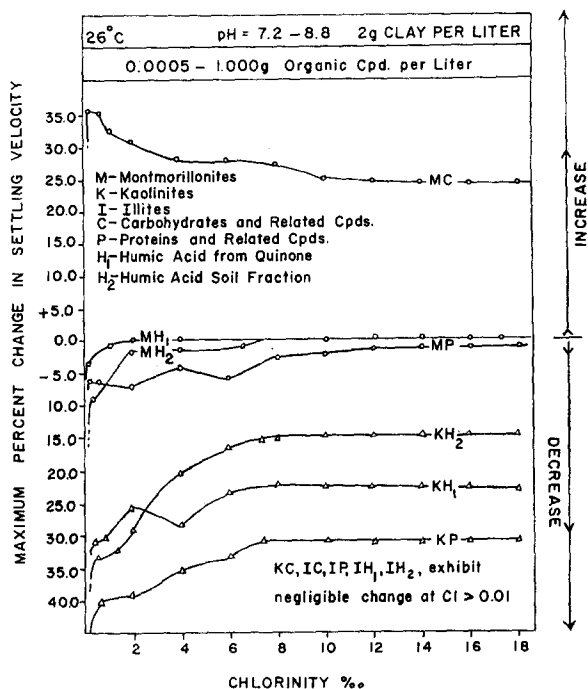


FIGURE 21.—General influence of dissolved, colloidal and suspended organic materials upon the settling velocities of clay minerals in artificial sea-water.

medium and the results summarized herein largely pertain to such alkaline media. Further, possible cementation effects of large quantities of organic materials upon clay minerals prior to marine transport and settling are not reflected in the tabulated results. Only the competitive tendencies of inorganic ionic exchange with organic adsorption or organic-inorganic ionic interactions along the transport path, or during active clay mineral sedimentation, are indicated by the results presented.

Kaolinitic clays tended to adsorb more simple carbohydrate material (mono- and disaccharides) than did the other clay minerals. Only montmorillonites adsorbed the trisaccharide, raffinose. While kaolinites extracted



TABLE 26.—GENERAL INFLUENCE OF DISSOLVED, COLLOIDAL AND SUSPENDED CARBOHYDRATES  
ARTIFICIAL  
(26°C, pH = 7.2–8.8, 0.0005–1.000 g

Compound	General Structure	Percent Change in Settling Velocity <sup>a</sup>					
		Cl% <sub>∞</sub> <sup>b</sup> =					
		0.5 K	18.0	0.5 I	18.0	0.5 M	18.0
1. Xylose	Aldopentose	0.0	0.0	0.0	0.0	+0.1	0.0
2. Arabinose	Aldopentose	0.0	0.0	0.0	0.0	+0.1	0.0
3. Galactose	Aldohexose	0.0	0.0	0.0	0.0	+0.2	0.0
4. Glucose	Aldohexose	0.0	0.0	0.0	0.0	+0.2	0.0
5. Mannose	Aldohexose	0.0	0.0	0.0	0.0	+0.2	0.0
6. Fructose	Ketohexose	0.0	0.0	0.0	0.0	+0.2	0.0
7. Sorbose	Ketohexose	0.0	0.0	0.0	0.0	+0.2	0.0
8. Fucose	Deoxyhexose	0.0	0.0	0.0	0.0	+0.1	0.0
9. Rhamnose	Deoxyhexose	0.0	0.0	0.0	0.0	+0.1	0.0
10. Desoxyribose	Deoxypentose	0.0	0.0	0.0	0.0	+0.1	0.0
11. Erythritol	Polyhydric alcohol	0.0	0.0	0.0	0.0	+0.1	0.0
12. Arabitol	Polyhydric alcohol	0.0	0.0	0.0	0.0	+0.1	0.0
13. Inositol	Hexahydrohexahydroxy benzene	0.0	0.0	0.0	0.0	+0.2	0.0
14. Xylitol	Polyhydric alcohol	0.0	0.0	0.0	0.0	+0.1	0.0
15. Sorbitol	Polyhydric alcohol	0.0	0.0	0.0	0.0	+0.1	0.0
16. Dehydroascorbic Acid	Oxidized dienol furanose (lactone)	-0.05	0.0	-0.02	0.0	-0.6	0.0
17. Lactose	Galactosidoglucose	0.0	0.0	0.0	0.0	+0.2	0.0
18. Sucrose	Glucosidofructoside	0.0	0.0	0.0	0.0	+0.2	0.0
19. Cellulose	Glucosidoglucose	0.0	0.0	0.0	0.0	+0.2	0.0
20. Melibiose	Galactosidoglucose	0.0	0.0	0.0	0.0	+0.2	0.0
21. Raffinose	Fructosidoglucosidogalactoside	0.0	0.0	0.0	0.0	+35.0	+25.1
22. Fucoidin	Polyfucose sulfuric ester	-0.4	0.0	+0.1	0.0	+35.1	+25.1
23. Agar	Polygalactose-arabinose sulfuric ester	-0.2	0.0	+0.1	0.0	+20.2	+12.2
24. Inulin	Polyfructoside	0.0	0.0	0.0	0.0	+30.1	+10.2
25. Starch, Dextrin	Phosphatopolyamyloso-glucosides	-0.2	0.0	-0.1	0.0	+0.05	0.0
26. Cellulose	Polyglucosidoglucosides	0.0	0.0	0.0	0.0	0.0	0.0
27. Heparin	Polysulfamic-acetyl amino-glucose	-0.1	0.0	0.0	0.0	-0.1	0.0
28. Hyaluronic Acid	Polyglucosamineglucuronic acid	-0.2	0.0	-0.05	0.0	+0.05	0.0
29. Quercetin	Pentahydroxyflavonol	0.0	0.0	0.0	0.0	-0.03	0.0
30. Pectin	Methyl galacturonic acid	-0.1	0.0	-0.03	0.0	+0.08	0.0

AND RELATED COMPOUNDS UPON THE SETTLING VELOCITIES OF CLAY MINERALS IN QUIET SEA-WATER<sup>1</sup>

organic epd. per l., 2 g clay per l.)

Percent Change in Settling Velocity				Maximum Degree of Adsorption					Percentage Wash Removable					Percentage Change in Ionic Strength	
Cl(‰) <sup>2</sup> =				(mg/g clay)										Cl(‰) <sup>2</sup> =	
0.5 C	18.0	0.5 V	18.0	K	I	M	C	V	K	I	M	C	V	0.5 <sup>3</sup>	18.0
0.0	0.0	+0.03	0.0	0.62	0.13	0.20	0.30	0.15	100	100	20	100	97		Negligible
0.0	0.0	+0.03	0.0	0.62	0.13	0.21	0.31	0.15	100	100	20	100	96		Negligible
0.0	0.0	+0.05	0.0	0.75	0.15	0.25	0.38	0.17	100	100	20	100	98		Negligible
0.0	0.0	+0.05	0.0	0.75	0.14	0.25	0.40	0.18	100	100	22	100	96		Negligible
0.0	0.0	+0.05	0.0	0.75	0.15	0.25	0.38	0.17	100	100	22	100	96		Negligible
0.0	0.0	+0.05	0.0	0.75	0.15	0.25	0.38	0.18	100	100	22	100	96		Negligible
0.0	0.0	+0.05	0.0	0.75	0.15	0.25	0.38	0.18	100	100	22	100	96		Negligible
0.0	0.0	+0.04	0.0	0.66	0.12	0.22	0.32	0.12	100	100	14	100	94		Negligible
0.0	0.0	+0.03	0.0	0.65	0.13	0.22	0.33	0.12	100	100	12	100	96		Negligible
0.0	0.0	+0.02	0.0	0.54	0.11	0.18	0.27	0.12	100	100	16	100	96		Negligible
0.0	0.0	+0.03	0.0	0.48	0.10	0.17	0.24	0.10	100	100	20	100	98		Negligible
0.0	0.0	+0.03	0.0	0.62	0.14	0.22	0.32	0.16	100	100	20	100	97		Negligible
0.0	0.0	+0.05	0.0	0.73	0.15	0.25	0.39	0.15	100	100	22	100	98		Negligible
0.0	0.0	+0.02	0.0	0.62	0.13	0.20	0.30	0.15	100	100	20	100	97		Negligible
0.0	0.0	+0.03	0.0	0.75	0.13	0.26	0.40	0.18	100	100	22	100	96		Negligible
-0.02	0.0	-0.2	0.0	0.00	0.00	0.00	0.00	0.00	—	—	—	—	—	-1.1	-0.03
+0.05	0.0	0.0	0.0	1.50	0.30	0.50	0.75	0.34	100	100	20	100	95		Negligible
+0.05	0.0	0.0	0.0	1.51	0.32	0.50	0.76	0.33	100	100	22	100	96		Negligible
+0.05	0.0	0.0	0.0	1.50	0.32	0.48	0.75	0.33	100	100	22	100	96		Negligible
+0.05	0.0	0.0	0.0	1.50	0.34	0.50	0.75	0.33	100	100	22	100	96		Negligible
0.0	0.0	0.0	0.0	0.00	0.00	0.38	0.0	0.0	—	—	12	—	—		Negligible
+0.1	0.0	0.0	0.0	3.33	1.40	1.16	1.72	1.43	12	14	12	16	12	-0.3	0.0
+0.1	0.0	0.0	0.0	3.62	1.51	1.28	1.89	1.56	12	14	12	16	12	-0.3	0.0
+0.2	0.0	0.0	0.0	3.71	1.55	1.32	1.94	1.62	100	100	12	100	96		Negligible
+0.05	0.0	0.0	0.0	6.65	3.92	3.31	3.31	3.86	100	100	35	100	60	-1.3	-9.02
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—		Negligible
-0.03	0.0	0.0	0.0	3.34	1.42	1.15	1.75	1.40	12	13	12	14	12	-0.5	0.0
-0.05	0.0	0.0	0.0	3.42	1.54	1.48	1.82	1.62	100	100	86	100	100	-0.2	0.0
-0.15	0.0	0.0	0.0	1.55	0.35	0.53	0.78	0.38	100	100	22	100	100	-0.8	0.0
-0.02	0.0	0.0	0.0	0.82	0.17	0.27	0.42	0.20	100	100	21	100	98	-0.3	0.0

<sup>1</sup> See also Table 27.<sup>2</sup> Reference velocities shown in Fig. 12. K = kaolinites, I = illites, M = montmorillonites, C = chlorites, V = vermiculites.<sup>3</sup> Cl = chlorinity of water.<sup>4</sup> Repeated organic-free sea-water wash.<sup>5</sup> Cl = chlorinity of water.

TABLE 27.—GENERAL INFLUENCE OF DISSOLVED, COLLOIDAL AND SUSPENDED AMINO ACIDS, CLAY MINERALS IN QUIET (26°C, pH = 7.2–8.8, 0.0005–1.000 g

Compound	General Structure	Percent Change in Settling Velocity <sup>a</sup>					
		Cl(‰) <sup>b</sup> =					
		0.5 K	18.0 <sup>c</sup>	0.5 I	18.0	0.5 M	18.0
1. Glycine	α-Amino-acetic acid	-0.8	-0.1	-0.6	0.0	-1.1	-0.1
2. Arginine	Basic-α-amino acid	-1.5	-0.05	-0.8	0.0	-1.3	-0.2
3. Histidine	Basic-imidazole-α-amino acid	-1.8	-0.1	-1.2	0.0	-1.3	-0.2
4. Lysine	Basic-α-amino acid	-0.6	0.0	0.0	0.0	-0.1	0.0
5. Valine	Neutral-α-amino acid (nonpolar side chain)	-0.9	0.0	-0.8	0.0	-1.2	-0.1
6. Alanine	α-Aminopropionic acid	-0.8	-0.1	-0.6	0.0	-1.5	-0.1
7. Isoleucine	Neutral-α-amino acid (nonpolar side chain)	-0.1	0.0	-0.1	0.0	-0.4	0.0
8. Leucine	Neutral-α-amino acid (nonpolar side chain)	-0.1	0.0	-0.1	0.0	-0.2	0.0
9. Tryptophan	Neutral-indole-α-amino acid (polar side chain)	-2.6	-0.2	-0.1	0.0	-0.4	0.0
10. Methionine	Neutral-thio-α-amino acid (polar side chain)	-0.05	0.0	-0.1	0.0	-0.2	0.0
11. Phenylalanine	Neutral-phenyl-α-amino acid (nonpolar side chain)	0.0	0.0	-0.1	0.0	-0.3	-0.05
12. Threonine	Neutral-α-amino acid (polar side chain)	-0.2	0.0	-0.1	0.0	-0.2	0.0
13. Cystine	Neutral-thio-α-amino acid (polar side chain)	-0.1	0.0	-0.1	0.0	-0.2	0.0
14. Tyrosine	Neutral-phenolic-α-amino acid (polar side chain)	-7.6	-3.0	-0.1	0.0	-0.2	0.0
15. Aspartic acid	Acidic-α-amino acid	-0.6	-0.05	-0.3	0.0	-0.8	-0.1
16. Ovalalbumen	Polypeptide	-2.1	0.0	-0.1	0.0	-0.1	0.0
17. Lab. peptone	Polypeptide	-1.6	0.0	-0.1	0.0	-0.1	0.0
18. Casein, Vitellin	Phosphoprotein	-41.2	-30.1	-0.2	0.0	-6.5	-1.0
19. Protamine Nucleinate	Protamine	-1.1	0.0	0.0	0.0	-0.2	0.0
20. Edestin	Globulin	0.0	0.0	0.0	0.0	-0.1	0.0
21. Keratin, Zein	Scleroprotein	0.0	0.0	0.0	0.0	0.0	0.0
22. Gelatin	Polypyrrrolidine peptide	-0.5	0.0	-0.1	0.0	-0.5	0.0
23. Desoxyribonucleate	Phosphate-purine-deoxy-ribose	-4.6	-0.1	-0.3	0.0	-0.3	0.0
24. Histone (thymus)	Basic protein	-0.5	0.0	-0.2	0.0	-0.05	0.0
25. Lecithin	Phospholipid	-3.8	0.0	-0.6	0.0	-0.2	0.0
26. "Humic acid", H <sub>1</sub>	Ox. prod. of Quinone	-32.2	-24.8	-0.2	0.0	-2.2	0.0
27. "Humic acid", H <sub>2</sub>	Soil humus fraction	-33.8	-16.2	-0.1	0.0	-8.9	0.0

PROTEINS AND SELECTED OTHER ORGANIC COMPOUNDS UPON THE SETTLING VELOCITIES OF ARTIFICIAL SEA-WATER<sup>1</sup>

organic cpd. per l., 2 g clay per l.)

Percent Change in Settling Velocity <sup>2</sup>				Maximum Degree of Adsorption					Percent Wash Removable <sup>4</sup>					Percent Change in Tonic Strength	
Cl(‰) <sup>3</sup> =				(mg/g clay)										Cl(‰) <sup>3</sup> =	
0.5	18.0	0.5	18.0	K	I	M	C	V	K	I	M	C	V	0.5	18.0
C		V													
-0.6	-0.1	-0.5	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-1.9	-0.2
-0.3	0.0	-0.3	0.0	0.70	0.14	0.22	0.36	0.14	92	92	88	94	92	-1.2	-0.1
-0.2	0.0	-0.1	0.0	0.72	0.16	0.24	0.35	0.15	90	90	86	92	94	-1.5	-0.05
0.0	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-1.2	-0.1
-0.4	-0.1	-0.5	-0.1	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-1.8	-0.1
-0.3	0.0	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-1.7	-0.1
-0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-0.5	0.0
-0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-0.6	0.0
-0.1	0.0	-0.1	0.0	0.84	0.0	0.0	0.0	0.0	100	—	—	—	—	-0.6	0.0
-0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-0.5	0.0
-0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-0.3	0.0
-0.1	0.0	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-0.6	0.0
-0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-0.4	0.0
-0.1	0.0	-0.1	0.0	0.79	0.0	0.0	0.0	0.0	88	—	—	—	—	-0.5	0.0
-0.2	0.0	-0.4	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	-1.8	-0.1
-0.1	0.0	-0.1	0.0	3.15	0.60	1.12	1.41	0.56	100	100	95	100	100	-0.8	-0.03
-0.1	0.0	0.0	0.0	2.23	0.42	0.76	1.08	0.37	100	100	100	100	100	-0.7	-0.05
0.0	0.0	-0.8	0.0	31.21	0.74	1.56	1.41	0.60	5	95	90	100	100	-1.3	-0.1
0.0	0.0	-0.1	0.0	0.41	0.68	1.72	0.15	0.98	100	98	95	100	100	-0.1	0.0
0.0	0.0	0.0	0.0	0.0	3.10	10.61	0.0	0.0	100	100	100	100	100	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—	—	0.0	0.0
0.0	0.0	-0.2	0.0	6.42	1.32	2.16	0.0	1.08	100	100	100	100	100	-1.6	0.0
-0.2	0.0	-0.4	0.0	1.42	0.21	0.46	0.72	0.25	12	82	65	100	100	-0.7	0.0
-0.1	0.0	-0.1	0.0	2.56	0.51	0.83	1.34	0.46	100	100	96	100	100	-1.4	-0.1
-0.5	0.0	-0.6	0.0	49.0	0.83	1.83	1.65	0.83	88	100	94	100	100	-2.4	-0.1
-0.1	0.0	-0.2	0.0	2.12	0.04	0.05	0.06	0.05	62	100	100	100	100	-0.8	-0.2
-0.03	0.0	-0.1	0.0	1.56	0.21	0.15	0.86	0.22	76	100	88	100	100	-1.6	-0.1

<sup>1</sup> See also Table 26.

<sup>2</sup> Reference velocities shown in Fig. 12; K = kaolinites, I = Illities, M = montmorillonites, C = chlorites, V = vermiculites.

<sup>3</sup> Cl = Chlorinity of water.

<sup>4</sup> Repeated organic-free sea-water wash.

<sup>5</sup> Cl = chlorinity of water.

greater quantities of the monosaccharides (e.g. galactose) than of the disaccharides (e.g. sucrose), the same concentration (m-moles) of each sugar per g of clay mineral are adsorbed. Such relative relationship for mono- and disaccharides was also observed for extraction of these carbohydrates by illites, montmorillonites, chlorites and vermiculites, although less quantity of carbohydrate was adsorbed. In terms of m-moles of organic material per unit lattice mole of clay material, the following approximate tendencies were noted: kaolinites, 2.1; chlorites, 1.5; montmorillonites, 1.0; illites and vermiculites, 0.6. In contrast, however, montmorillonites adsorbed only 0.6 m-mole of raffinose per unit lattice mole of clay mineral. Such adsorption tendencies do not necessarily reflect the relative strengths of the affinities at the adsorption interface.

When a clay mineral is exposed to sea-water its ion exchange positions, both interlamellar and interlattice, tend to be occupied by such ionic constituents as  $Mg^{2+}$ ,  $Na^+$  and  $K^+$ . Such occupation tendencies not only compete with or inhibit entry of the organic molecules but also restrain the expansion of the clay mineral lattices. In addition, the extraction of organic material from the saline water can also be a function of the water content adsorbed or occluded within a coacervated settling clay mass. Consequently, all clay minerals containing extracted organic material were exposed to repeated washing with organic-free artificial sea-water. Kaolinitic, illitic and chloritic clays surrendered "adsorbed" mono- and disaccharides completely via such treatment. Vermiculitic clays retained very little, if any, extracted material after such washing procedure. Montmorillonites, on the other hand, retained approximately 80 percent of the adsorbed material.

The adsorption of raffinose is a special case. No detectable adsorption tendencies of kaolinites, illites, chlorites and vermiculites for this trisaccharide were observed. Montmorillonites exhibited some adsorption affinity but did not extract a quantity comparable to the molar weight ratio of trisaccharide to monosaccharide. Such adsorption inhibition would be anticipated if the adsorption is interlamellar in character. The size and shape of the trisaccharide may prevent its entry between unit cells of kaolinites, illites, chlorites and vermiculites under sea-water conditions while the more expandable framework of montmorillonites may permit limited entry of the carbohydrate. The settling velocity results obtained (Table 26) also reflect this possibility, and the diagenetic inhibition shown by Whitehouse and McCarter (1958) indicates that this carbohydrate, as well as the polysaccharide, fucoidin, is adsorbed within montmorillonite threads, such as are shown in Fig. 4, and thus decreases the expansion tendencies of the threads to facilitate coalescence or interweaving of the threads by coulombic forces of the sea water inorganic ions. The results listed for adsorption of the polysaccharides agar and inulin support this hypothesis. The stronger adsorption affinity of other clay minerals for fucoidin and agar possibly reflects the effects of the sulfuric acid groups of these carbohydrates.

The general adsorption tendencies of clay minerals for carbohydrates do

not follow the relative cation exchange capacity tendencies of the clay minerals. The adsorption, particularly that which is interlattice or on micelle solid surfaces, follows more directly the probability of hydrogen bonding via hydroxyl centers on the clay mineral surfaces. Similar adsorption tendencies for some monosaccharides would be anticipated since the enol forms are often the same in alkaline solution and equilibria between the enol form and all related monosaccharides simultaneously exist (e.g. between fructose, mannose, galactose and the same enol form).

The adsorption of proteins and related compounds apparently is related directly to the amphoteric character of such materials and seems to proceed, if at all, via organic carboxyl group interaction with adsorbed inorganic cations, via hydrogen bonding through  $\text{—NH—}$  group (not  $\text{NH}_2$ ), or via phosphato group interactions with positively charged broken edges of the solid clay. Ordinary phosphoric acid groups have minor effect in this connection but attachment via phosphato-linkages to long-chain aryl and alkyl organic structure apparently is essential for significant influence on settling rates. Note the influence (Table 27), of phosphoproteins such as casein and vitellin upon the settling rates of kaolinites. This follows the idea that adsorption at positive edges of the solid clay inhibits flocculation and settling. The influence of lecithin, a phospholipid, is also important in this connection, even though it is removed more readily from the clay minerals by washin. In some clay minerals, particularly montmorillonite, choline (from lecithin) possibly is adsorbed to some extent via  $\text{N}^+(\text{CH}_3)_3$  electrostatic bonds.

In many instances, small decreases in settling rates are intimately associated with decreases in effective ionic strength. Such decrease can be assigned to the formation of organic-inorganic ionic complexes via the organic carboxyl group; the  $\text{NH}_2$  group of proteins is relatively inactive in this connection in alkaline media. For a full discussion of such effects see Cohn and Edsall (1943) or similar treatises.

The general influences of "humic acids,"  $H_1$  and  $H_2$  cannot be assigned to any particular effect since these materials are complex and heterogeneous in molecular components. However, hydrogen bonding via keto and hydroxyl groups, and some ionic interaction probably directs the influences on settling rates shown in Fig. 21 for  $H_1$ .  $H_2$  contains some material of poly-amino acid nature and phospho-proteins, and hydrogen bonding via  $\text{—NH—}$  groups as well as inorganic cation-organic carboxyl group and phosphato linkages are active relative to kaolinite surfaces and exert minor effects on montmorillonites at low chlorinities or ionic strengths.

Although the magnitudes of the effects observed do not negate the over-all relative differential settling tendencies of clay minerals, the relative settling tendencies are modified to make the differentiation between kaolinites and other clay minerals more pronounced and increase the settling rates of montmorillonites by 25 to 35 percent. This latter influence does not introduce significant complexity into differential settling rate concepts since montmorillonites settle much less rapidly than other clay minerals above a chlorinity of 2‰.

## CONCLUSIONS

On the basis of all evidence collected and presented in this report, it is concluded that both differential settling and differential transport of clay minerals occur in estuarine and marine environments. Such differential settling within clay mineral mixtures is, to a marked degree, a function of differences in individual clay mineral types. However, minor quantities of single settling phases, containing specific intimate associations of different clay minerals, are sometimes developed during the flocculation of fresh-water source clay mixtures or by aging within sedimentary deposits on the marine floor.

Settling of clay minerals across fresh-water-saline-water transient interfaces occurs differentially or not at all. The clay mineral content of sedimentary deposits will reflect such differential settling laterally outward or inward from the saline water interface if net forward transport of the clay minerals is or has been active. However, vertical stratification of different clay mineral types or associations with depth within sedimentary deposits does not arise or persist as a consequence of differential settling. Such stratification can occur only as a result of definite environmental changes. In fact, repeated resuspension and subsequent outward transport of clay minerals may often modify the *relative* content of clay minerals within deposits such that the relative content of the more rapidly settling clay minerals will increase outward from shore as far as such continuous scouring of the deposits persists. Such effect is a direct consequence of either continuous leaching of the slower-settling materials from the deposits by repeated differential settling fractionation or lack of leaching of aged or viscous gels of the slower settling materials. Such processes also can increase effectively the relative content of those settling phases that contain more than one clay mineral type.

Clay mineral concentration gradients modify differential settling in quiet saline waters, and localized high concentrations of clay minerals (10–15 g/l.) in near-surface water may fall rapidly to the floor of shallow quiet saline water zones without appreciable differential settling if below-surface waters contain less than 1–2 g clay per l., i.e. a density gradient becomes active.

Clay minerals are not transported and do not settle as single solid grains or in irreversible solid states of aggregation in saline water. The settling unit is a thermodynamically reversible assembly of solid grains or threads, in association with occluded water and water of hydration, and has been termed herein a “coacervate.” The largest solid units or crystals are commonly within the slowest settling coacervates of any particular clay mineral type and any observations of increasing solid size with increasing distance from shore is a direct substantiation of active differential settling rather than a negation of such settling activity.

Rapidly moving turbulent water can transport clay mineral types without differential transport over long distances but eventually differential transport and differential settling will occur. Deposition requires such differential action unless a marked density gradient is active.

The factors of clay mineral lattice type, clay mineral physical structure, initial solid particle size and shape, cation exchange capacity, and cation fixation tendencies interrelate to control the settling rates of the clay minerals by determination of the extent of hydration and coacervation of the settling entities. The degree of coacervation and specific associations of the solid grains within the settling entities are subsequently determined by the ionic ratio composition, temperature and ionic strength of the saline water in which settling occurs.

No organic material has yet been found which inhibits the differential sedimentation tendencies of clay minerals via adsorption mechanisms along the transport path. Complex carbohydrates, in general, increase the settling rates of montmorillonitic clay minerals and phosphoproteins tend to decrease the settling rates of kaolinitic clay minerals. Such action modifies velocity magnitudes but does not alter the general relative order of settling of individual clay mineral types or clay mineral associations.

At an ocean water chlorinity of 18‰, illitic and kaolinitic clay minerals settle in quiet, 26°C, water at rates of about 15.8 and 11.8 m/day, respectively. Chlorites settle slightly faster than kaolinites and vermiculites slightly faster than illites. Vermiculites fall less rapidly than illites, however, when the chlorinity is below 10‰. Montmorillonites exhibit a much slower settling velocity, 1.3 m/day under the conditions previously cited for illites and kaolinites. Some illite-montmorillonite associations settle at intermediate rates. A general summary of these relative rates is given in Fig. 12 and in Table 16. These results, which are based upon 1534 different clay mineral samples, apply to the average transport and sedimentation of natural deposit, soil and marine sedimentary matter. The largest deviations from such average values occur in saline water of chlorinity less than 2‰. Over the chlorinity range 0-20‰, the settling-rate changes of clay minerals may be expressed in terms of an exponential expression of Gompertz type.

Strontium, as well as potassium and magnesium, is fixed within montmorillonitic clay mineral threads by saline water flocculation and subsequent aging of deposited material. The magnesium-strontium and magnesium-potassium ionic ratios in saline water govern the general characteristics of montmorillonitic settling rates to greater extent than the ionic strength of the water does.

The probability of clay mineral transformations, particularly of montmorillonites, in marine environments is accepted but indirect evidence collected to support such transformations will become more significant when it is reconciled with, or combined with, differential settling and transport concepts.

All factors relative to differential settling of clay minerals have not yet been fully evaluated. The influence of bacterial action upon adsorbed organic matter, and the cementation of clay particles by exposure to large quantities of organic matter prior to exposure to saline water need considerable investigation. Further study of organic adsorption tendencies, of mineralogical transformation, of silt size, fresh-water, clay mineral aggregate



influences, and of the resuspension and turbulent transport of aged or biologically disturbed clay mineral deposits is needed. Something has been done but there is much more yet to do in order that the transport, distribution, chemical transformations, adsorption tendencies and physical properties of clay minerals in estuarine and marine environments may be adequately understood from various disciplinary points of view.

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