

ADJUSTMENT OF CLAYS TO CHEMICAL CHANGE AND THE CONCEPT OF THE EQUIVALENCE LEVEL

by

MAURICE C. POWERS

Shell Oil Company, Houston, Texas

ABSTRACT

Further x-ray and chemical work on suspended sediment samples and cored samples from the James River and its estuary support earlier proposals by the author. A chlorite-like clay is forming from weathered illite through a mixed-layer illite-vermiculite-chlorite stage, and some illite is seemingly regenerated to a better illite by potassium fixation.

Chemical analyses of interstitial water, hydrochloric acid-leachate, and fused samples offer explanations regarding the chemical changes occurring in clays as composition of the environment changes.

Magnesium is adsorbed by clays to a far greater degree than potassium in the marine and brackish environment.

The variance between clays found in Recent and ancient sediments is related to and explained by the concept of the equivalence level. It is suggested that K^+ is adsorbed preferentially to Mg^{2+} by clays when they have been buried to a depth that is greater than that of the $Mg^{2+} - K^+$ equivalence level; above this level Mg^{2+} is preferentially adsorbed by the clays.

The trifold nature of clay minerals in terms of their origin and distribution is briefly discussed.

INTRODUCTION

Earlier work (Powers, 1954) showed that a diagenetic chlorite (chlorite-vermiculite) is forming in the Patuxent estuary, Chesapeake Bay, and Atchafalaya Bay on the Gulf of Mexico, and more recent work showed similar results for clays collected off the coast of southern California. It was proposed that the diagenetic chlorite formed from a weathered illite in the Chesapeake Bay area and from montmorillonite and illite in the Atchafalaya and Pacific areas. It was shown that the thermal stability of the diagenetic chlorite increased and the chlorite and illite in the samples were better crystallized in the direction of increasing salinity. Grim and Johns (1954) found similar results of diagenesis in Gulf of Mexico sediments.

This paper presents additional evidence for the diagenesis of clays in Recent marine sediments. An important purpose in the paper is to define and explain diagenesis that takes place after deposition. A study of the diagenesis of clay minerals after burial is important to the student interested in the origin and distribution of clays yet practically nothing has been written on the subject. A hypothesis is presented to account for the general quantitative relationships of the clays with relation to geologic age.

CLAY MINERALS OF THE JAMES RIVER AND ITS ESTUARY

In the James estuary a chlorite-like clay is forming from weathered illite through a mixed-layer illite-vermiculite-chlorite stage, and some illite is seemingly reconstituted to a better illite by potassium fixation. The diagenetic chlorite increases in thermal stability seaward through the estuary.

The mechanism accounting for the diagenesis involves the adsorption of Mg^{2+} by the clays preferentially to potassium, but not to the complete exclusion of potassium. The result is the increased occurrence of a chlorite-like and vermiculitic clay, and to much less extent illite, in the direction of increasing salinity.

Chemical analyses were made on three fractions of each core sample collected through the estuary. (1) The interstitial water from various intervals along the core was analyzed for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and chlorinity. (2) The clays (less than 2μ) were washed free of water-soluble chloride and leached with 1.0 N HCl for one hour, and analyses were made on the leachate for Na^+ , Ca^{2+} , K^+ and Mg^{2+} . (3) The HCl-leached samples were then analyzed for total Mg^{2+} , Ca^{2+} , Na^+ and K^+ . These chemical analyses afford explanations of the chemical changes occurring in the clays as the chemical composition of the environment changes.

The important observation has been made that in estuarine and marine waters and in shallow estuarine and marine sediments magnesium is adsorbed by the clays to a far greater degree than potassium. Actually, the amount of magnesium in fused samples increased exponentially with relation to the amount of magnesium and chloride in the interstitial water of the samples within a chlorinity range of about 2–18 parts per thousand (Fig. 1), whereas a similar curve for potassium was nearly flat. In strongly reducing estuarine muds ferrous iron may very well be adsorbed by montmorillonite and weathered illite to produce a high iron chlorite-vermiculite clay.

A plot of salinity of the overlying water against the ratio of Mg^{2+}/K^+ in the clay fraction of the sediments shows that magnesium clays increase relative to potassium clays in the direction of increasing salinity (Fig. 2).

Suspended sediment samples were obtained from the upper and lower water layers through the James estuary. These samples showed the same diagenetic changes as did the bottom sediment samples. The suspended sediment samples were collected during the course of one afternoon when there were no abnormal weather or tide conditions, and it is therefore unlikely that flood stage versus normal runoff can explain the diagenesis described. It seems likely that heavy rains would merely wash *more* soil into the streams rather than a different type of clay. It is also of interest that the literature seems rather barren of examples relating either thin layers or entire lithotopes of distinctive clay types to flood versus normal runoff. If indeed the rivers in flood carry more crystalline chlorite (higher thermal stability) than during normal runoff, surely some of this clay is dropped out all along the estuary, as it is hardly reasonable to expect that the *entire* suspension load

would by-pass the upper and middle reaches of the estuary. Yet detailed analyses of cores taken along the course of the estuary channel do not show evidence for flood-deposited layers of anomalously more crystalline chlorite. We may infer from this information that the diagenesis described for the area studied cannot be explained by flood versus normal runoff, and some other cause must be sought to explain the data.

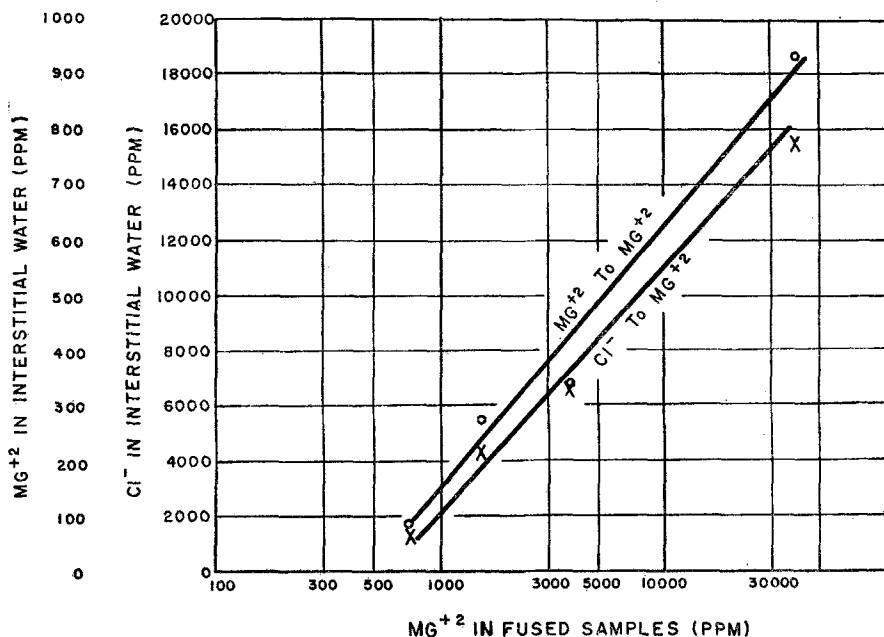


FIGURE 1.—Relation of Mg^{2+} in fused sample to Mg^{2+} and Cl^{-} in interstitial water.

Different salinity values in different parts of an estuary can not be called upon to account for the diagenesis by differentially flocculating the clays along its length. Even the most obstinate clays are flocculated when the electrolyte concentration is raised to a salinity equivalent of no more than three or four parts per thousand. See, for example, the work by Whitehouse and Jeffrey (1955, especially Figs. 3, 4 and 5). It would seem therefore that the clays are in the flocculated state almost immediately upon entering the estuary and surely before they have traversed any considerable salinity change (Powers, 1954, p. 74).

Explanation of the orderly and interrelated mineralogical and chemical changes observed requires a hypothesis which correlates the several variations mentioned. It appears that a combination of unaltered detrital clays, characteristic of the source soil, and altered diagenetic clays, characteristic of the sedimentary chemical environment, can account for the observations on marine and estuarine clay mineral distributions in Recent sediments.

RECENT-ANCIENT CLAY DISCREPANCIES

The formation of diagenetic chlorite and vermiculite from weathered illite and montmorillonite in a saline environment is most likely a general feature of clay diagenesis and may even overshadow the admixed detrital fraction. Diagenesis should therefore result in the occurrence of large amounts of chlorite and vermiculite in ancient sediments, yet in them we seldom find large concentrations of either clay mineral.

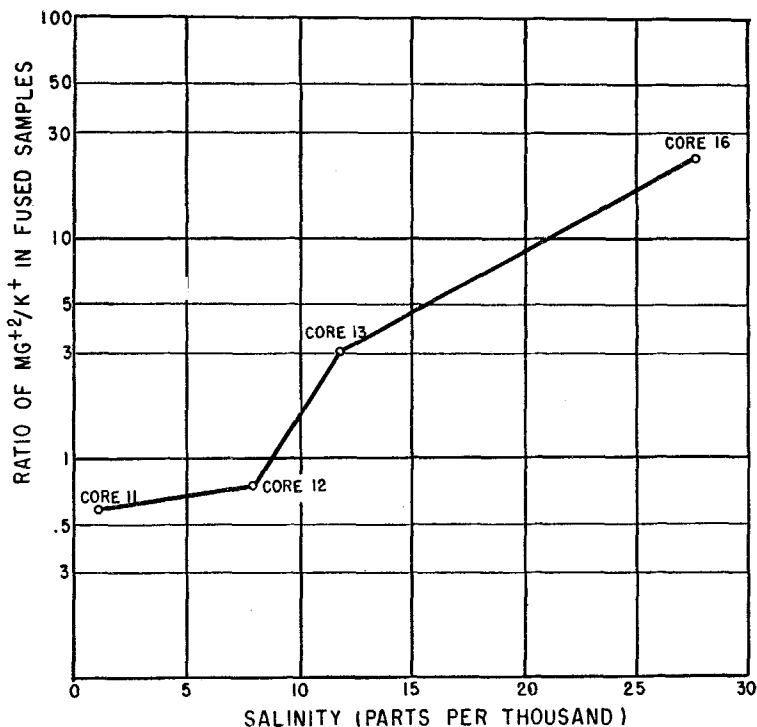


FIGURE 2.—Relation of Mg^{2+}/K^{+} in fused samples to salinity of interstitial water.

The general lack of abundant chlorite and vermiculite in ancient sediments has probably caused some wonder on the part of those persons investigating them as to the validity of some of the statements of the student of Recent sediments concerning the diagenesis of clays.

Although there are notable exceptions, the direction of study for most students of clay origin has been limited either to the Recent or the ancient sediments, whereas important answers to some of the problems lie somewhere between the very Recent and the very ancient.

It has been known for some time that montmorillonite is not common in sediments older than Cretaceous and, in fact, quite rare in Paleozoic shales.

It appears now that it was a mistake to relate this variance in montmorillonite to geologic age, for the time connotation masked the important factor, namely depth of burial.

DEPTH FACTOR AND THE EQUIVALENCE LEVEL

Tieing chemistry and chemical equilibrium in with diagenesis in Recent marine clays and, much more important, diagenesis occurring after the clays are deposited to a depth of several hundred feet, brings to light some interesting observations.

The relation of hydration capacity and ionic potential to the order of preference that clays have for cations in exchange reactions is not completely understood. Wiegner and Jenny (1927) and Wiegner (1935) performed experiments to show that the size of the hydrated ion, rather than the size of the nonhydrated ion, controls replaceability in clays. According to this concept K^+ might be expected to replace Mg^{2+} because of the lower hydration capacity of K^+ ; however, there are objections to this hypothesis (Hendricks, Nelson and Alexander, 1940). Experiments have shown that for the elements Na^+ , Mg^{2+} and K^+ the order of uptake by clays is the order given. The amounts of uptake of the three elements relative to each other showed essentially no variation for Georgia kaolinite, Polkville (Mississippi) bentonite, Patuxent River clay and Chesapeake Bay clay, regardless of the salinity of the solutions used (Table 1). No attempt was made to saturate the clays with a cation before performing the tests. The procedure consisted

TABLE 1.—UPTAKE OF ELEMENTS FROM SEA WATER ONTO CLAYS

Salinity of Solution ‰	Uptake ‰ ¹											
	Georgia Kaolinite			Polkville Bentonite			Patuxent River Clay			Chesapeake Bay Clay		
	Na ⁺	K ⁺	Mg ²⁺	Na ⁺	K ⁺	Mg ²⁺	Na ⁺	K ⁺	Mg ²⁺	Na ⁺	K ⁺	Mg ²⁺
5.03	0.36	0.00	0.00	0.36	0.00	0.01	0.36	0.00	0.00	0.00	0.00	0.01
10.07	0.42	0.01	0.01	0.37	0.01	0.04	0.42	0.01	0.00	0.42	0.01	0.03
20.14	0.69	0.01	0.02	0.69	0.01	0.02	0.69	0.01	0.04	0.58	0.01	0.03
30.21	0.00	0.01	0.06	0.84	0.01	0.08	0.00	0.01	0.06	0.00	0.01	0.07
Total Uptake by Clays ‰	1.47	0.03	0.09	2.26	0.03	0.15	1.47	0.03	0.10	1.35	0.03	0.14

¹ ‰ = parts per thousand.

of allowing 0.5 g of the air-dried $<2\mu$ fraction of each clay to stand for one and one-half hours in 300 ml of sea water having salinity of 5.03 parts per thousand. The samples were then washed once with distilled water and transferred to beakers containing solutions of 10.07 parts per thousand, then 20.14 parts per thousand, and finally 30.21 parts per thousand salinities.

Sodium, magnesium and potassium were determined in each solution before and after the clay was added. The figures for K^+ and Mg^{2+} are reliable to 1 percent and Na^+ to 2 percent of the amount reported. They support the conclusion of Grim (1953, p. 145) that cation exchange is a stoichiometric reaction in which the laws of mass action hold.

The explanation of the greater adsorption of Mg^{2+} than K^+ lies in part in the relative concentration of Mg^{2+} and K^+ in sea water. The ratio of Mg^{2+} to K^+ in sea water, in numbers of atoms, is about 5 : 1, assuming complete ionization.

At considerable depth, temperature may be important in affecting exchange reactions. According to Grim (1953, p. 149) :

At elevated temperatures, when there is little or no water present between basal layers in addition to the sorbed cations, the size of the ion and its geometrical fit into the structure of the oxygen layers are probably major factors in determining replaceability.

Excellent reviews of cation and anion exchange phenomena on clays are given by Kelley (1948) and Wiklander (1955). Wiklander (1955, pp. 137–138) concludes that relative replacing power of cations is determined by the exchange material, exchange capacity, nature of the ions (valence, hydrated and nonhydrated ion size), concentration of the solution, and relative concentration of the ions in solution. Kelley (1948, p. 60) arrives at essentially the same conclusions, pointing out that “. . . it is doubtful whether any purely mechanical or kinetic explanation of cation exchange will ever be found adequate to explain all the facts.”

We may speculate logically as to the role of Mg^{2+} and K^+ in the diagenesis of clay minerals relative to increasing depth of burial. Published analyses of both ancient and Recent shales (Murray and Sayyab, 1955 ; Grim and Johns, 1954 ; Powers, 1954) suggest some important geochemical processes as regards the history of marine and brackish shales. The 5 : 1 concentration ratio of Mg^{2+} to K^+ in sea water explains the observed exchange preference of clays in sea water for magnesium. In this way we can account for the diagenesis of chlorite and illite in brackish and marine environments. That is, the latter is adsorbed preferentially as long as the ratio of Mg^{2+}/K^+ is in the vicinity of 5 : 1. This does not mean that K^+ is not adsorbed onto the clays, but that the amount of adsorption is less than if the concentrations of Mg^{2+} and K^+ were equivalent. In equivalent concentrations K^+ may be adsorbed preferentially to Mg^{2+} if exchange is actually dependent on the radius of the hydrated ion.

By reasoning as above in terms of ionic potentials and equivalence, it is recognized that the *preferential* adsorption of Mg^{2+} over K^+ with depth

cannot continue beyond a certain concentration ratio of Mg^{2+}/K^+ . In other words, the Mg^{2+} will have a greater likelihood of being adsorbed the nearer the sediment is to the surface because of the greater value of Mg^{2+}/K^+ , and the K^+ will gain in its adsorption potential with depth (Fig. 3). That level

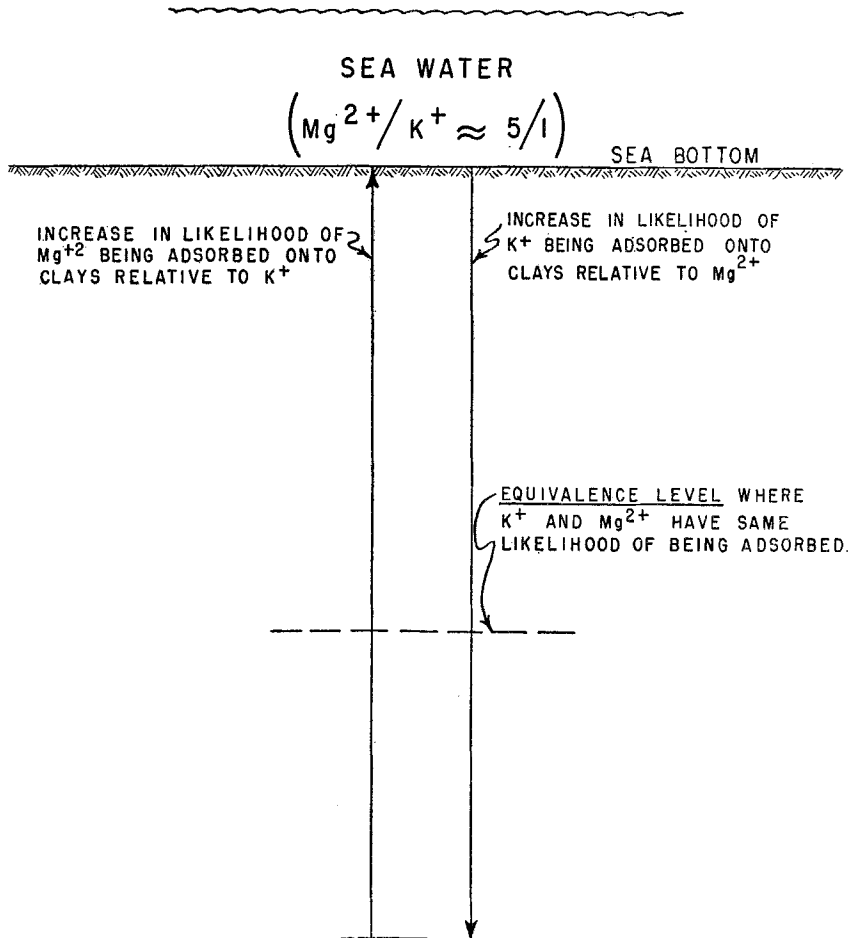


FIGURE 3.—The magnesium-potassium equivalence level.

below which K^+ is adsorbed to a greater extent than Mg^{2+} may be thought of as the *equivalence level for Mg^{2+} and K^+* . The depth of the equivalence level will depend principally upon the difference in the ionic potential of the two ions and their relative concentrations and should not exceed several hundred feet. The physical properties of the sediment, such as compaction characteristics, will play an important part in determining the depth of the equivalence level.

Below the equivalence level, one of two possibilities seems likely :

1. The Mg^{2+} (and Fe^{2+}) may move into the octahedral layer of the lattice and replace Al^{3+} which possibly moves into the tetrahedral layer expelling Si^{4+} . At the depths considered, the temperatures are probably great enough to account for the migration of Mg^{2+} from exchangeable positions between the layers to octahedrally co-ordinated sites within the lattice, as suggested by Hofmann and Endell (1939). The former sites of Mg^{2+} (and Fe^{2+}) are replaced by K^+ . Substitution of Mg^{2+} for Al^{3+} in octahedral co-ordination may be ion for ion as suggested by Foster (1951). The depth of this reaction is probably considerable and spread over a depth range of at least a few thousand feet. Substitution of Fe^{2+} or Mg^{2+} for Al^{3+} in the gibbsite sheet of montmorillonite would decrease the tendency of the clay to expand as demonstrated by Foster (1953, 1954, 1955). The substitutions suggest that little or no Mg^{2+} would be lost from the clays as they are compacted into shales and slates; the amount of K^+ should show a slight overall increase in the clay; and Al^{3+} should show a slight increase relative to Si^{4+} as the muds are compacted into tight shales and slates. All three of these predictions are well borne out by the work of two prominent Russian geochemists, Vinogradov and Ronov (G. V. Chilingar, 1957). Their results are based on the analysis of 252 composite samples, representing 6804 single samples and ranging in age from Tertiary to Precambrian. Relative to increasing age of the clays investigated, they find an increase in K^+ , essentially no change in Mg^{2+} , and a decrease in the SiO_2/Al_2O_3 ratio. An increase in illite relative to the other clay minerals would result from these substitutions and the mineral outcome is expected to consist of the unaltered clay fraction plus reconstituted and diagenetic illite, mixed-layer complexes involving illite, chlorite, vermiculite, and montmorillonoid, and minor chloritic clay. The nature of the mixed-layer clays would depend largely upon the source material. The significance of an increase in illite with depth of burial is related to its predominance in ancient sediments, whereas chlorite is rarely the dominant clay in ancient sedimentary rocks. Illite formed in this manner would almost surely contain more Mg^{2+} and probably more iron than continentally formed illite.

C. S. Ross and S. B. Hendricks suggested as early as 1943 (Ross and Hendricks, 1945) that there may be a complete gradation between the beidellite-type clay minerals and moderately high potassium mica-like minerals. They state (1945, p. 61) :

As the beidellite end of the montmorillonite-beidellite series is approached there is a decided tendency toward the formation of mixed-layer type minerals containing potassium. In more fundamental terms the number of nonexchangeable interlayer ions, essentially of K^+ , increases with the increase in replacement of silicon by aluminum in tetrahedral coordination.

The reaction outlined above by the present author corresponds to the reaction outlined by Ross and Hendricks, differing essentially in the role of replacement of Al^{3+} by Mg^{2+} in the octahedral layer. In this sense beidellite is merely a diagenetic stepping stone in the transition from montmorillonite

to illite and is not a necessary component of the detrital montmorillonoid clay fraction. Actually it is rather unlikely that beidellite is a common constituent of soil clays as proposed by Ross and Hendricks (1945), because the nature of its excess negative charge (strong in the tetrahedral layer) is such that the mineral would probably convert easily to illite, vermiculite or chlorite. Some doubt has been cast as to the purity of beidellite (Grim and Rowland, 1942; Foster, 1953), and the natural material having the formula proposed by Ross and Hendricks (1945) has not yet been found and described. It would seem from these indications and the magnitude of the diagenesis that the transition from a montmorillonoid to illite with depth of burial does not depend on having beidellite as the starting clay mineral. The diagenesis described applies to the entire montmorillonite–beidellite series but may, as stated earlier, develop a beidellite-type of montmorillonoid penecontemporaneously during the process of converting from a montmorillonite to an illite.

2. A less likely possibility of change in the clays with depth involves a slow but persistent replacement of Mg^{2+} by K^+ . Once K^+ is adsorbed onto the clay surfaces it is more difficult to replace than Mg^{2+} . Some of the more loosely held Mg^{2+} would be “outmaneuvered” by the K^+ , resulting in about the same set of clay minerals as mentioned for the first possibility but in a different chemical composition for the illite. This hypothesis is less realistic than the first one from the point of view of accounting for a concentration of charge in the tetrahedral layer and the consequent fixation of potassium in the clay.

It is seen from the foregoing that the concept of the equivalence level and the results it has on the clays ties together the diagenetic changes we observe in Recent marine sediments with the high percentage of illite and mixed-layer clays and common occurrence of only small amounts of chlorite in ancient shales. It also explains the general absence of montmorillonoids in ancient shales; they are converted to illite and mixed-layer illite–montmorillonite. These diagenetic changes will occur at a depth below the surface, depending on the permeability, porosity, chemistry, and probably the temperature of the sediment from the time of its deposition to the time of its greatest depth of burial. Continentally deposited montmorillonoids may remain as such if K^+ content is too low to effect diagenetic changes. Clays deposited with limestones follow a pattern similar to marine shales, according to our data. Exceptionally rapid deposition of sediments, especially volcanics, into orogenic basins that are subsequently highly faulted and folded offer special problems. For example, 17 Å montmorillonite occurs at depths of as much as 15,000 ft in the Ventura Basin of California. The montmorillonite disappears at greater depth in these sediments (K. Hsu, personal communication).

Once K^+ has replaced Mg^{2+} in the clays to the extent that illite and mixed-layer illite–chlorite–montmorillonite have formed, it is not likely that the reaction would be reversed if the sediment were then lifted up to a near-surface position by diastrophism. There is a bit of evidence for this statement.

A sample of shale dredged from the bottom of the Gulf of Mexico was interpreted by R. W. Barker (personal communication) on the basis of faunal evidence as lower Miocene age. This age suggests a depth of burial of about 25,000 ft. The shale, now at the surface of the Gulf bottom, was apparently pushed up by a salt dome. Examination of the clay content revealed no 17 Å montmorillonite, and the clay is generally quite similar to that in the deepest samples investigated in Gulf Coast wells; although it contains somewhat more illite in the mixed-layer fraction of the clay and in this respect suggests a depth of burial even greater than indicated by Barker's interpretation. Quite possibly the forces necessary to shear the surrounding sediment, in the process of raising the shale to a higher level, imposed a compressional force on the clays equivalent to a somewhat greater depth of burial than actually existed.

The only likely reversible process in the proposed diagenetic sequence is the weathering environment. The geochemical implications of the equivalence level on K^+ are well worth considering.

OBSERVATIONS

Following the theoretical development of the foregoing *equivalence level* hypothesis, some important substantiating observations were made on samples from several deep wells in Gulf Coast Tertiary sediments.

Clay minerals in the shallow sediments at depths of burial less than about 5000 ft consist predominantly of montmorillonite with only small amounts of illite, chlorite, and mixed-layer clay. The chlorite is probably highly faulted (Bradley, 1955), becoming better crystallized with increasing depth, thus explaining the sharper and higher 4.75 Å and 14 Å peaks occurring at considerable depth. Care must be taken, therefore, not to confuse the increased peak heights with increase in abundance of chlorite. Kaolinite varies in the shallow sediments from only traces to moderate amounts. The kaolinite does not vary in concentration with depth except locally in the wells, and the variation does not seem to be related to a diagenetic cause.

With increasing depth there is a slight increase in the amount of 10 Å illite and a pronounced increase in mixed-layer illite. There is no discrete 17 Å montmorillonite below 9000–12,000 ft. The mixed-layer illite occurs principally with montmorillonite, but vermiculite and chlorite are also observed in mixed-layer form with illite.

Probably all the kaolinite and montmorillonite and most of the 10 Å illite have a detrital origin, whereas the remaining clays are diagenetic, forming either in the depositional environment or postdepositionally. The vermiculite and chlorite may have formed penecontemporaneously to deposition by diagenesis of montmorillonite and developed into a well crystallized chlorite postdepositionally. Part of the diagenetic chlorite, vermiculite and montmorillonite is altered to illite and the balance of the montmorillonite to a mixed-layer illite-montmorillonite. A small amount of mixed-layer illite-chlorite is evident in deep samples.

The changes in the clays take place gradually over a considerable depth range of several thousand feet. These gradual changes are not readily apparent from a plot of the 17 Å peak height, but require an integrated study of the 5.0–5.65 Å area and the 10–17 Å region.

Burst (see paper, this publication) discusses the Wilcox clays and their diagenesis after burial.

Discussion of Results

An abundance of evidence suggests that the disappearance of montmorillonite and the appearance of a mixed-layer illite–montmorillonite are related to depth of burial; these changes are not related to age of the sediment, a change in the detrital clay component sedimented into the basin of deposition, or directly to the depositional environment.

Generally speaking, the Gulf shoreline has been regressive since at least Late Cretaceous time. Superimposed on this grand-scale regression of the sea have been numerous smaller-scale transgressions and regressions. At first the idea was put forward that the increase in illite and disappearance of montmorillonite with depth might be related directly to environmental effects, and the crossing of time lines by the general regression of the sea would account for the fairly constant depth at which the major clay changes took place. This hypothesis was found to be untenable for numerous reasons. In the first place if this hypothesis is to explain the clay mineral changes, then the Recent sediments of the Gulf should show similar relations because of the striking similarity of the geologic setting of the Recent versus most of the Tertiary. Recent sediments in the Gulf of Mexico have been studied and no major clay alterations such as those described above have been observed. Furthermore, superimposed transgressions and regressions, as for example the Anahuac shale wedge, should reveal at least some indication of a relationship to montmorillonite, illite, and mixed-layer clay percentages. No anomalous relations were observed even though several transgressive and regressive deposits, including the Anahuac, were penetrated by the wells studied.

Finally, samples from the Porters Creek sections in two deep wells have been examined for their clay content. The interval in which the Porters Creek occurs in well A is 6200–7100 ft, in well B from 8600–9500 ft. The environment of deposition is thought to be the same for the sections in the two wells (E. H. Rainwater, personal communication). The Porters Creek shale penetrated by well A contains an abundance of 17 Å montmorillonite, whereas the deeper section penetrated by well B does not contain 17 Å montmorillonite. In view of the similarity of the environment of deposition of the two sections suggested by the stratigraphers, it is felt that the clay changes observed are related to some cause other than the environment at the time of deposition. The conversion of all the 17 Å montmorillonite to illite and mixed-layer clay at about the same depth in the Porters Creek as observed for the other wells studied, again offers evidence for the relation of depth to clay mineralogy.

The present study offers ample evidence that the clay mineral changes are not related to geologic age of the sediment except as age is coincidentally related to depth of burial.

There is no evidence for relating the observed clay changes to a change in the detrital clay component sedimented into the basin of deposition. To do so would necessitate calling upon drastic changes in climate locally within given time planes and changes of drainage basins and stream directions. Stratigraphic and paleontologic studies do not warrant the climatic and geomorphic changes necessary to account for the major clay mineral changes noted.

According to C. E. Weaver (personal communication) the disappearance of a discrete 17 Å montmorillonite at about 9000–12,000 ft is in fact common to all studies carried out to date by the clay petrology section of Shell Oil Company where the issue is applicable. These studies include rocks of various geologic age and lithologic type and suggest the general nature of the diagenesis.

The hypothesis put forth to explain the major clay changes states that the relation is limited to sediments containing saline interstitial waters and therefore would not necessarily apply to continental sediments. That is, montmorillonite may occur at any depth in continental shales not impregnated with potassium-bearing saline water.

DIAGENESIS AND CHEMICAL REQUIREMENTS

The question of whether there is enough K^+ trapped in the marine muds to account for the diagenesis of montmorillonite to illite and mixed-layer clay involves considerably more complex problems than first meet the eye. Gulf Coast sediments may be used as a model to study this question.

The principal variables in such a model are percent clay mineral in the sediment, amount of K^+ in the trapped interstitial water, amount of interstitial water in the muds within the depth range considered, percent of clay in the clay fraction of the sediment that must undergo K^+ adsorption, amount of illite formed after burial, and amount of adsorbed K^+ inherited from the suspension period of the clay history. Specific surfaces of clays, formation of authigenic nonclay minerals, adsorption phenomena involving organic constituents, and chemical kinetics are necessarily left out of the model.

A rough estimate of the average percent clay in the western Gulf Coast Tertiary sediments, according to H. A. Bernard (personal communication), is about 10–30 percent. R. H. Nanz, Jr. (personal communication) gives a rough estimate of 30–40 percent less than 4μ size in the total stratigraphic interval of the regressive facies in the Gulf Coast Tertiary, and not all the clay-size fraction is clay mineral. Nanz (personal communication) says further that at Seeligson and other places the “shaleline” of the electric logs is characteristic of clayey sands, silty sands and silts, as well as clay rocks ($<4\mu$ particle size). The average clay *size* content of Seeligson continental

shales is about 25-30 percent, and in another area the inner-to-middle neritic shales average about 25-30 percent clay size particles. The almost total lack of reliable grain size analyses on Tertiary shales prompted the sieve and pipette analysis of a few carefully chosen shales. Table 2 shows

TABLE 2.—GRAIN SIZE ANALYSIS OF SELECTED TERTIARY SHALES
(Results in Weight Percent of Original Samples)

Sample Number	Sand Size > 62 μ	Silt Size 4-62 μ	Clay Size < 4 μ	Soluble in HCl and H ₂ O ₂	Remarks
1	Trace	32.7	34.8	32.5	Transgressive phase. Water depth 100-300 ft.
2	Trace	31.3	40.2	28.5	Regressive phase. Water depth 60 ft.
3	1.0	43.1	30.9	25.0	Transgressive phase. Water depth 200 ft.
4	3.2	32.3	18.1	46.5	Upper slope.
5	1.8	32.6	9.7	55.8	Middle neritic to edge of upper slope.
Average of above :					
	1.0	34.4	26.7	37.6	

the results of the analysis from cored samples. The first three samples were chosen as typical Tertiary shales. Note that the sample from the shallowest water contains the most clay, contrary to observations on the Recent sediments of the Gulf of Mexico. Some thin beds of sandy material are interbedded with the shale of sample 4 but the shale layers remain typical of the upper slope facies (R. Lagaay, personal communication). The interbedded sandy layers were eliminated from the composite shale. Sample 5 may be middle neritic to edge-of-the-upper-slope (personal communication, E. H. Rainwater and B. S. Parrott). Most of the soluble material is removed by the action of the dilute hydrochloric acid and consists principally of carbonate minerals and microfossil tests. The weight percent of organic carbon (hydrogen peroxide soluble) is probably 2 percent at most. The prominent percentage of acid solubles is typical of most Recent marine muds. The average percent of clay for the five samples (26.7 percent) falls close to the estimates of Nanz and Bernard for average clay content of Gulf Coast Tertiary shales.

Part of the clay-size fraction consists of nonclay minerals and the amount probably varies over wide limits. In the compositional analysis of the Gulf Coast model, it is assumed that the Tertiary section in the Gulf Coast contains an average of about 20 percent clay *mineral*.

Diffraction analyses of Gulf Coast sediments show that about 30 percent of the *clay fraction* deposited is altered to illite, corresponding to about 6 percent of the total sediment sample.

The amount of K^+ assigned to the interstitial water is simply that which occurs in sea water, namely 0.038 percent, assuming complete ionization. Six layers of water in montmorillonite correspond to about 60 per cent water, calculated as :

$$\text{percent water} = \frac{\text{weight wet} - \text{weight dry}}{\text{weight dry}} \times 100$$

Unpublished work by the present author and reports by Grim and Cuthbert (1945) and White (1955) show that this value is very near the plastic limit. It probably corresponds to the value at the depth at which muds become shales. As the surface of the sediment is approached, so is the liquid limit which is never more than a few feet below the surface. At the liquid limit a Ca^{2+} -saturated montmorillonite contains about 165 percent water, or 1.65 g of water for each 1.00 g of sediment. It is unlikely that K^+ escapes from the muds once they are in the plastic state because of the strong filtering effect of the muds on the potassium ion as water is squeezed out of the system. The ratio of sediment to water at the liquid limit is used in the Gulf Coast model.

It is assumed in the model analysis that 6 percent K_2O is necessary in the composition of illite, although illites may contain somewhat less than this amount in their composition.

Some of the K^+ used in the reaction is inherited from the suspension period in an available exchange position on the clays. The quantity of K^+ supplied in this manner is difficult to determine, but uptake experiments and chemical analyses of clays in the Chesapeake Bay area by the author indicate that up to 0.0024 g of K^+ per gram of clay may be available.

Using the figures arrived at above by rough compositional and dimensional analysis, it is possible to estimate whether enough K^+ is available in exchange position on clays and in the interstitial water to convert 30 percent of the clay in a 20 percent clay-bearing shale from a montmorillonite to an illite. Summary figures and arithmetic follow.

1. Clay fraction = 20 percent of sample.
2. Diagenetic illite in clay fraction = 30 percent.
3. Diagenetic illite in sample = 6 percent.
4. Therefore in 1.000 g of sample 0.060 g is altered illite.
5. Assume illite has about 6 percent K_2O .
6. 0.60 g illite has 0.0036 g K_2O or 0.003 g K^+ .
7. Therefore 1.000 g sample requires about 0.003 g K^+ for the diagenesis.
8. Sea water contains 0.004 g K^+ per g of water.
9. Ratio of sediment to interstitial water at liquid limit is about 1.000 : 1.650 g.
10. Therefore $1.650 \times 0.0004 = 0.00066$ g K^+ is available from the interstitial water for each gram of sediment. This amount is about one-fourth the amount required in the composition of an illite bearing 6 percent K_2O .
11. Chesapeake Bay samples showed 0.0024 g of exchangeable K^+ per gram of clay. The clay makes up one-fifth of the total sample. Therefore $0.0024 \div 5 = 0.00048$ g K^+ is the amount available for diagenesis.
12. The K^+ in interstitial water plus the K^+ in available form on the clays totals 0.0011 g K^+ per gram of sediment. This is about one-half the amount needed for the diagenesis suggested, but it will be shown later on that the sediments actually contain about *four times* this amount of K^+ .

There are many sources of error in the figures given here. Chief among the errors are the percent interstitial water, the amount of K^+ in exchangeable position, and especially the amount of K^+ needed to produce from montmorillonite a clay that responds to x-ray diffraction as an illite, or in other words, a clay that maintains a 10 \AA peak after glycolation. For the most part, therefore, the figures are speculation, and before any reliance is placed in them they must await confirmation.

A more dependable test than the compositional analysis outlined above involves actually analyzing the K^+ content of the sediments from Gulf Coast wells with relation to depth of burial in order to determine whether enough K^+ is trapped during sedimentation to account for the diagenesis of montmorillonite to illite, estimated from diffraction analyses of the clays, by simply rearranging the K^+ present. As long as the K^+ content does not vary appreciably with depth below the sediment surface, it seems reasonable to assume that attending mineralogical variations involving that element are justified, as far as the amount of K^+ required is concerned, without calling on additions of K^+ after burial of the sediment. The analyses in Table 3

TABLE 3.—POTASSIUM IN BULK SAMPLES FROM TWO DEEP WELLS IN GULF COAST MIOCENE SEDIMENTS

Sample	Depth in Feet	Percent K^+ by Wt.	Percent K_2O by Wt.	Remarks	Nature of Sample
1	3170	1.5	1.81	Slightly sandy and silty shale	Core
2	4170	1.6	1.93	Shale	Core
3	6855	1.9	2.28	Shale	Core
4	9600	1.7	2.05	Shale	Core
5	8950	1.8	2.17	Shale	Core
6	11,950	1.6	1.93	Shale	Core
7	17,000	1.8	2.17	Shale	Cuttings

show that there is essentially no change in the potassium content with increasing depth below the surface. Analyses were made on bulk samples from core chips or cuttings, as indicated in the table. Sample 1 contains an excess of silica, suggesting considerably more sand (quartz) than the other samples, and in this way accounts for the low K^+ value. The percentages given in the table do not deviate from true values by more than about 5 percent of the amount reported. The average K^+ content in the wells is 1.7 percent with a deviation of less than ± 0.2 percent if sample 1 is not counted. If all the K^+ is assumed to be concentrated in the illite clay fraction (about 13 percent of the sample), 15.8 percent K_2O is contained therein. This value is of course much higher than was indicated in the compositional analysis of the Gulf Coast model and points out the limitations in the reliability of such a model. These analyses amply demonstrate that there is more K^+ in the samples than is needed for the diagenesis proposed. There is essentially no

deviation of K^+ content with depth, and this is taken as supporting evidence for diagenesis after burial, rather than a change in the detrital clay composition, to explain the observations on clay changes with relation to depth of burial. The question then does not involve whether there is *enough* K^+ for the diagenesis proposed but rather *how* the K^+ occurs in relation to the minerals and water in the sediment. It is possible, for example, that large quantities of K^+ are tied up in exchange position by bacteria or associated with the ionization of residual COOH groups in materials such as ligno-proteins (V. P. Sokoloff, personal communication; Mitchell, 1955, p. 264; Kelley, 1948, p. 21). This and other problems remain unsolved as the lack of knowledge on the subject of K^+ in sediments and minerals is brought into the open.

Again the question arises, how much K^+ is necessary to convert a montmorillonite to an illite as determined by x-ray diffraction, remembering of course that the x-ray diffraction technique employed does not analyze quantitatively for K^+ . The technique used to differentiate illite from montmorillonite depends on the inability of ethylene glycol to expand the unit layers of clay to a value greater than 10 Å. Indeed, we do not know how much fixed K^+ is necessary to resist interlayer expansion by ethylene glycol. Surely this is a fundamental defect in the technique of clay mineralogical identification with x-rays and one that should be remedied.

The Trifold Nature of Clays

We are led by our reasoning into recognition of the trifold nature of clay minerals in terms of their origin and distribution in marine sediments. The three categories are as follows:

1. The detrital component forms the first category of clays. They are unchanged in the depositional environment or postdepositionally and may or may not form a large fraction of the final clay product in sedimentary rocks, depending on the type of original clay mineral and its consequent postdepositional alteration. A wide range of clay types is included here. The types of clay are determined by the source rock and weathering characteristics in the source area and *en route* to the depositional basin.

2. The second category of clays is formed by diagenesis within the depositional environment and includes at least that fraction of the sediment that is above the liquid limit or subjected to the circulation of overlying water. These clays are determined by the type and nature of the clays brought into the depositional environment; that is, the degree of weathering and the conditioning by the transporting medium, as well as the physicochemical conditions of the environment. These clays may include illite, chlorite, vermiculite, and especially mixed-layer complexes of these clays. The author hesitates to coin terms, but perhaps it would lead to better clarification by referring to these clays as *hydro-diagenetic* as opposed to those in the next category which are referred to as *petrodiagenetic*, having been formed by postdepositional alteration.

3. Those clays formed by diagenesis after burial comprise the third category. The process of diagenesis takes place over a long period of time and through a depth range that is defined principally by the chemistry of the initial interstitial water, permeability of the sediments, and type of clays present. Diagenesis of these clays may include considerable lattice replacement as well as surface exchange reactions and, in this way, differs from hydro-diagenesis, which seemingly is primarily a surface reaction.

The clay minerals in this category are predominantly mixed-layer illite-montmorillonite-chlorite complexes and illite. Intermediate depths reveal abnormal amounts of mixed-layer clays which become more illitic with greater depth. More perfect crystals in the petrodiagenetic chlorite produce sharper diffraction peaks at considerable depth and may be mistaken for an increase in the *abundance* of chlorite.

These clays form the *petrodiagenetic* fraction or the alterations which take place after the muds have become consolidated into shales. Petrodiagenesis differs from metamorphism in having as its primary cause the chemistry of the interstitial water and having as its product a shale rather than a slate. The pressure effect is indirect in that it may diminish or increase the absolute concentration of the elements in the interstitial water, thereby affecting the depth at which a reaction is completed as well as the reaction rate. Membrane filtering may be an important process in changing the chemistry of the interstitial water in special instances and thereby may play an important role in clay diagenesis.

SUMMARY

It is seen that diagenesis proceeds in different directions in Recent marine sedimentary environments during hydro-diagenesis and, after burial to considerable depths, during petrodiagenesis.

The concept of the equivalence level is of importance in studying clay minerals in sediments that have been buried to considerable depths; these are normally the more ancient sediments simply because the older sediments have, on the average, been buried to greater depths than younger sediments. The relationship of depth and time is probably coincidental in the explanation of petrodiagenesis.

The common occurrence of mixed-layer clays and illite in deeply buried sediments is accounted for in large part by the formation of these materials during petrodiagenesis.

REFERENCES

- Bradley, W. F. (1955) Structural irregularities in hydrous magnesium silicates: in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 395, pp. 94–102.
- Chilingar, G. V. (1957) Evolution of chemical composition of clays of the Russian platform: by A. P. Vinogradov and A. B. Ronov, *Geokhimiĭ ja*, reviewed in *Geochim. Cosmochim. Acta*, v. 12, pp. 172–175.
- Foster, M. D. (1951) The importance of exchangeable magnesium and cation-exchange capacity in the study of montmorillonitic clays: *Amer. Mineral.*, v. 36, pp. 717–730.

- Foster, M. D. (1953) Geochemical studies of clay minerals : II—Relation between ionic substitution and swelling in montmorillonites : *Amer. Mineral.*, v. 38, pp. 994–1006.
- Foster, M. D. (1954) The relation between “illite,” beidellite and montmorillonite : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 386–397.
- Foster, M. D. (1955) The relation between composition and swelling in clays : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 395, pp. 205–220.
- Grim, R. E. (1953) *Clay Mineralogy* ; McGraw-Hill, New York, 384 pp.
- Grim, R. E. and Cuthbert, F. L. (1945) Some clay-water properties of certain clay minerals : *J. Amer. Ceram. Soc.*, v. 28, pp. 90–95.
- Grim, R. E. and Johns, W. D. (1954) Clay mineral investigation of sediments in the northern Gulf of Mexico : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, p. 81–103.
- Grim, R. E. and Rowland, R. A. (1942) Differential thermal analysis of clay minerals and other hydrous materials. Part 2 : *Amer. Mineral.*, v. 27, p. 801–818.
- Hendricks, S. B., Nelson, R. A. and Alexander, L. T. (1940) Hydration mechanism of the clay mineral montmorillonite saturated with various ions : *J. Amer. Chem. Soc.*, v. 62, pp. 1457–1464.
- Hofmann, U. and Endell, J. (1939) Die Abhängigkeit des Kationenaustausches und der Quellung bei Montmorillonit von der Vorerhitzung : *Ver. deut. Chemiker Beihefte*, v. 35, p. 10.
- Kelley, W. P. (1948) *Cation Exchange in Soils* : Reinhold Publishing Corporation, New York, 144 pp.
- Mitchell, R. L. (1955) Trace elements : in *Chemistry of the Soil*, Reinhold Publishing Corporation, New York, Ch. 9, pp. 253–286.
- Murray, H. H. and Sayyab, A. S. (1955) Clay mineral studies of some Recent marine sediments off the North Carolina coast : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 395, p. 430–441.
- Powers, M. C. (1954) Clay diagenesis in the Chesapeake Bay area : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 68–80.
- Ross, C. S. and Hendricks, S. B. (1945) Minerals of the montmorillonite group : their origin and relation to soils and clays : *U.S. Geol. Survey*, Professional Paper 205–B, p. 23–79.
- White, W. A. (1955) Water sorption properties of homoionic montmorillonite : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 395, pp. 186–204.
- Whitehouse, U. G. and Jeffrey, L. M. (1955), Peptization resistance of selected samples of kaolinitic, montmorillonitic and illitic clay materials : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 395, pp. 260–281.
- Wiegner, Georg (1935) Ionenumtausch und Struktur : *Trans. Third International Congress Soil Sci.*, Oxford, England, v. 1, p. 5–28.
- Wiegner, Georg and Jenny, Hans (1927) Ueber Basenaustausch an Permutiten (Kationenumtausch an Eugelen) : *Kolloid-Zeits.*, v. 42, pp. 268–272.
- Wiklander, L. (1955) Cation and anion exchange phenomena : in *Chemistry of the Soil* : Reinhold Publishing Corporation, New York, Ch. 4, pp. 107–148.