DIAGENESIS IN CLAY MINERALS—A REVIEW

by

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ABSTRACT

Diagenesis refers to the process, and the changes (usually excluding cation exchange) that take place in sediments after deposition, but definitions of the process vary widely over which changes, and what part (or all) of the time between the transportation of the sediment and the time that the sediment(ary rock) is studied, should be included in diagenesis. Furthermore, Weaver, Griffin, and others, have favored alternative explanations to account for many clay mineral distributions that previously have been interpreted as representing changes in clay minerals in both recent and ancient sediments, and which were referred to diagenesis.

Although agreeing that such alternative explanations account best for many distributions of clay minerals, additional evidence that presumably is convincing of diagenesis is presented herein to account for the formation of certain other occurrences of glauconitic mica, glauconite, illite, corrensite, kaolinite, and vanadiferous micaceous clay. A two-stage mechanism is proposed for a possible process by which illite and probably corrensite are formed: (1) cation sorption driven by energy (activities) of the ions in solution, and binding energy of the clay minerals, and (2) subsequent rearrangement of ions in the clay mineral to produce illite. It is finally proposed that diagenesis of clay minerals is characterized by the addition to and incorporation into them of Me ions, such as Mg, K, Ca, Na, Al, Fe, V, SiO_2, and others, driven mainly by chemical energy and aided by mechanical and thermal energy, but as the latter two become more effective the process is designated metamorphism (anamorphism).

Long-time, diagenetic reactions after burial of sediments are probably less important, volume-wise, than provenance and terrestrial weathering in determining the mineralogy of argillaceous sedimentary rocks in the geologic column.

INTRODUCTION

Notably different connotations are attached to diagenesis by different geologists, as is shown by the different definitions of the process. Howell (1957) records diagenesis in one definition as: "the chemical and physical changes that sediments undergo during and after their accumulation, but before consolidation takes place"; but another extends it through lithification, "... changes occurring between the time of deposition and the time at which complete lithification takes place".

Sujkowski (1958) emphasizes temperature and pressure, as follows: "In this paper 'diagenesis' is used to include all the processes which turn a fresh sediment into stable rock of some hardness, under conditions of pressure and temperature not widely removed from those existing on the earth's surface."

Sujkowski further notes that there is no clearcut line between diagenesis and low grade metamorphism on the one hand, and no sharp boundary between diagenesis and weathering on the other, to which I will agree wholeheartedly (Keller, 1957, p.6).

Packham and Crook (1960) state that, "Diagenesis may be subdivided into halmyrolysis, early diagenesis, and epigenesis, being, respectively, alteration before and during deposition, immediately after burial, and under deep-seated conditions."

Within the area of argillaceous sediments, surface phenomena, ion exchange. and colloidal properties must be reckoned with. Powers (1959, p.234), writing about clay sediments, states that he hesitates to coin new terms, but hopes clarification will result by proposing: "Hydro-diagenetic" clays are "formed by diagenesis within the depositional environment and include at least that fraction of the sediment that is above the liquid limit or subjected to the circulation of overlying water." "Petro-diagenetic" clays are "formed by diagenesis after burial."

Weaver (1959) separates ion exchange from diagenesis as follows:

> "Thus, chemical diagenesis would be restricted to modifications of the basic lattice, and alterations affecting the interlayer material would not be considered as diagenetic processes but as absorption or exchange. . . . Syngenetic alterations occur while the clay is still in contact with sea water, and epigenetic alterations occur later. Epigenesis eventually passes into low-grade metamorphism."

It is not the purpose in this paper to reconcile the differences in definition of diagenesis; instead, the natural history (apart from artificially erected boundaries) of changes in clay minerals from the stage of their transportation to the time of study in the field and laboratory will be considered. At the end of the paper, these processes will be summarized into a somewhat definitive and descriptive statement.

Before launching into a catalog of individual changes, the geochemical causes for the occurrence of any changes may be examined. Sujkowski (1958) wrote to the point as follows:

> "Most sediments are mixtures of many heterogeneous compounds and are chemically unstable. Low temperature and pressure may permit a sediment to remain in metastable conditions for hundreds of millions of years, but normally changes occur, leading to the separation of different chemical compounds, with water and organic matter as the chief agents of change."

Packham and Crook (1960) emphasize the environmental pH-cation concentration effecting diagenetic changes and note that minerals which have abrasion pH above 7 will be in contact with others whose abrasion pH is below 7 (Stevens and Carron, 1948) and therefore will tend to react, that the concentrations of metal cations (salinity of the fluid phase) in relation to H^+ ion concentration may control the direction of mineral change, that these relationships may change with different pressures and temperatures if the pH is dependent on CO_2 content of the fluid phase, and that environmental Eh is variable and important in effecting mineral changes until it stabilizes after burial. Sujkowski (1958) calls especial attention to several environmental changes, such as unmixing of compounds, changes (usually an increase) in concentration of fluid phase as the water (solvent) is expressed, and the development of lamination in shales.

From the foregoing background of reasons and reactions by which diagenesis is expected to occur, it is dangerously easy to conclude without further supporting evidence that clay minerals in sediments do undergo diagenesis. Weaver, however, in several papers (1958a, b, c, 1959), challenged the interpretations of distributions of clay minerals as arising from diagenesis. He wrote (1959, p.170), "The general distribution of clay minerals through the geologic section is probably first a function of tectonics and the type of source rock," and with respect to Recent sediments (1959, p.182), "Studies of Recent marine muds suggest to the author that the clay minerals are primarily detrital in origin and reflect the composition of the source area". Therefore, it is desirable that the evidence on which diagenesis has been inferred should be reexamined and the validity of the interpretation of it be reassessed.

Evidence from which diagenesis was inferred

When one reflects on trends which led to inferences of diagenesis of clay minerals he goes back even to the paper on, "Clay Minerals and Their Identity", published by Ross and Kerr in 1931, who wrote, "The recent work has shown definitely that kaolinite is one of the less important clay minerals of sediments, and that calculations based on the assumption of its presence are nearly always in error." The dethroning of King Kaolin who had long worn the crown of clay minerals was more of a mineralogic revolution than most of the younger statesmen in clay mineralogy appreciate. This rather radical (at that time) statement sharpened the accuracy of clay mineral identification and stimulated geologic thinking about argillaceous sediments.

A subsequent surge in the number of clay mineral identifications yielded data which were summarized by Grim in his textbook (1953) to the effect that illite dominated the clays in ancient sediments, that kaolinite was scantily present in the older ones, and the suggestion by Grim that illite may have been formed at the expense of other clay minerals. The dominantly monomineralic character of enormous volumes of Paleozoic shales was considered good geologic evidence of response of clay minerals to such sedimentologic regimen—hence a diagenetic response. Four years earlier, Grim, Dietz, and Bradley (1949) concluded that, in the Gulf of California and off the coast of California, kaolinite was lost during diagenesis and altered probably to illite or a chloritic mineral. Montmorillonite occurred widely spread in those sediments and "In general very little montmorillonite seems to be lost during marine diagenesis" (Grim, Dietz, and Bradley, 1949). Millot (1949) published in the same year his researches relating clay mineals to environments of formation and occurrence.

From 1949 to 1958 many good papers were published on clay minerals in sediments, mostly Recent sediments, which described the distribution of clay minerals with respect to their transport from fresh water into marine water and within a marine depositional basin. These papers are ably reviewed and summarized by Weaver (1959), and it would be superfluous to recount their contents here. Some of the authors attributed the clay mineral distribution to diagenetic changes, whereas others interpreted the distributions to be occasioned by clay mineral sources, either parent rock, or the rivers which transported them.

In 1958 and 1959, Weaver (1958a, 1958b, 1958c, 1959) surveyed the evidence on which previous interpretations had been based and concluded (1959, p.158) that proposed clay mineral alterations in Recent deposits were not proven as being alterations but that they more probably were segregations whose "tendencies can equally well be explained by such things as preferential flocculation, current sorting, effects of different source areas, floods, periodic variations in composition and concentration of river detritus, and probably numerous factors of which we are not aware". Griffin, in 1962 (see also Griffin, 1960), described how different clay mineral suites, from parent rocks and the several rivers delivering detritus to the Gulf of Mexico, augmented by currents in the Gulf, accounted for most of the clay mineral distribution observed.

Since the appearance of Weaver's papers, Pryor and Glass (1961) have applied the principle of differential flocculation of kaolinite, illite, and montmorillonite by action of cations in ocean water to account for the distribution in clay minerals in 9 formations in the Upper Cretaceous and Tertiary-age sediments in the Upper Mississippi Embayment. They concluded that kaolinite was deposited dominantly in the fluviatile environment, nearly equal amounts of kaolinite, illite, and montmorillonite in the inner neritic environment, and that montmorillonite was dominant in the outer neritic environment. That kaolinite is most easily flocculated, followed by illite and montmorillonite, was shown by Beavers and Marshall (1951) who studied the cataphoresis of clay minerals in the presence of polyvalent chlorides ($LaCl_3$, $ThCl_4$, and six-valent "hexol", $(Co(OH_2)Co(NH_3)_4\ {}_3Cl_6$. Curiously (and of interest to clay sedimentologists), montmorillonite is flocculated in the presence of starch, such as potato starch, although the mixture remains negative in charge. "This action", according to Beavers and Marshall (1951), "is not well understood. It may be a property or a particular fraction of the starch." Whitehouse, Jeffrey, and Delbrecht (1960, p.73) report that, "Complex carbohydrates, increase the settling rates of montmorillonitic clay minerals and phosphoproteins tend to decrease the settling rates of kaolinitic minerals." Parenthetically, it appears to me that the possible effect on the coagulation, or alternatively the prolonged dispersion, of clay minerals by various organic substances occurring in environments of transportation and deposition of sediments is a fertile field for further investigations.

The arguments of Weaver, augmented by the work of Griffin, make a strong and convincing (to most persons) case against diagenesis of clay minerals as they move from fresh to marine water. Cation exchange, and reconstitution of previously degraded illite and chlorite, which may occur here, are held by

Weaver as being changes not sufficiently profound to be classified as diagenetic. Thus, immediate diagenesis of Recent clay minerals as they enter an ocean environment from weathering and fresh water environments is usually unfounded.

The evidence of clay minerals in respect to diagenesis of ancient sediments was also reviewed by Weaver (1959, p.154) who concluded that, "illite is the dominant clay mineral of the pre-Upper Mississippian sediments. Post-Lower Mississippian clay suites are more variable in composition; illite becomes less abundant and montmorillonite and kaolinite more abundant." Weaver is less specific about the genesis of the pre-Upper Mississippian clay suites than that of the post-Lower Mississippian, the change of which he states, "is best related to a change in regional tectonics".

To the contrary, however, several papers in support of diagenesis of ancient sediments have appeared in the last 5 years, including one by Weaver in 1961. These will be reviewed, and the evidence from them for diagenesis examined critically, and finally a two-stage mechanism for diagenesis will be elaborated.

DIAGENETIC ILLITE AND GLAUCONITIC MICA IN THE MORRISON FORMATION

The first field example of diagenesis to be cited is the development of illite and glauconitic mica from montmorillonite in the Brushy Basin member, the upper member of the Morrison (Jurassic) formation on the Colorado Plateau in Utah and Colorado. Part of the data on this occurrence was presented to the Fifth Conference of this Group (Keller, 1958), and a more complete documentation is in press (Keller, U.S.G.S. Bull. 1150). The Brushy Basin member is a bentonitic mudstone, commonly 300 to 500 ft thick, that is spread over hundreds of square miles on the Colorado Plateau. It composed dominantly of montmorillonite (the variety not easily collapsible by treatment with KOH) derived by alteration of volcanic ash (network, not a phyllosilicate) structure. The evidence for the ash is relics of shards, and some mica and feldspar, remaining in the clay. The montmorillonite weathers on the outcrop to a typical frothy, "popcorn" surface. Over most of the Colorado Plateau region the Brushy Basin is off-white, gray, pink, yellowish red, red, or purple in color. Its composition, Table 1, 55–223, significant to the subject discussion, is characterized by 3.07 per cent Fe_2O_3, 0.35 per cent FeO, 4.51 per cent MgO, and 0.39 per cent K_2O.

At one locality, however, on Lone Tree or Blue Mesa, eleven miles northwest of Uravan, Colorado, and extending several miles in each direction, the Brushy Basin clays are anomalously blue in color instead of pink to red and yield a 10 Å basal spacing—here they are illite. These blue Brushy Basin clays on Blue Mesa are stratigraphically continuous and interfinger with the gray and yellowish red bentonite surrounding them. That the blue clay had the same parent volcanic ash as the yellow-red clay is unquestioned geologically. Microscopically, relic shards are present in clays of both colors, and partially decomposed residual silt particles washed out of the blue clay yield poorly developed diffractograms of expanding type clay (with ethylene glycol). The physical evidence seems entirely sound that volcanic ash was the parent rock of the montmorillonite in the clay of all colors in the Brushy Basin member, and that further change to blue color on Blue Mesa is an outgrowth of mineralogic transformation, or diagenesis, to illite.

TABLE 1.—ANALYSES OF MUDSTONES FROM THE MORRISON FORMATION

	Sample 55–180	Sample 55–177	Sample 55–223
SiO_2	49.03	56.64	58.40
Al_2O_3	17.93	20.99	24.16
Fe_2O_3	13.11	3.90	3.07
FeO	1.31	0.66	0.35
MgO	2.79	2.95	4.51
CaO	0.39	0.65	0.69
Na_2O	0.10	0.45	0.51
K_2O	7.84	7.11	0.39
TiO_2	1.06	0.61	0.44
P_2O_5	0.37	0.22	0.13
H_2O^+	6.00	5.77	7.29
Total	99.93	99.95	99.94

Sample 55–180: Glauconitic mica. Blue Mesa, Uravan, Colorado.

$$(\mathrm{Si}_{3.49}\,\mathrm{Al}_{0.51})\,(\mathrm{Al}_{0.99}\,\overset{-0.27}{\underset{2.07}{\mathrm{Fe}^{3+}_{0.70}}}\,\mathrm{Fe}^{2+}_{0.80}\,\mathrm{Mg}_{0.30})\,(\mathrm{K}_{0.71}\,\overset{0.78}{\mathrm{Na}_{0.01}}\,\mathrm{Ca}_{0.03})\,\mathrm{O}_{10}\,(\mathrm{OH})_2$$

Sample 55–177: Blue mudstone. Hydrous mica, analcime, chlorite (slight). Blue Mesa.
Sample 55–223: Pink bentonite. Montmorillonite with small amount of quartz and hematite. Near Thompson (Floy), Utah.

Approximate Only $$(\mathrm{Si}_{3.79}\overset{-0.21}{\mathrm{Al}_{0.21}})\,(\mathrm{Al}_{1.63}\,\overset{0.30}{\underset{2.26}{\mathrm{Fe}^{3+}_{0.15}}}\mathrm{Fe}^{2+}_{0.04}\mathrm{Mg}_{0.44})\,(\mathrm{Ca}/2\mathrm{NaK})\,\mathrm{O}_{10}(\mathrm{OH})_2$$

Excess plus charge due to free SiO_2 and to Fe_2O_3.

Analyses by Bruce Williams Laboratory, Joplin, Missouri. The cost of these was defrayed by Grant No. 541 of the University of Missouri Research Council.

The chemical composition of the blue clay is shown by analysis of sample 55–177 in Table 1, which is characterized by 3.90 per cent Fe_2O_3, 0.66 per cent FeO, 2.95 per cent MgO, and 7.11 per cent K_2O. The chemical change accompanying the color change was the addition and incorporation of more than 6.5 per cent K_2O throughout a thickness of about 400 ft of clay. The source of the potassium is postulated to be from solutions from evaporites which have risen through salt-cored anticlines in the vicinity of Blue Mesa.

The blue color in the clay is interpreted to arise from resonance between iron atoms (ions) occurring in the clay structure in two states of valence, the two-valence representatives being separated by a distance of not more than 10 ionic radii (Weyl, 1951; Shively and Weyl, 1951), an interesting story in itself. The blueness is significant in several ways, (1) it was an anomalous color and therefore drew special attention to, and extra work on, this clay resulting in the discovery of the 10 Å phase, illite, and (2) in the development of a new 10 Å phase from montmorillonite the Fe‴–Fe″ iron was left in appropriate reorganized association from which blue arose. Thus, the change in basal spacing from that of montmorillonite to that of illite is interpreted to have been accompanied by other intracrystalline arrangement which included the blue-producing Fe‴–Fe″ adjustment, which is held to be sufficiently basic and profound to categorize the change as diagenetic. This occurrence is interpreted, therefore, to be a valid demonstration of illite converted from montmorillonite that was derived from a non-phyllosilicate parent.

DIAGENETIC GLAUCONITIC MICA FROM MONTMORILLONITE–ILLITE

Further diagenesis of the Brushy Basin clays to glauconitic mica, which approached closely to glauconite, is shown in a clayey sandstone about 15 ft thick near the top of the Brushy Basin member on Lone Tree-Blue Mesa. The sandstone is friable, fine-grained, and clayey. It is composed of angular to subangular quartz grains commonly ranging in size from 0.25 mm to 0.1 mm in cross section (the latter size predominating), and sparse alkali feldspar. The green pleochroic glauconitic mica coats the sand grains, wraps around them, and fills intergranular spaces. Where it is well developed, it covers an estimated 20 per cent of the thin section area in the rock. The glauconitic mica shows a microcrystalline, clayey texture similar to that exhibited by montmorillonite and aluminous hydrous mica, which are the typical clay minerals in the sandstones of the Brushy Basin member. The clay fraction of glauconitic mica is pleochroic and green, typical of galuconite. Indices of refraction were measured as 1.578 and 1.600, approximately, for X and Z, respectively. These index values are slightly lower than the indices recorded for most glauconite.

A diffractogram of the glauconitic mica, designated "180", is shown with the diffractogram of typical glauconite, designated "00", from the Bonneterre dolomite, Missouri (Hendricks and Ross, 1941), in Fig. 1. The similarity in patterns is close. In order to increase the registry of the X-ray, using k_α radiation, the scale factor was reduced by one-half in the range of 2θ above 30°. To obtain the *hkl* reflections, less fluorescent but weaker Co radiation was used. The oriented clay flakes on a porous tile base show a strong 001 d spacing at 9.97 Å, a very weak 002 spacing at 5.01 Å, and a strong 003 spacing at 3.34 Å. From a specimen of more nearly randomly oriented, pulverized material additional peaks were recorded on a diffractogram at 4.53 Å, 3.67 Å, 3.52 Å, 3.059 Å, 2.91 Å, 2.58 Å (004), 2.409 Å, 1.665 Å, and 1.510 Å (060). The *hkl* reflections are not strongly developed on the diffractogram, probably indicating incomplete or imperfect crystallization. The glauconitic is 1 M (Dr. Herbert Glass, personal communication, October 1956), dioctahedral.

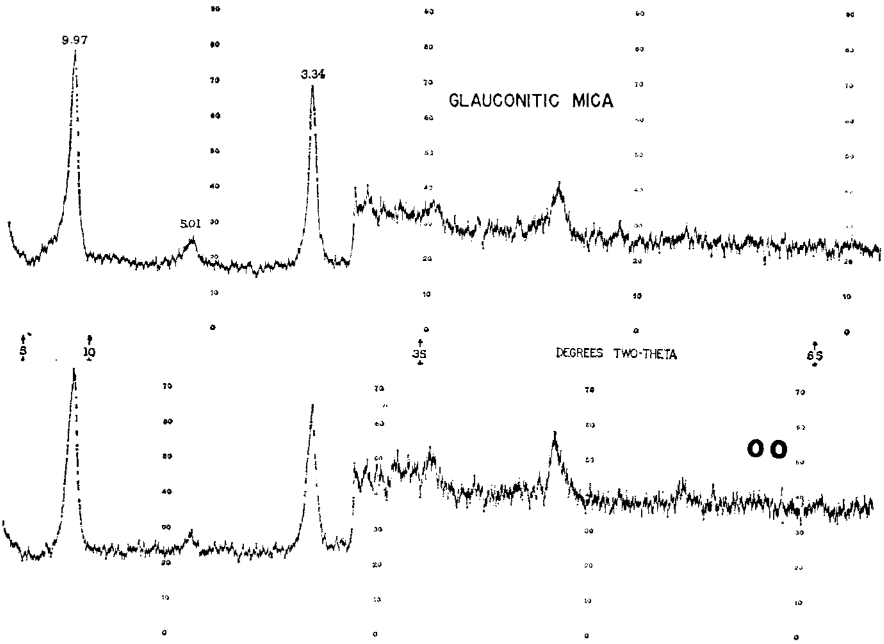

Figure 1.—X-ray diffractograms of the glauconitic mica, "180," from Blue Mesa, Montrose County, Colorado, and of typical glauconite, "00," from the Bonneterre dolomite, Flat River, Missouri. Ni-filtered Cu K_α radiation. The scale factor was reduced one-half at 30° 2–theta to increase the registry.

A chemical analysis, sample 55–180, Table 1, shows that the change of the clays to glauconitic mica was accompanied by enrichment in Fe_2O_3 to 13.11 per cent, K_2O to 7.84 per cent, and a decrease in MgO and Al_2O_3. The formula for the glauconitic mica was computed, including TiO_2, by M. D. Foster (personal communication, May 1956) as follows:

$$\underset{1.99}{(Al_{0.88}Ti_{0.06}Fe^{3+}{}_{0.68}Fe^{2+}{}_{0.08}Mg_{0.29})}(Si_{3.40}Al_{0.60})O_{10}(OH)_2Ch_{0.95}$$

This formula is intermediate between those of typical glauconite and muscovite. Foster (1956, p.66) indicates that substitution of Al for Si in typical glauconite is of the order of $(Si_{3.67}Al_{0.33})$, and that substitution in muscovite is in the range $(Si_{2.98\ \text{to}\ 3.11}\ Al_{1.02\ \text{to}\ 0.89})$, whereas the tetrahedral substitution of Al for Si in the glauconitic mica is intermediate between Foster's values for glauconite and muscovite. The Al and Fe^{3+} in octahedral coordination in muscovite are found by Foster to be of the order of 1.9 and 0.03 in ratio respectively, and in glauconite to

> be 0.18 and 1.1 to 1.2 in ratio, respectively. In the glauconitic mica, octahedral Al and Fe^{3+} are of the order of 0.9 and 0.7 in ratio, respectively; hence this is intermediate between muscovite and glauconite, for which reason the mineral is called glauconitic mica.

Iron oxides and other compounds are abundantly available in the Brushy Basin rocks, so the source of iron for diagenetic incorporation into glauconitic mica is no problem. It is essential, however, that a favorable oxidation potential was present. The pelletal glauconitic mica may have been induced organically, but the details of the environment of the matrix flakes are less easily inferred or assignable. Nevertheless, the validity of diagenesis here is considered to be established.

Diagenesis of Illite Since Early Paleozoic Time

The origin of glauconite, apart from some of it being detrital (Light, 1952), is usually considered to be diagenetic—including the observation by Weaver (1958a, p.166) who in writing about illite polymorph stated that, "In view of the fact that the glauconite mineral, which is considered to form diagenetically under marine conditions appears to exist only as the 1 M polymorph. . . ."

Of special interest to the present inquiry into diagenesis is a paper by Hurley, Cormier, Hower, Fairbairn, and Pinson (1960) who were investigating the reliability of glauconite for age measurement by K–Ar and Rb–Sr methods. They concluded from this entirely different and independent approach that glauconite was being formed in sediments during geological time (since the Lower Paleozoic)—a straightforward criterion of diagenesis—and that K was being incorporated, timewise, into the crystals of glauconite. A pertinent paragraph of the paper (Hurley *et al.*, 1960, p.1793) is cited, following:

> "Glauconites have interlayered structures. The interlayering involves mainly non-expandable 10 Å layers and expandable (montmorillonitic) layers. The potassium content of glauconites is inversely proportional to the percent expandable layers. Furthermore, the percentage of expandable layers is greater in younger glauconites than in older. This suggests that the glauconite pellets continue to develop into purer mineral grains over long periods of time, with a decrease from 30 per cent or more of expandable layers in your glauconite to about 10 per cent in glauconite of early Paleozoic age. Almost without exception Lower Paleozoic glauconite was found to contain more than 5 percent potassium."

It is significant that the formation (crystallization) of glauconite and incorporation of K was time dependent over a long time.

Diagenetic Alteration of Montmorillonite to Illite in Ancient Marine Rocks

Burst (1959) studied the clay mineral relationships in the subsurface of the Wilcox (Eocene) formation which extends continuously from outcrop in southern Illinois and Missouri to a depth in excess of 13,000 ft in Louisiana, and found "progressive diagenetic conversions with depth. Montmorillonite, a common constituent of Wilcox outcrop material, becomes less evident below 3000 ft and is not normally found in an unmixed state below the 9000–10,000 ft overburden level. At depths between 3000 and 14,000 ft, montmorillonite lattices are commonly interspersed with illite components, the frequency of which increases with depth to a virtual elimination of montmorillonite swelling characteristics below 14,000 ft."

Powers (1959, p.318) observed

> "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. . . . 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 post depositionally."

Furthermore, Weaver, who suggested that illite in the pre-Upper Mississippian shales is compatible with the probably *non-diagenetic* illite in associated carbonate rocks (Weaver, 1959, p.170) wrote in regard to clay minerals in the Late Cretaceous rocks of the Washakie Basin of Wyoming (Weaver, 1961), "Montmorillonite, when buried to depths of several thousand feet, starts to be converted to a mixed-layer illite-montmorillonite as a portion of the montmorillonite layers contract to form illite-like layers. At a depth of approximately 10,000 ft no discrete montmorillonite remains (Burst, 1959; Powers, 1959; Weaver, 1959, 1960). This can be seen in the Lewis of the Washakie Basin."

Thus, from the foregoing documentation, the evidence appears sound that diagenesis of illite from montmorillonite does take place. Burst de-emphasized the importance of time in the diagenesis of the Wilcox illite, as follows (Burst, 1959, p.28): "Geologic age, however, does not seem to be the controlling feature in the reduction of clay swelling capacity. . . . This paper shows that anomalies of this type may be related to differences in burial depth and geothermal gradient." Recalling that Hurley *et al.* (1960) did find time to be important in the diagenesis of glauconite, it is suggested that all three factors, time, burial depth, and geothermal gradient, in addition to activities of essential ions, contribute significantly to the diagenetic formation of 10 Å clay minerals.

Diagenetic Formation of Corrensite

The preceding examples have been centered about incorporation of K during diagenesis, but equally sound evidence is found from Mg-minerals, notably corrensite, whose diagenetic formation has been documented from two, well-investigated occurrences. Grim, Droste, and Bradley (1960) reported a range of mixed-layer clay minerals sequences of the corrensite type from clay partings in the ore beds in a New Mexico evaporite section. Pertinent to the origin of the minerals in the partings, they state:

> "They clearly represent material that accumulated in, and has remained in, an environment of high Na, K, and Mg activity from Permian time to the present" (p.228). Furthermore (p.234), "It seems highly unlikely that so nearly monomineralic detrital chlorite could ever have been introduced into an evaporite environment, to serve as parent for these specimens, but intermittent influxes of montmorillonite minerals and similarly constituted degradation products are easily conceived."

The highly monomineralic character of this occurrence meets a basic requirement which Weaver reasoned for diagenetic response of a mineral to a particular environment.

Peterson investigated the mineralogy and petrology of upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee (Peterson, 1962) and found corrensite in association with both calcite and dolomite, and chlorite–vermiculite and montmorillonite containing mixed 10 Å layers with calcite.

He has written with notable perception of the geochemical problems (and their probable solutions) of the genesis and diagenesis of the clay minerals and dolomite. Particularly significant are the following quotations.

> "electron micrographs of well-ordered corrensite show that it is crystallized in flat plates that have distinct crystal outlines, some of which suggest the pseudohexagonal outline common to macroscopic crystals of micaceous minerals. In addition, corrensite is a mineral that is not found in sediment loads of modern streams. This fact alone suggests that it was formed either in the depositional environment or during diagenesis. . . . Diagenetic chemical reactions take place in response to a trend toward chemical equilibrium, not away from it. . . . (Peterson, 1962, p.28).

In further relationship to diagenesis, Peterson wrote in 1961 (p.1265):

> "The demonstration that minerals have formed or altered during deposition or that they have been in some form of reactive equilibrium, does not prove that the rock in which they are found constitutes an equilibrium assemblage. Such a demonstration, however, does illustrate the importance of chemical processes in producing the properties of the carbonate rocks, and of the minerals forming them, even those minerals regarded traditionally as detrital. . . . It is clear that diagenetic readjustment of sedimentary mineral constituents does take place, and can be thought of as the very beginning of metamorphism."

Thus Mg, as well as K, may be incorporated diagenetically into clay minerals. A two-stage process will be suggested as the mechanism by which diagenesis is achieved, following a brief description of the addition of silica and vanadium to clay minerals during diagenesis.

ADDITIONAL DIAGENETIC REACTIONS

Silicification of clay minerals was postulated by Keller (1957, p.79) to occur by the condensation (although perhaps only transitory or loosely attached) of dissolved or colloidal silica tetrahedra onto colloidal clay particles by way of oxygen bridges. Upon burial of these loosely combined or articulated companions, the silica would become "permanently" attached, and siliceous mudstones would result. This postulation is now supported by observation of silicified illite by Bisque (1960/1962) who reported, "Certain dolomitic carbonate rocks containing disseminated illitic clay are shown to be susceptible to a type of 'silicification' whereby the clay particles are polymerized into a 3-dimensional network by the introduction of silicon from an outside source". Bisque and Lemish (1959) described the silicification process as, "the 'tying together', or polymerization of clay particles" by hydrated silica tetrahedra. It is also possible that some siliceous illitic shales might have been montomorillonites originally, from which silica was expelled as Al substituted for Si in the tetrahedral layer (Towe, 1962).

Kaolinization of gibbsite by combination with silica may well be included in diagenetic processes (Harrison, 1934; Gordon, Tracey, and Ellis, 1958).

The development of vanadiferous micaceous clays (also mixed layer illite-montmorillonite and chlorite) in uranium–vanadium ore minerals of the Colorado plateau was probably a diagenetic process (Hathaway, 1959; Foster, 1959). Foster (1959, p.121) reported that increase in V^{4+} was accompanied by a decrease in Al^{3+} (and Si^{4+}).

MECHANISM OF CLAY MINERAL COLLAPSE AND INCORPORATION OF POTASSIUM, MAGNESIUM, OR ALUMINUM

A two-stage mechanism will next be proposed to describe a probable way by which montmorillonite is transformed to illite, glauconite, or perhaps corrensite. This transformation is apart from the reconstitution of degraded illite and chlorite to their original counterparts.

The first stage is the cation exchange occurring when clay minerals are transported from a fresh-water environment to the ocean. These have been studied first hand. Powers (1959) measured the uptake of elements from sea water in 1.5 hr by Georgia kaolinite, Polkville (Miss.) bentonite, Patuxent River clay, and Chesapeake Bay clay, and found that Na^+, Mg^{2+}, and K^+ were taken up in that order. The amounts of uptake of the three elements relative to each other showed no variation in those clays.

Carroll and Starkey (1960) immersed montmorillonite (Osage, Wyo.), mixed-layer illite-montmorillonite (Highbridge, Ky.), illite (Fithian, Ill.), kaolinite (Bath, S.C.), and halloysite (Tintic, Utah) in sea-water for 10 days, and additional samples of the first three for 150 days. They found that Mg^{2+} ions from sea-water moved into the exchange positions in the minerals in preference to Ca^{2+} and Na^+ ions. Part of their data are shown in Table 2.

Potts (1959), in a small number of experiments, immersed clays (less than 5.5 microns e.s.d.) collected from suspension in the Missouri River (Easley, central Missouri), in ocean water 36 and 86 hr. The original river clay contained dominantly montmorillonite (expanding clay) and lesser amounts of 14 Å,

TABLE 2.—EXCHANGEABLE Ca^{2+}, Mg^{2+} and Na^2, TOTAL CATION EXCHANGE CAPACITY AND PERCENT OF EXCHANGE CAPACITY COMPLETED WITH CATIONS OTHER THAN H– OF THE EXPERIMENTAL CLAY MINERALS UNDER VARIOUS CONDITIONS IN SEA WATER (modified from Table 3 of Carroll and Starkey, 1960, p. 87).

Mineral	Exchangeable Cations Mg/100 g				CEC Determined		Percentage Exchange Positions Filled
	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sum		
Montmorillonite							
Natural	11	15	54	—	80	89	90
Sea-Water 150 d.	8	32	21		61	76	80
Mixed-layer							
Natural	26	7	—	—	33	33	100
Sea-Water 150 d.	5	7	5	—	17	28	61
Illite							
Natural	17	3	—	—	20	20	100
Sea-Water 150 d.	8	8	—	—	16	28	57
Halloysite							
Natural	1.8	1.7	0.6	—	4.1	11	37
Sea-Water 10 d.	4.1	5.4	0.6	—	10.1	31	32
Kaolinite							
Natural	0.5	0.4	—	—	0.9	5	18
Sea-Water	1.4	1.7	—	—	3.1	16	19

TABLE 3.—EXCHANGEABLE CATIONS, MISSOURI RIVER CLAY TREATED IN OCEAN WATER
Meq in 100g dry clay

Cations	Untreated Clay	36 hours in ocean water	86 hours in ocean water	HCl treated,* 86 hours, in ocean water
Ca^{2+}	60.7	38.3	17.3	12.9
Mg^{2+}	20.1	29.7	39.3	36.2
Na^+	1.7	1.8	3.4	3.8
K^+	1.4	1.4	2.0	1.9

* Treated with 5 N HCl for 3 min to remove $CaCO_3$

10 Å, and 7 Å clay. Data on the exchangeable cations in the clay before, and after treatment as indicated, are given in Table 3.

The observations and data of Carroll and Starkey, and Potts, are similar in that: treatment of land-derived clay in ocean water resulted in (1) a marked increase in exchangeable Mg, and (2) decrease in total exchangeable ions and exchange capacity in the 3-layer clays, but (3) an increase in exchangeable ions and exchange capacity in the 2-layer, halloysite and kaolinite. The increased sorption of Mg was attributed by Carroll and Starkey to the fact that "there is more magnesium than calcium in sea water and, in addition, calcium is tied up in the buffer mechanism of sea water (1960, p.99). Powers noted that "the ratio of Mg^{2+} to K^{+} in sea water, in numbers of atoms, is about 5:1, assuming complete ionization" (1959, p.314).

The exchange and sorption of cations from sea-water by river-borne clays may be examined in terms of energies that drive the process in 2 different ways: (1) energies of the solutions involved, and (2) energies of binding of cations by the clays. Consideration of the solution energies is approached as follows. It is assumed that the clay carried in the rivers is in equilibrium with the ions dissolved in the river water. The James River, of which an analysis is recorded in Clarke's Data of Geochemistry (Clarke, 1924, analysis L, p.77) will be taken as a typical example of river water carrying clay to the ocean. The composition of the river solution, recalculated in mols per liter is as follows:

Ca^{2+}	0.000506 mols/liter
Mg^{2+}	0.0001957
Na^{+}	0.0001113
K^{+}	0.00003438

It is assumed that ionization is approximately 100 per cent at these low concentrations, and these represent activities likewise. When clay carried by that solution is poured into the ocean, it comes into equilibrium with ocean water. Molal activities of the free ions in the ocean water may be calculated using the data from Garrels and Thompson (1962), as follows:

Ion	Molality	% Free Ion	Activities Free Ions	Molal Activity Free Ions
Ca^{2+}	0.0104	91	0.00264	0.00002498
Mg^{2+}	0.0540	87	0.0169	0.000794
Na^{+}	0.4752	99	0.356	0.1675
K^{+}	0.0100	99	0.0036	0.00006237

The solutions may be used as measuring instruments, modifying Woodruff's method used to study ionic equilibria between soil clay and dilute salt solutions (Woodruff, 1955a, b) to measure the free energy per chemical equivalent, that would accompany the transfer of the river solution (ionic activities) to the ion activities in sea water. The following equations are applicable, where *a* refers to the activity of a given ion in the solution.

$$\Delta F = RT \ln \frac{a_{\text{river}}}{a_{\text{ocean}}},$$

or

$$\Delta F = 1364(\log a_{\text{river}} - \log a_{\text{ocean}})$$

Since the clay minerals are in equilibrium with their suspending solution (a reasonable assumption), there will be zero difference of free energy between clay and solution; and the ΔF for the hypothetical solution transfer will be similar for the clay, i.e. per equivalent of cation exchanged, as follows:

		ΔF
Ca^{2+}	James River to ocean	891 cal.
Mg^{2+}		-415
Na^{+}		-4332
K^{+}		-353

A minus value indicates that the spontaneous change will tend to be in the direction of increase in sorption by that ion from ocean water; a plus value indicates a tendency to decrease the sorption of that ion. Potts found that the clay transferred from river water to sea water for 86 hr exchanged ions percentagewise in relation to those held in river water as follows:

Ca^{2+}	decreased to	34%	of original
Mg^{2+}	increased	195%	of original
Na^{+}	increased	200%	of original
K^{+}	increased	140%	of original

This direction and order of change is qualitatively in accord with the solution chemistry; it is another way of expressing what Carroll and Starkey, and Powers reported as differences in concentration.

The actual ions held by the clay, and the strength by which they are held, includes also the binding energy of the clay for the several ions. Marshall and students have investigated over 40 different clay-ionic systems, homionic and polyionic (documented on pp.376–377 of Marshall, 1954), part of which are applicable to the question in hand. Marshall pointed out immediately, however (p.377), that, "Evidently it is not possible to predict cationic activities in polyionic clays from data obtained only on homionic systems." Instead, Jarusov's rule (Jarusov, 1937) that, "the cation with the higher mean free bonding energy preempts those surface positions which manifest greater mean free bonding energy" (Marshall, 1954, p.383), applies best to polyionic clay systems.

Fortunately some of the work in Marshall's laboratory is applicable to clay such as is carried by the Missouri River—for example the clay from the Putnam soil, an expanding, beidellitic clay, which is presently being eroded by tributary streams of the Missouri River, was studied by McLean (1950) in K–Na systems. In K–Na mixed systems the bonding energy of potassium to Putnam clay is about 30 per cent higher than in single systems, and the reduction of the bonding energy of sodium is even greater (Marshall, 1954, p.377). On Wyoming bentonite, the effect of Ca is to reduce the bonding energy for K—thus, in the ocean water where Ca is lower in concentration than in river water, the binding of K will increase. Arizona bentonite showed stronger bonding energy for K than did Wyoming bentonite.

Of highest importance to the question of K sorption and fixation in regard to the problem at hand was the discovery by Barber and Marshall (1951, 1952) that in K–Ca, K–H–Ca, and K–H systems, the bonding energy for K was higher when present at less than 10 per cent saturation than when present in larger amounts in two illites, Putnam clay, attapulgite, and impure halloysite; that the bonding energy for K appears to rise almost asymptotically for very small fractions of saturation; and that it is indeed quite high in the limit (Marshall, 1954, Fig.10, p.383).

It is most significant and important that in these polyionic systems as the saturation of the clay becomes lower with potassium, the higher the bonding energy between the two! When this concept is extrapolated to 3-layer clays carried by a river into the ocean it is understandable why K moves into a position of fixation. Marshall wrote of this, "These are fixation effects" (p.381), although he was not discussing diagenesis.

Powers (1957, 1959) attacked this problem of K sorption, and suggested that at an increased depth of burial the sorption of K^+ would increase until it equalled that of Mg^{2+}, which he called an "equivalence level". However, as is being proposed in this paper, the sorption of K is a function of both availability from solution and also from bonding energy between K and the clay, and the fixation of K by a 3-layer clay does not call for a high concentration of K—indeed the opposite is desired—and the relatively low saturation of exchangeable K on clay minerals in the ocean makes for tightest holding and fixation.

Attention has been directed in a preceding paragraph to the decrease in cation exchange capacity of river-borne montmorillonite and mixed-layer illite-montmorillonite after being treated with ocean water, as observed by both Potts, and Carroll and Starkey. This decrease is interpreted as being due to conversion of easily exchangeable cation sites to fixed cation sites or to some on which tightly bonded ions, such as K, are being held too tightly to be exchanged by ordinary cation exchange capacity reactions.

The source of adequate amounts of available K to produce illite from montmorillonite or degraded illite was considered by Powers (1959, p.322). He found inadequately low the amount of K available on exchange positions and in interstitial water, but analyses of bulk samples of clay yielded more than enough, and he suggested sources in bacteria or ligno-proteins. Can it be that more K resided in tightly bonded positions on the clay than was detected by Powers using ordinary cation exchange capacity reactions?

Thus, the following model is suggested for the reactions undergone by river-borne 3-layer, Ca-rich clays when poured into the ocean. The change in ionic concentrations in solutions pulls Ca from the exchange positions and tends to substitute Na, Mg, and K in that order of abundance. Because of the bonding energies of clays, reacting in the polyionic systems as described by Jarusov's rule, Mg is sorbed in a maximum of exchange positions.

Mg may be retained as an interlayer brucite sheet, $Mg(OH)_2$, the formation of which is aided by the alkaline environment of the ocean. A reverse action is set up by the protons that are set free as each Mg^{2+} ion combines with $2OH^-$ from $2H_2O$. Thus not all montmorillonite is converted to chlorite or corrensite. The amount of conversion is influenced probably by the charge characteristics of the clay, and certainly by the activity and continued availability of Mg, as specified by Grim, Droste, and Bradley (1960) in the first sentence of the quotation from them on page 145, and by Peterson (1962, p.28), "The compositional variations of the complex chlorite minerals are the result of adjustment to the original bulk chemical composition of the sediment, including the solutions trapped in the pores of the sediment."

The hydroxides of Ca, Na, and K, unlike $Mg(OH)_2$, do not form a relatively insoluble hydroxide mineral compound in ocean water, and do not precipitate interlayer within the clay minerals. The K^+ ion, however, is tightly bound (as has been stated) by the clay, and thereafter becomes "permanently" fixed and incorporated in the clay mineral crystal, as has been shown by the development of glauconitic mica (Keller, 1958), glauconite (Hurley *et al.*, 1960), and illite under deep burial (Burst, 1959; Powers, 1957; Weaver, 1961).

That Al can be precipitated interlayer to montmorillonite has been shown in the laboratory by Slaughter and Milne (1960), and in soil clays by Coleman (1961) and Shen and Rich (1962). Hahn (1954) found chlorite (?), which is probably Al-chlorite, in a boehmite deposit in Missouri. Quite probably Al-chlorites will be found to be more common in soils and sedimentary rocks than heretofore recognized, and it is likely that a diagenetic origin will be inferred for some of them.

Details of the second stage in diagenesis, i.e., the ways in which change occurs in the basic lattice and the charge on it accompanying the "permanent fixation" of K, brucite layers, or gibbsite layers, are not adequately known. It has been suggested inferentially that Al moves from the octahedral to tetrahedral layer, displacing silica, and that this silica contributes to the silicification of shale (Towe, 1962). Perhaps Mg that has been sorbed strongly because of solution energy moves into the octahedral layer. Changes inferred to occur in the clay crystals, phyllosilicates, during diagenesis are not entirely visionary, for they have precedence and a counterpart in the solid state changes undergone by olivine transformed to iddingsite, as described by Gay and Le Maitre (1961) as follows:

> " 'Iddingsitization' is a continuous transformation in the solid state during which the original olivine crystal may pass through various stages of structural and chemical change; it may be possible at any stage to recognize embryonic structural arrangements, some of which approximate to normal ordered mineral structures, but the altered olivine is at all times a disordered, irregular arrangement which cannot be described as a simple sub-microscopic mineral intergrowth."

Thus, even though details of the mechanism can not be delineated, the fact that profound changes have occurred in order that the existing secondarily formed minerals (e.g. the blue illite, glauconitic mica, corrensite, the 10 Å mineral in the Wilcox shale) occur, cannot be denied; and (for the purposes of this paper) it seems that these changes are justifiably called diagenesis because of their relative permanence. Presumably this is another example of a geologic observation of which the physical and crystal chemistry awaits working out.

GENERALIZATIONS ON THE PROCESS OF CLAY MINERAL DIAGENESIS

Two, or possibly three, requirements must be met in order that clay mineral diagenesis may proceed. Adequate amounts of the element(s) such as K, Mg, Al, Si, V, etc., that are incorporated within the clay mineral must be available. A clear-cut example of such dependence is shown at Blue Mesa where blue illite was formed only in the place where K was available but failed to form outside the K-rich zone.

Second, the combining ion must be accompanied by energy of sufficient intensity to activate the reaction. Presumably this energy may be chemical, i.e. high activity of the ion, or strong binding energy by the clay mineral; high intensity of mechanical energy in the form of pressure (which conduces Al substitution for Si in the tetrahedral layers); or high intensity of thermal energy, i.e. increased temperature. Obviously as the pressure and temperature increase, the environment approaches that classified formally as metamorphism.

A possible third requirement, or a factor in the rate of diagenesis that brings potentiality of reaction into actuality when energy intensities are low or availability slow, is time—geologic time. Long time may not be necessary for the reaction under all circumstances, but it may be a characteristic of a particular geologic system and thus be a "special-case" requirement.

Diagenesis is typically a process that bridges between weathering and metamorphism in the rock cycle. It may be located in a sedimentary-metamorphic subcycle as shown in Fig. 2. Chemical weathering with respect to clay minerals is characterized by the addition of H^+ ions in which the process is driven dominantly by the chemical energy (activity) of H^+ ions. In an analogous manner, it may be said that, diagenesis of clay minerals is characterized by the addition and incorporation in them of Me ions, such as Mg, K, Ca, Na, Al, V. Fe, SiO_2 and others, driven mainly by chemical energy and aided by mechanical and thermal energy; but as the latter two become more effective the process is designated metamorphism (anamorphism).

Clay minerals tend to indicate, as do other minerals, the environment under which they were *formed*, but not necessarily the environment of the deposit in which they were *found* (Keller, 1956, p.2690). If the two environments are different, the activation energy of clay mineral reaction may bar clay mineral transformation to the last environment of deposition. The importance (in terms of volume of clay minerals) of environments in determining the clay mineral present in a sediment appears at this time to be in decreasing order, first, sites of provenance and terrestrial weathering, second, long-time reactions after burial, and third, short-time anamorphic reactions during transportation to deposition.

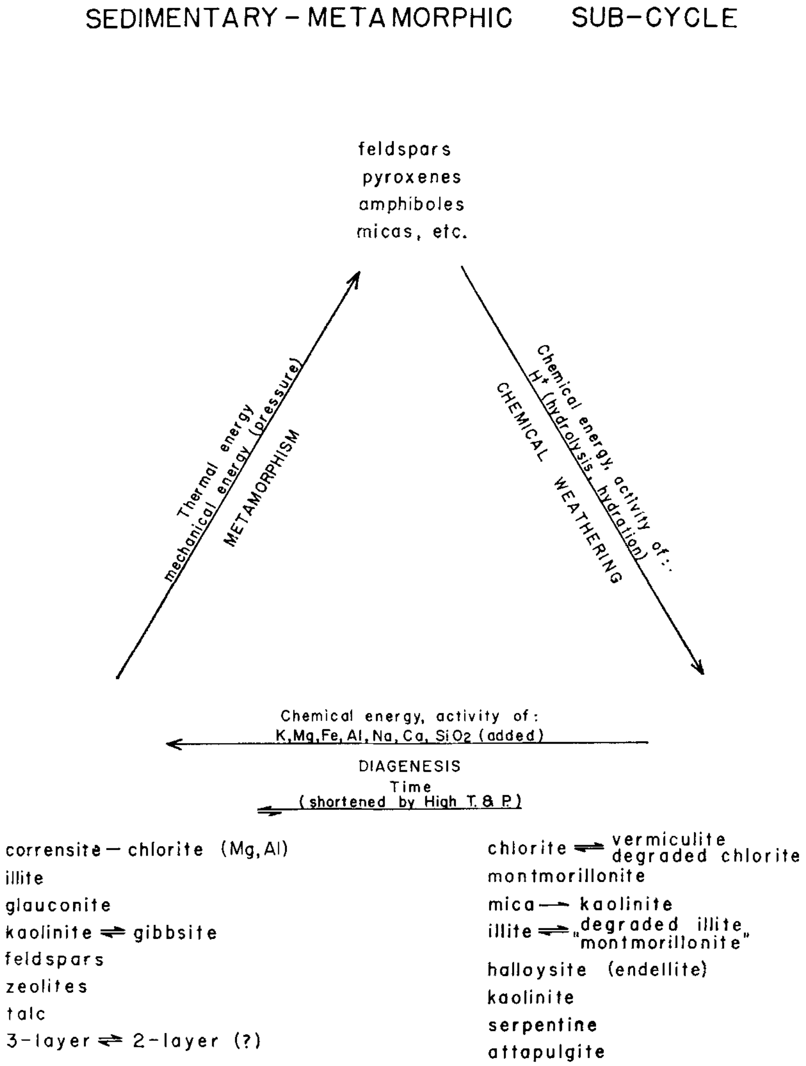

FIGURE 2.—Graphic subcycle illustrating weathering of primary minerals by addition of H ions driven by chemical energy; diagenesis by addition and incorporation of Me ions, such as K, Mg, Fe, Al, V, Ca, Na, and SiO_2, driven mainly by chemical energy; and metamorphism in which the driving energy is mainly thermal and mechanical (high pressure).

Clay mineralogists, geologists, and other earth scientists may ultimately describe mineral responses most precisely in terms of the physical chemical parameters present in the reacting system. The description and inference of climate, marineness, biogenic milieu, etc., when expressed conventionally (as in geologic terms) will be valid, accurate, and precise to the extent and precision that the geologic description represents the physical chemical parameters.

REFERENCES

Barber, S. A., and Marshall, C. E. (1951) Ionization of soils and soil colloids: II Potassium-calcium relationships in montmorillonite group clays and in attapulgite: *Soil Sci.*, v.72, pp.373–385.

Barber, S. A., and Marshall, C. E. (1952) Ionization of soil and soil colloids: III Potassium-calcium relationships in illite, kaolinite, and halloysite: *Soil Sci.*, v.73, pp.403–413.

Beavers, A. H., and Marshall, C. E. (1951) The cataphoresis of clay minerals and factors affecting their separation: *Proc. Soil Sci. Soc. Amer.*, v.15, pp.142–145.

Bisque, R. E. (1962) Clay polymerization in carbonate rocks: *Clays and Clay Minerals*, 9th Conf., Pergamon Press, pp.365–373.

Bisque, R. E., and Lemish, J. (1959) Silicification of carbonate aggregates in concrete: *Highway Res. Board Bull.* 239, pp.41–55.

Botinelly, T., and Fischer, R. P. (1959) Mineralogy and geology of the Rifle and Garfield Mines, Garfield County, Colorado: in Geochemistry and mineralogy of the Colorado Plateau uranium ores: *U.S. Geol. Survey, Prof. Paper* 320, pp.213–230.

Burst, J. F., Jr. (1959) Postdiagenetic clay mineral environmental relationships in the Gulf Coast Eocene: *Clays and Clay Minerals*, 6th Conf., Pergamon Press, pp.327–341.

Carroll, D., and Starkey, H. C. (1960) Effect of sea-water on clay minerals: *Clays and Clay Minerals*, 7th Conf., Pergamon Press, pp.80–101.

Clarke, F. W. (1924) The data of geochemistry: *U.S. Geol. Survey, Bull.* 770.

Coleman, N. T. (1961) Decomposition of clays and the fate of aluminum: Abst., program, 1961 meeting, *Geol. Soc. Amer.*, p.30A.

Foster, M. D. (1956) Correlation of dioctahedral potassium micas on the basis of their charge relations: *U.S. Geol. Survey Bull.* 1036-D, pp.57–67.

Foster, M. D. (1959) Chemical study of the mineralized clays, in Geochemistry and mineralogy of the Colorado Plateau uranium ores: *U.S. Geol. Survey Prof. Paper* 320, pp.121–132.

Garrels, R. M., and Thompson, M. E. (1962) A chemical model for sea water at 25°C and one atmosphere total pressure: *Amer. J. Sci.*, v.260, pp.57–66.

Gordon, Mackenzie, Jr., Tracey, J. I., Jr., and Ellis, M. W. (1958) Geology of the Arkansas bauxite region, *U.S. Geol. Survey Prof. Paper* 299.

Griffin, Geo. M., (1960) Clay mineral facies development in recent surface sediments of the northeastern Gulf of Mexico: Unpublished Ph.D. Thesis.

Griffin, G. M. (1962) Regional clay-mineral facies—products of weathering intensity and current distribution in the northeastern Gulf of Mexico: *Bull. Geol. Soc. Amer.*, v.73, pp.737–768.

Grim, R. E. (1953) *Clay Minerology*: McGraw-Hill, New York, 384pp.

Grim, R. E., Dietz, R. S., and Bradley, W. F. (1949) Clay mineral composition of some sediments from the Pacific Ocean off the California coast and the Gulf of California: *Bull. Geol. Soc. Amer.*, v.60, pp.1785–1808.

Grim, R. E., Droste, J. B., and Bradley, W. F. (1960) A mixed-layer clay mineral associated with an evaporite: *Clays and Clay Minerals*, 8th Conf., Pergamon Press, pp.228–235.

Hahn, G. W., (1954) Clay mineral relationships in the Ochesky fireclay pit: Unpublished Master's thesis, Library, University of Missouri, Columbia, Mo.

Harrison, J. B. (1934) The katamorphism of igneous rocks under humid tropical conditions: British Guiana, Imp. Bur. Soil Sci., Rothamsted Exp. Sta. Harpenden, Pub., St. Albans.

Hathaway, J. C. (1959) Mixed-layered structures in vanadium clays, in Geochemistry and mineralogy of the Colorado Plateau uranium ores: *U.S. Geol. Survey Prof. Paper* 320, pp.133–138.

Hendricks, S. B., and Ross, C. S. (1941) Chemical Composition and genesis of glauconite and celadonite: *Amer. Min.*, v.26, pp.683–708.

Howell, J. V. (1957) Glossary of Geology and related sciences: *Amer. Geol. Inst.*, under NAS–NRC, Washington, D.C.

Hurley, P. M., Cormier, R. F., Hower, J., Fairbairn, H. W., Jr. (1960) Reliability of glauconite for age measurement by K–Ar and Rb–Sr methods: *Bull. Amer. Assn. Petrol. Geol.*, v.44, pp.1793–1808.

Jarusov, S. S. (1937) Mobility of exchangeable cations in the soil: *Soil Sci.*, v.43, pp.285–303.

Keller, W. D. (1957) *Principles of Chemical Weathering*: Lucas Bros., Pub., Columbia, Mo., 111pp.

Keller, W. D. (1958) Glauconitic mica in the Morrison formation in Colorado: *Clays and Clay Minerals*, Nat'l. Acad. Sci.–Nat'l. Res. Council pub. 566, pp.120–128.

Keller, W. D. (1961b) Mineral and chemical alluviation in a unique pedologic example: *J. Sed. Pet.*, v.31, pp.80–86.

Keller, W. D. (1962) Clay minerals in the Morrison formation on the Colorado Plateau: *U.S. Geol. Survey Bull.* 1150, 90pp.

Keller, W. D., and Frederickson, A. F. (1952) Role of plants and colloidal acids in the mechanism of weathering: *Am. J. Sci.*, v.250, pp.594–608.

Light, M. A. (1952) Evidence of authigenic and detrital glauconite: *Science*, v.115, pp.73–75.

Marshall, C. E. (1954) Multifunctional ionization as illustrated by the clay minerals: *Clays and Clay Minerals*, Nat'l. Acad. Sci.–Nat'l. Res. Council pub. 327, pp.364–385.

McLean, E. O. (1950) Interrelationships of potassium, sodium, and calcium as shown by their activities in a beidellite clay: *Proc. Soil Sci. Soc. Amer.*, v.15, pp.102–106.

Millot, Georges (1949) Relations entre la constitution et la genese des roches sedimentaires argileuses: *Bull. l'Assn. des Ingen. Geol. de l'univ. Nancy*, Tome II, pts. 2, 3, 4, Nancy, France.

Packham, G. H., and Crook, K. A. W. (1960) The principle of diagenetic facies and some of its implications: *J. Geol.*, v.68, pp.392–407.

Peterson, M. N. A. (1961) Expandable chloritic clay minerals from upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee: *Amer. Mineral.*, v.46, pp.1245–1269.

Peterson, M. N. A. (1962) The mineralogy and petrology of upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee: *J. Geol.*, v.70, pp.1–31.

Potts, R. H. (1959) Cationic and structural changes in Missouri River clays when treated with ocean water: Unpublished Master's thesis, University of Missouri, Library, Columbia, Mo.

Powers, M. C. (1957) Adjustment of land-derived clays to the marine environment: *J. Sed. Pet.*, v.27, pp.355–372.

Powers, M. C. (1959) Adjustment of clays to chemical change and the concept of the equivalence level: *Clays and Clay Minerals*, 6th Conf., Pergamon Press, pp.309–326.

Pryor, W. A., and Glass, H. D. (1961) Cretaceous-Tertiary clay mineralogy of the upper Mississippi embayment: *J. Sed. Pet.*, v.31, pp.38–51.

Ross, C. S., and Kerr, P. F. (1931) The clay minerals and their identity: *J. Sed. Pet.*, v.1, pp.55–65.

Shen, M. J. and Rich, C. I. (1962) Aluminum fixation in montmorillonite: *Proc. Soil Sci. Soc. Amer.*, v.26, pp.33–36.

Shively, R. R., Jr., and Weyl, W. A. (1951) The color change of ferrous hydroxide upon oxidation: *J. Phys. and Colloid Chem.*, v.55, pp.512–515.

Slaughter, M., and Milne, I. H. (1960) The formation of chlorite-like structures from montmorillonite: *Clays and Clay Minerals*, 7th Conf., Pergamon Press, pp.114–124.

Stevens, R. E., and Carron, M. K. (1948) Simple field test for distinguishing minerals by abrasion pH: *Amer. Min.*, v.33, pp.31–50.

Sujkowski, Zb. L. (1958) Diagenesis: *Bull. Amer. Assn. Petrol. Geol.*, v.42, pp.2692–2717.

Towe, K. M. (1962) Clay mineral diagenesis as a possible source of silica cement in sedimentary rocks: *J. Sed. Pet.*, v.32, pp.26–28.

Weaver, Chas. E. (1958a) A discussion on the origin of clay minerals in sedimentary rocks: *Clays and Clay Minerals*, Nat'l. Acad. Sci.–Nat'l. Res. Council pub. 566, pp.159–173.

Weaver, Chas. E. (1958b) The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material: *Am. Mineralogist*, v.43, pp.839–861.

Weaver, Chas. E., (1958c) Geologic interpretation of argillaceous sediments: *Bull. Am. Assn. Petrol. Geol.*, v.42, pp.254–271.

Weaver, Chas. E. (1959) The clay petrology of sediments: *Clays and Clay Minerals*, 6th Conf., Pergamon Press, N.Y., pp.154–187.

Weaver, Chas. E. (1960) Possible uses of clay minerals in search for oil: *Bull. Amer. Assn. Petrol. Geol.*, v.44, pp.1505–1518.

Weaver, Chas. E. (1961) Clay Mineralogy of the Late Cretaceous rocks of the Washakie Basin: Guide book sixteenth Ann. Conf. Wyo. Geol. Assn., pp.148–154.

Weyl, W. A. (1951) Light absorption as a result of two states of valency of the same element: *J. Phys. and Colloid Chem.*, v.55, pp.507–512.

Whitehouse, U. G., Jeffrey, L. M., and Delbrecht, J. D. (1960) Differential settling tendencies of clay minerals in saline waters: *Clays and Clay Minerals*, 7th Conf., Pergamon Press, N.Y., pp.1–80.

Woodruff, C. M. (1955a) Ionic equilibria between clay and dilute salt solutions: *Proc. Soil Sci. Soc. Amer.*, v.19, pp.36–40.

Woodruff, C. M. (1955b) The energies of replacement of calcium by potassium in soils: *Proc. Soil Sci. Soc. Amer.*, v.19, pp.167–171.