FORMATION AND OCCURRENCE OF CLAY MINERALS

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INTRODUCTION

Clay minerals may be significant indicators of earth processes. They form through a range which involves at one extreme the action of compressed water vapor at a temperature of several hundred degrees centigrade, and at the other extreme, the action of atmospheric agencies at an ordinary temperature. Not recognized as original products of magmatic crystallization, clay minerals are *prima facie* evidence of a process subsequent to the original crystallization. Yet their relation to the magmatic process may be close: the last of the fluids and vapors of the magma may react with wall rock to form clay-mineral masses. This is probably the extreme of high-temperature, hypogene clay-mineral formation. Between this and the low temperature limit the transition is gradual, the minerals formed falling into gradational groups. In time clay aggregates of hydrothermal origin become distinguishable with difficulty from clay aggregates formed under atmospheric conditions—that is, those of supergene origin.

HYPOGENE PROCESSES

Clay minerals formed by hypogene processes result from the action of gases, vapors, or solutions that originate below and force their way upward through rocks of the earth's crust. Most of the elements of the clay minerals are contributed by the invaded rocks; few, other than water, are derived from deeper sources. The chief materials removed from the crustal rocks are alumina, silica, alkali or alkaline earth elements, and iron; these are transformed into clay minerals at a temperature ranging from slightly below 100°C to about 450°C in an environment that may be acid, neutral, or alkaline, depending upon the pH of the invaded rocks and the acidity of the vapors from the magma.

In the conduits of fumaroles, geysers, and volcanic vents the wall rock may be altered to clay; also, compressed vapors or mixed liquids and vapors (it is not easy to be certain which) may alter rock-forming minerals to clay in cavities in pegmatite dikes or in igneous masses. The most extensive hypogene clay deposits, however, have resulted from the action of thermal waters; although some of them are limited to the borders of metal-carrying veins, others are disseminated over a wide area.

Temperature

Data on temperature prevailing during clay-mineral formation are of three types: (1) measurements in drill holes penetrating hydrothermally active areas; (2) measurements of surface emanations; and (3) temperature recorded during experiments in clay-mineral synthesis. These data give little information on the temperature of formation of clay minerals in a natural environment, but they are all that are available.

Temperature in Drill Holes. Fenner (1934) has given measurements of the temperature in holes drilled in hydrothermally active geyser-basins of Yellowstone Park. A temperature of 180°C was noted in the bottom of a hole in Norris basin drilled to a depth of 265 feet; another hole, drilled to a depth of 406 feet in the Upper Geyser Basin, measured 205°C at the bottom.

In Italy during the course of power development at Larderello and adjacent regions in Tuscany (Ippolito, 1947) holes were drilled that yielded emanations and steam adequate for a major industrial installation. Keller and Valduga (1946) reported a temperature of 205°C and a pressure of 63.5 pounds per square inch in a representative Larderello well drilled to a depth of 876 feet. Brannock et al. (1948) reported that at Steamboat Springs, Nevada, the temperature in the bottom of one well, 156 feet deep, was 138°C. MacDonald (1944) has reported that gas collected from drill holes adjacent to a solfatara at the Kilauea volcano, Hawaii, had the temperature of 95.5°C. The temperatures recorded in these hydrothermal areas are well above the increase attributable to the thermal gradient, and are generally attributed to magmatic activity.

Temperature of Surface Emanations. A number of measurements of the temperature of hot springs or fumaroles have been recorded. One of the most elaborate programs of measurement was carried on by Zies and associates (1924) in the Valley of Ten Thousand Smokes, Alaska, following the Katmai eruption in 1912. There the temperature of gases escaping from fumaroles ranged from less than 100°C to 650°C. At Parícutin, Mexico, Zies (1946) observed temperatures up to 640°C in fumaroles of the older Zapicho flow. The estimated temperature of the lava at its source was given by Zies as 1200°C, in the same range as observed for other basaltic lavas.

Barth (1950) has reported temperature measurements for the springs, geysers, and fumaroles of Iceland. There superheated steam is a great rarity. Although it occurs in hot lava flows and around active craters, it has been reported only twice from hot-spring areas. Temperature at these springs was measured at 118°C and 120°C, but temperature in all other steam vents was very close to the boiling point of water; slight superheating probably occurred, but was not conspicuous.

Byers and Brannock (1949) observed variations in temperature of the emanations from Cone A in Okmok Caldera on northeastern Unmak Island. Temperature dropped from 320°C on July 19, 1946, to 90°C on September 5, 1946.

Temperature of Synthesis. Kaolinite has been produced synthetically at different temperatures and under a variety of conditions. It was formed by Noll (1934) at 320°C in the presence of 0.5N HCl. Noll expressed the opinion that kaolinite would form below 200°C in the proper acid concentration, if given sufficient time. Early experiments by Collins (1887) were said to have produced kaolinite by alteration of orthoclase in dilute HF in 96 hours at 16°C. Schwarz and Walcker (1925)

stated that kaolinite must form between pH 4.5 and 5.2, the best range being 4.8 to 5.0. In later experiments, Schwarz (1933) prepared kaolinite through the alteration of feldspar by treating with 0.5N to 1.0N HCl or H_2SO_4 at 300°C for 250 hours. According to Noll (1936), kaolinite forms below 400°C in a neutral solution free of alkali metals or in an acidic solution containing ions of alkali metals. The mineral was produced under acidic, neutral, or slightly alkaline conditions at 300°C and at a pressure of 87 atmospheres.

Folk (1947, p. 393), who has studied the alteration of feldspars and their products in the laboratory to gain information on the origin of kaolinite, writes ". . . . kaolin forms in acid solutions up to about 350°C if Al is rather high and K is low; muscovite forms from as low a temperature as 200°C, through 525°C in slightly basic and rather acid solutions if K and Al are high; and pyrophyllite forms from about 300°C up to 550°C if Al and K are both low. It appears thus that the Al: Si ratio and the K concentrations are very important in determining which mineral will form, since, if the temperature and acidity are proper, that mineral will be stable whose formula most closely resembles the composition of the solution around it."

Gruner (1944) reported that in about 30 experiments, largely with feldspars, using HCl solutions at 300°C to 400°C and in one case at 525°C, muscovite formed above 350°C and kaolinite below; and that pyrophyllite commonly formed throughout the range of experiments.

The experiments by Ewell and Insley (1935) in which kaolinite was formed from Al_2O_3-SiO_2 gels in a bomb at 310°C are in accord with other recent syntheses.

Experiments in synthesis, therefore, indicate that kaolinite may form under pressure at about 300°C. Under acid conditions and given an abundance of time—both of which nature provides—kaolinite may form at normal surface temperature and atmospheric pressure. The dehydration curve for kaolinite indicates that a temperature of formation greatly in excess of 400°C is unlikely. Thus, kaolinite probably does not form at the extreme upper limit of temperature prevailing in fumaroles.

Montmorillonite was synthesized by Noll (1935) at 300°C and 87 atmospheres; he used ratios of alkali: alumina: silica of 0.02: 1: 4 to 1: 1: 4. The alkalis used were NaOH, KOH, and $Ca(OH)_2$, under conditions slightly more alkaline than required for kaolinite. Noll concluded that montmorillonite forms when solutions are alkaline and alkali-earth metals are present. If an excess of $Mg(OH)_2$ is present, the magnesium enters into the composition of the montmorillonite up to 15.3 percent MgO; this is thought by Noll to correspond to fuller's earth.

Beidellite has been formed by Norton (1939) at 275-325°C by the action of CO_2-charged water on albite; in 1937 he developed sericite by the same method, using orthoclase, anorthite, and albite. Finely ground orthoclase was altered with H_2O and CO_2 in 33 days at 280°C and 1800 psi pressure, and in 150 days at 320°C and 2950 psi pressure. Noll (1932) found that sericite forms in greatest amount at 250°C, the lowest temperature of formation being 225°C.

Ewell and Insley (1935) synthesized dickite from hydrous alumina-silica gels at 350° and 365°C. Differential thermal curves indicate that dickite is stable at higher temperatures than kaolinite.

Thugutt (1894) reported that hydrated nepheline gave a product similar to nacrite.

Nontronite was produced in a bomb at 350°C by Ewell and Insley (1935) from coprecipitated gels using Fe_2O_3.$2SiO_2$.

Halloysite, according to Noll (1936), is unstable above 50°C; however, complete dehydration is obtained only by heating to about 400°C. Partial dehydration occurs readily at temperatures as low as about 75°C, or in a dry atmosphere, or under pressure. The intermediate states of dehydration appear to be quite stable because many specimens occur in nature in this form.

Adularia is not a clay mineral, but it may be found under similar conditions and may be an anhydrous associate of clay minerals. Morey and Ingerson (1937) indicate that the temperature needed for the synthesis of adularia is in the range 245-300°C. Gruner (1936) heated montmorillonite in gold-lined pressure bombs in aqueous solutions of $KHCO_3$ (10 percent). Seven days at 300°C produced very good orthoclase that gave an X-ray powder photograph identical with that of adularia. At 272°C the feldspar pattern became distinct after 10 days. At 245°C the stronger lines of orthoclase appeared after 42 days of heating. No changes were noticeable after 4 weeks at 200°C.

Alunite is another mineral frequently associated with clay. Leonard (1927) formed 60 to 90 percent alunite in 7 days in sealed pyrex tubes with 0.1M solutions of H_2SO_4, K_2SO_4, and Na_2SO_4 with ammonium sulphate at a temperature of 200°C. Alunite (50 to 99 percent) was formed at 100°C in 0.05M solutions with 50g of aluminum sulphate by heating for 100 days. With similar solutions, 40 to 60 percent alunite resulted in 60 days at 22°C.

Zeolites are reported by Noll (1936) to form under more alkaline conditions than either montmorillonite or sericite. In the same type of experiment which produced montmorillonite, analcime was formed with an excess of NaOH, $Ca(OH)_2$, and $Mg(OH)_2$.

Gaseous Emanations

The vapors from fumaroles and fissure emanations or hot springs are composed essentially of steam that contains some acidic materials. Zies (1929) has given the percentages of acid constituents for the vapors of the Valley of Ten Thousand Smokes as follows: HCl—0.117 percent; H_2S—0.029 percent; HF—0.032 percent.

Byers and Brannock (1949) report the constituents of the fumarole gases on northeastern Umnak Island as water vapor, carbon dioxide, and sulphur dioxide, and the water from thermal springs to contain as high as 159 ppm of boron and a few ppm of arsenic and antimony.

Residual gases in freshly erupted volcanic rock were studied at the time of the eruption of Mt. Pelée by Shepherd and Merwin (1927). Samples were heated in vacuo and the gases identified were thought to be characteristic of the eruption. The chief volatiles found were: H_2O—80 percent; CO_2—9 percent; and Cl, S, and F in smaller amounts.

Thermal Waters

Character of Hydrothermal Solutions. The character of the solutions responsible for the alteration of a rock to clay depends upon the original source material and the effects of wall-rock contamination. Both are important.

Though fluids from the magmatic source may be acidic, containing the vapors of HCl, HF, and H_2S, reactions with ground-water and wall rocks often produce a neutral or alkaline environment for the formation of clay minerals. On the other hand, there is good evidence that clay minerals may be formed under acid conditions.

Singewald (1932), in studying the alteration of diabase in igneous intrusions at Loveland Mountain, Park County, Colorado, concluded that the agents causing the alteration were contained in the magma itself and followed the same paths as the intruded porphyry. Alteration was an end of the intrusion cycle of each porphyry. Mineralizers within the sills were augmented by mineralizers from more deep-seated magma.

Acceleration of alteration as a result of acid conditions has been noted in volcanic regions. Payne and Mau (1946) call attention to two types of chemical decomposition in basalt around Kilauea crater. At steam vents where no sulphur dioxide is present, silica and soluble bases are leached away, leaving the hydrated oxides of aluminum and iron. At the solfatara, where sulphur dioxide is present, alteration is accelerated, and alkali and alkaline-earth elements are removed, leaving a yellow siliceous residue.

MacDonald (1944) has reported the development of opal and a lesser amount of kaolinite as the result of the action of thermal solutions weak in carbonic, sulphurous, and sulphuric acids. Many cavities were lined with sulphur crystals, and the other minerals deposited include alum, gypsum, mirabilite, kieserite, epsomite, and aphthitalite.

Allen (1935), in studying the geyser basins and igneous emanations of Yellowstone Park, found it necessary to account for bicarbonates of the alkalis in the thermal water. He concluded that there must have been an attack by CO_2 upon the wall rocks at depth.

Fenner (1936) found two different processes causing alteration to clay at Yellowstone Park. Near the surface, by the attack of acid sulphate on the feldspars, kaolinization results. At depth, where an attack of CO_2 was probably involved, the alteration produced beidellite. An interesting feature described by Fenner is the close association of pyrite with the beidellite. Casts of feldspars replaced by clay contain bright little cubes of pyrite, which were probably introduced by alkaline solutions responsible for the clay.

Acids of sulphur on the outlet side of an alteration zone, as pointed out by Lovering (1949, p. 53), would yield a quartz-alunite rock. At a greater distance from the source of the solutions, or nearer the surface, alunite would be expected to give way to diaspore. This sequence was described long ago by Whitman Cross (1896) in the alteration of rhyolite on Mount Robinson, Colorado.

In discussing the East Tintic district, Lovering (1949, p. 49) suggested that alunite forms in a less acid environment than that in which the kaolin minerals form.

He postulated precipitation from cooling, nearly spent acid solutions, with the pH increased to a little less than 7 by contact with bases in the rocks traversed.

Sulphate-bearing solutions, acting on kaolinitic clay, are believed by Ross and Kerr (1934) to form halloysite. Halloysite is often formed within or near masses of carbonate rocks. The mineral is also characteristic of vein deposits formed under acid conditions (see Lovering, 1949). Halloysite deposits at Liège, Tintic, and Park City may be the result of precipitation brought about by acid solutions acting on a carbonate rock. At low levels, in siliceous or argillaceous-siliceous wall rocks, kaolinite results from the action of acid solutions; but in the carbonate rocks higher up, halloysite forms.

In solfataric action described by MacDonald (1944), in which kaolinite was formed, the vapors responsible for the alteration contained sulphur dioxide, sulphur vapor, and a trace of hydrochloric acid.

Nutting (1945) reported that soil minerals, particularly those of the montmorillonite group, are known to dissolve or disperse readily in water solutions containing 0.01 to 0.04 percent acid.

Hydrothermal Deposits

Clay Minerals in Active Thermal Regions. Knowledge of clay minerals in active thermal localities is fragmentary. The solfataric action reported by MacDonald (1944) has resulted in the formation of kaolinite at the expense of olivine basalt lava and ash. As early as 1851, Bunsen (1851) observed that the transformation of a basalt to clay was no simple soaking process, but that certain constituents might be added, others subtracted. The alteration usually starts in the glassy or microcrystalline groundmass, leaving the phenocrysts intact. The rock eventually becomes soft. Barth (1950, p. 49) found the rocks in Iceland to be "profoundly altered by hot-spring action; most intense and rapid is the alteration caused by acid springs. The end product consists of opal with small amounts of clay minerals. The mechanical action of boiling and gas exhalation breaks up the rock into a finely divided claylike substance. In areas of intense acid-spring activity such slippery warm clay deposits cover large areas. . . . The basaltic lava is attacked by acid steam and vapors emanating from cracks and fissures in the lava. Around such cracks incrustations usually occur, and the pores and vesicles of the rock are filled with secondary minerals. Simultaneously the primary minerals are altered by metasomatic action, inducing changes in the bulk chemistry of the rock."

The dome around Geysir, Iceland, he described (Barth 1950, p. 97) as having "been built up by precipitation of silica from the hot-spring water as it flowed out of the basin. It is stratified (consisting chiefly of alternating layers of clay and silica sinter.) . . . The clay (layers) are identical (in composition) with the decomposition product formed by the action of acid hot-spring water on basaltic rocks at other places in Iceland, and it appears that only acid waters can produce this kind of clay. On the other hand, only alkaline waters deposit silica sinter. . . . The hot spring activity in this place has changed many times from alkaline to acid and vice versa."

Rock alterations in the Kilauea region of Hawaii have been described by MacDonald (1944) and by Payne and

Mau (1946). The resultant rock is composed largely of opal, with smaller amounts of kaolinite or related clay minerals, and relict magnetite and ilmenite. It has approximately the same volume as the unaltered rock, and original structures and textures are surprisingly well preserved.

Anderson (1935) has described and given many important details of the alteration of the lavas surrounding the hot springs in Lassen Volcanic National Park. Opal, accompanied by minor amounts of kaolin and alunite, is the chief product in the altered exteriors of all lava fragments collected where active decomposition is taking place. The muds from the hot-spring basins are similar in composition except that they usually contain more kaolin; the mud pots and the sediments from Boiling Lake consist largely of kaolin. Day and Allen (1925) suggested that two types of lava decomposition are in progress: ". . . The one producing kaolin and some silica without aluminum sulphate, the other producing silica with aluminum sulphate. In the fact that kaolin is decomposed by strong sulphuric acid into silica and aluminum sulphate, the key to the difference is doubtless to be found. If the acid forms in a place where sufficient water is percolating, its concentration is kept down to such a value that the decomposition of feldspars, volcanic glass, and possibly other minerals is incomplete. The intermediate and comparatively stable compound kaolin results, and this generally occurs in the springs, together with very dilute acid.

"On the other hand, if sulphuric acid forms in nearly dry ground, it will accumulate by progressive oxidation of the sulphur gases and the concentration may reach comparatively high values—probably in the form of sirupy films."

Anderson (1935) believes there is considerable evidence in support of this conclusion, namely the high alumina content of the sediments from Boiling Lake where one might expect the greatest dilution of sulphuric acid. Moreover, opal is being formed from lavas that are being attacked by steam where the acid may be more concentrated.

Clay Minerals as Cavity Fillings in Pegmatites. Presumably cavities in pegmatite dikes, signifying gaseous conditions, may provide channels along which thermal fluids permeate and alter the feldspars. They represent a late, probably hydrothermal, stage in pegmatitic activity. The alteration could be largely either the result of compressed vapors or thermal solutions. Silva and Neiva (1948) attribute montmorillonite formed in granite pegmatites to hydrothermal solutions.

Clay Minerals in Metalliferous Deposits. In recent years the importance of clay minerals as indicators of mode of origin of metal-bearing deposits has come to be generally recognized. Many of the metal-bearing deposits associated with late Mesozoic or Tertiary volcanism, particularly in the Cordilleran region of the continent, have associated with them prominent zones containing clay minerals. Deposits of tungsten, molybdenum, zinc, lead, copper, and uranium have been observed in a number of instances to occur in sites where the wall rocks have undergone partial or complete replacement by clay minerals. In particular, montmorillonite, kaolinite, halloy-

site, hydromica (illite), and dickite are coming to be recognized as significant by-products of the ore-forming process.

The initial stages of hydrothermal alteration may not involve clay minerals, as in the stages described by Lovering et al. (1949) at Tintic, Utah, where the ferromagnesian minerals of igneous rocks are converted to chlorite, and limestone is dolomitized. However, Sales and Meyer (1949) consider the montmorillonite at Butte one of the earliest indicators of hydrothermal alteration. Kerr (1951) reports the formation of chlorite at Silver Bell prior to the clay-mineral stage, and also at the copper deposit at Santa Rita (Kerr et al., 1950).

The initial stage represents the greatest penetration of the solutions and vapors from the magma into the fresh wall rock. It is here also that the alkali and alkaline-earth ingredients of the wall rock react most strongly with acidic fluids from the magma to produce alkaline or approximately neutral conditions. Sales and Meyer (1949) have given a summary of numerous analyses of the rocks of this stage, indicating particularly the release of alkaline earth elements from quartz monzonite bordering the Butte veins. The outer reactive zone in hydrothermal alteration encloses a zone of somewhat lower pH in which hydromica (illite) rather than montmorillonite becomes the dominant clay mineral. On the inner boundary of the hydromica zone, kaolinite becomes the dominant clay mineral. Located concentrically within the kaolinite zone is an inner zone in which sericite predominates.

The chemical and physical conditions giving rise to the formation of the concentric zones of alteration are the same conditions involved in the processes of metallic mineralization. The evidence of the mineral constituents observed indicates an increase in temperature toward the center; pressure conditions which are more or less uniform and characteristic of open fractures from a few hundred to a few thousand feet below the surface; and variations in pH from a slightly alkaline periphery, to neutral, to slightly acid, to slightly alkaline, from the edge to the center.

Montmorillonite is found in the border zone along the margins of hydrothermal veins, cutting intrusive igneous masses in the Cordillera of the United States. Sales and Meyer (1949) report that at Butte it is the first clay mineral to develop in the hydrothermal alteration of the quartz monzonite.

Field studies in the Marysvale district, Utah, have demonstrated that montmorillonite and hydromica (illite) may be formed by the hydrothermal alteration of glassy volcanic dikes. In the vicinity of Lovelock, Nevada, solid masses of volcanic glass have been found altered to montmorillonite, apparently by hydrothermal solutions. Volcanic ash is believed to be even more susceptible to alteration in areas of hydrothermal activity.

Among the clay minerals, dickite seems likely to form under conditions of highest temperature. The breaks in the static dehydration curve are slightly higher, and field relationships suggest an extension to deeper-seated conditions of occurrence. Exceptions exist, and although is has been suggested that dickite may be formed under supergene conditions, most, if not all of it is hydrothermal; it is ordinarily the high-temperature kaolin mineral.

The original dickite of Anglesey, dickite from three localities near Columbia, Missouri, dickite in the lead ores of southeastern Missouri (Tarr and Keller, 1936), the dickite at San Juanito, Mexico, dickite formed in the alteration of the Gilman porphyry at Gilman, Colorado, and dickite reported (Frankel, 1949) from the gold-bearing rocks of Witwatersrand are all hydrothermal in origin. Dickite in the veins of Cerro de Pasco coats coarse crystals of enargite; at Ouray, Colorado, dickite coats sulphide minerals. Sales and Meyer (1949) found dickite in the higher temperature or central zone in the deepest levels of the Butte, Montana, mines. In the Daggafontein mine on the Witwatersrand (Frankel, 1949) the dickite was associated with a greenish-gray clay, a chloritic mineral, pyrrhotite, gersdorffite, and a lustrous hydrocarbon, identified by Davidson and Bowie (1951) as thucholite, probably also of hydrothermal origin.

Where dickite and kaolinite are found together in hydrothermal veins, evidence points to dickite as the earlier of the two. It is a less abundant clay mineral, and only in a few places such as San Juanito and Ouray have masses of any considerable size been found.

Honess and Williams (1935) have reported dickite from the Pine Knot Colliery in Schuylkill County, Pennsylvania. The material is well crystallized and occurs, for the most part, as a white, glistening powder, or in small lumps composed of transparent tabular monoclinic crystals, many of exceptional beauty, ranging in size from 0.1 to 0.5 mm along the major axis. Of the associated species, clear transparent quartz is most common, although a small amount of pyrite and magnetic material is present. The quartz crystals are everywhere completely coated with dickite that impregnates the crystal surfaces in a manner suggestive of replacement.

The association of dickite with sulphides, such as in the southeastern Missouri lead ores, may indicate neutral or slightly alkaline conditions of precipitation. At Butte, sericite is an associated mineral; at San Juanito, pyrite may have been precipitated with dickite.

In the Tintic district, Utah, Lovering (1949) found an abundance of supergene kaolin in the oxidized zone of ore shoots. Argillic alteration is found below the lava near channels followed by later mineralizing solutions.

In origin, nacrite is probably more closely associated with dickite than with kaolinite. At St. George, Utah, and at San Juanito, Mexico, nacrite and dickite are closely associated. Both occurrences are believed to be hydrothermal, as is the well-known occurrence at Brand, Saxony.

The sequence of clay minerals appears most significant in hydrothermal veins. Individual minerals may occur under a variety of conditions, but the progressive alteration from fresh rock on the wall through a sequence such as montmorillonite, illite, kaolinite, sericite, and dickite is probably characteristic of hydrothermal veins.

SUPERGENE PROCESSES

The processes by which clays are formed on or near the surface have received much less experimental attention than have the processes of hypogene clay formation. It seems clear, however, that atmospheric conditions are responsible for the formation of clay minerals under a variety of conditions.

Clay-mineral development under normal surface conditions may require periods that are long even in terms of geologic time unless some accelerating conditions prevail. Under even slightly favorable conditions, however, leaching and deposition, together with weathering and soil formation, do take place. The chemistry of supergene processes is complex. It is generally thought, however, that even weak concentrations of acid or alkali solutions together with small amounts of alkali or alkaline-earth elements, alumina, silica, and other chemical constituents, given sufficient time, may produce clay deposits, some of which are very large. Special conditions, such as a more concentrated chemical action or moderate increase in temperature, may greatly decrease the time factor.

In saline or brackish bodies of water, clay minerals are thought to be often subject to diagenesis. In regions of heavy rainfall and high temperature, organic acids are apt to accumulate in unusual concentration, accelerating the formation of clay. Even organic concentrations in bogs where the temperature is not extreme may form clay minerals.

The formation of clay minerals originally, by either hypogene or supergene action, followed by removal, transportation, and redeposition at a new site, is simple in general concept but involves many features that should receive further scrutiny—particularly the extent to which the alteration or direct precipitation of clay minerals may take place in the cycle.

Normal Surface Action

Normal surface action in clay formation involves leaching and deposition, and weathering and soil formation. Leaching and deposition may take place as a result of special chemical conditions existing in fractures in rock masses considerably below the zone of weathering and soil formation. The distinguishing of clay minerals formed by leaching and deposition from those formed by low-temperature hydrothermal processes may not always be possible, but the attempt is worthwhile. In clay accumulations formed by mechanical transport, the presence or absence of chemical precipitates and the origin of the introduced clay minerals prior to transport are the most interesting features.

Leaching and Deposition. In the formation of bentonite, for example, supergene leaching and deposition are probably involved. As defined by Ross and Shannon (1926) bentonite is formed by the chemical alteration of glassy igneous material usually tuff or volcanic ash. One large group of bentonite deposits found in the lower Mississippi Valley and Gulf Coast region (Hagner, 1939) has probably been formed under supergene conditions. Even in many volcanic areas of the western United States, the actual formation of clay may have resulted from supergene action. In recent years, as a result of the search for bentonite to be used as an adsorptive clay, thousands of other bentonite occurrences have been discovered.

Nutting (1945) has pointed out that the complete replacement of shells by montmorillonite at Pontotoc, Mississippi, indicates that alumino-silicate sols may be deposited under conditions that allow removal of the original bases present in the shell-forming material.

Allen (1944) emphasizes the importance of sedimentary processes in clay-mineral formation in certain Pacific Coast areas where volcanic materials predominate. Sedimentary processes are more important than volcanic processes at Ione, California; Castle Rock, Washington; Whiteware, Montana; Hobart Butte and Molalla, Oregon. Clays derived directly from volcanic materials are composed dominantly of montmorillonite; but these clays, with the exception of the beidellite-nontronite varieties, have relatively low percentages of available alumina. In contrast, clays derived through leaching of various aluminous rocks in thoroughly drained areas are composed dominantly of kaolinite; furthermore, the depositional structure of these sedimentary clays favors the formation of gibbsite by weathering or the formation of dickite or kaolinite by hydrothermal action.

Large accumulations of fuller's earth that contain attapulgite as the effective clay mineral have been worked for many years in the Georgia-Florida region (Kerr, 1937). The sediments which contain the clays have been derived from the erosion of the crystalline rocks of the highlands. On the other hand, no such accumulation of attapulgite as is found in the sedimentary layers has been reported in the source area. It seems likely that the accumulation of attapulgite may represent more than simple transport and deposition; perhaps waters unusually high in magnesium, or long-continued action of waters low in magnesium, contributed to the formation of this unusually high-magnesia clay.

The unique clay mineral hectorite described by Foshag and Woodford (1936) is found in the Mojave Desert, California, in folded sediments of Tertiary age. Relic textures are abundant in the clay matrix; they include minute collapsed cavities lined with layers of the clay mineral, and curved structures which may be altered pumice shards. The rock is probably a greatly altered dacite tuff. The clay mineral of which the rock is now chiefly composed, is chemically and optically almost identical with the magnesian clay mineral, but differs from it by swelling greatly in water. In origin, therefore, this bentonitic magnesian clay is not essentially different from most normal bentonites. Chemical analyses of this clay show that it is essentially a magnesium silicate with only an insignificant amount of alumina. Noteworthy are the high soda content (3 percent) and the lithia content (1.12 percent).

According to Tarr and Keller (1937), kaolinite found in several localities in Missouri gives evidence of having been deposited from solution. Kaolinite occurs in the Orongo Circle mine as thin veins in nearly vertical joints of the Pennsylvanian shales, as well as in cavities and as a replacement mineral. The kaolinite at the National Pigment barite mine was deposited in joints in dolomite that had been enlarged by solution. At the Reavis mine, kaolinite occurs dominantly in solution cavities and along joints in the Jefferson City dolomite. This mine and the National Pigment mine are in sink holes. Kaolinite in the Keokuk, Iowa, area occurs in quartz geodes and in small solution cavities in siltstone.

Allen (1937) has described kaolinite derived from limestone by supergene processes. The Cheltenham clay of Missouri had its source in an earthy limestone subject to the action of carbonic-acid waters. Erosion into a choked sink hole or closed basin has resulted in the accumulation of a sedimentary clay deposit.

MacKenzie (1949) has described a clay mineral of possible supergene origin, which differs somewhat from illite but belongs to the same group. The material occurs at Ballater, Aberdeenshire, in a crush-band in the altered rock along a vein in a granite outcrop exposed in road-widening. The alteration is apparently a result of the action of water, but since the band was still highly altered at the base of the exposure (about 25 feet from the surface), it is not certain from the field relationships whether the water was of hydrothermal origin or whether it percolated from the surface.

As pointed out by Ross and Kerr (1934) halloysite forms many times by supergene processes. Callaghan (1948) has described halloysite $4H_2O$ from Bedford, Indiana, which represents a supergene reorganization of deposited material. Other halloysite deposits were apparently at one time a residual soil. Halloysite from Wagon Wheel Gap, Colorado (Cross, 1896), formed as an alteration product of rhyolite, and may have been deposited from solution or suspension by downward-moving waters.

Lovering (1949) has described kaolinite, halloysite, and allophane in the East Tintic district, Eureka, Utah, which formed when weathering of sulphide ores produced acid solutions. Away from the sulphide bodies, montmorillonite and beidellite are the common products of weathering.

Bates et al. (1950) have made a number of interesting observations on the morphology of halloysite. Halloysite $4H_2O$ (endellite) is believed to consist of well-developed tubes which split upon dehydration to halloysite $2H_2O$. Study with an electron microscope has revealed that halloysite $2H_2O$ crystals consist of hollow tubes which have collapsed, or have split and partially or completely unrolled. It is suggested that this change in morphology explains the irreversibility of the dehydration process. There is no apparent morphological transition from these crystals to the pseudo-hexagonal plates characteristic of kaolinite, dickite, and nacrite.

Stringham and Taylor (1950) ascribe the formation of nontronite occurring in a contact metamorphic zone to the action of slightly acid solutions. This clay is probably a weathering product of diopside, tremolite, and pyrophyllite. Nontronite (Main, 1950) occurs within fissures and fills cracks and spaces between polygonal joints in basalt in the vicinity of Garfield and Manito, Washington. The mineral occurs chiefly as a filling, although in some cases the basalt is altered to nontronite. The nontronite contains a small amount of sericite, pyrite, and quartz. Presumably neutral or alkaline solutions at normal temperature and supergene in origin, acted on the basalt and deposited nontronite in openings.

Weathering and Soil Formation. Clay minerals are produced in various areas on the earth's surface where the normal temperature is low; at such a temperature, however, special physical or chemical conditions are essential, and small differences may be significant. The clay minerals form slowly by rock decomposition. Varve clays deposited during Pleistocene glaciation along the Hudson Valley are essentially rock flour with a minor clay-mineral content; working near Newburgh, New

York, Allen (1947) found a relatively small clay-mineral content in the glacial clay—a feature found elsewhere by other investigators.

In contrast, weathering in Brazil under tropical or semitropical conditions has produced kaolinitic masses which may extend for hundreds of feet in depth. Kerr (1942) has described granite at Fazenda, Pacú, which decomposed in place, forming kaolinite; the texture of the granite was preserved in the weathered material.

Residual clays formed by weathering of granite and pegmatite in the southern Appalachian region furnish mixtures of kaolinite and halloysite in varying proportions. According to Sand and Bates (1952) halloysite is formed only from the weathering of feldspars and, under conditions of intense leaching, is formed from both plagioclase and potash feldspars. Primary mica, however, always alters to vermicular kaolinite. Potash feldspars, where leaching is not intense, pass through an intermediate stage of secondary mica, changing finally to vermicular kaolinite. On the other hand, halloysite forms from plagioclase, apparently without passing through an intermediate stage.

Rocks can be decomposed by action of normal surface waters when sufficient time exists for the completion of the process. Water in soil may occur in cavities and capillaries as adhering water, hygroscopically combined water, chemically combined water, and even water vapor. The total water content of a soil changes constantly through additions and subtractions. (Mohr 1944, p. 41) has pointed out in his discussion of tropical soils that the pH may vary from a figure lower than 3 to higher than 9. Even quartz (Mohr, 1944, p. 75), which is resistant at less than pH 7, dissolves in time at a pH greater than 7.5.

In tropical weathering, acid water may be responsible for the formation of extensive kaolinite deposits. Mohr concluded that kaolinite would form in tropical soils as a result of weathering of feldspar, under the influence of pure water or water containing carbonic, sulphuric, or humic acid. Under the influence of alkali or OH⁻ ions, montmorillonite is more likely to form. In the same climate, if the rocks undergoing weathering are highly calcic, montmorillonite develops; alkali-rich rocks yield kaolinite. Wherever weathering takes place the possibility of an accelerating chemical action always exists.

Correns and Engelhardt (1938) have investigated the mechanism of weathering of potash feldspar and conclude that potash, alumina, and silica are all at first removed in ionic form with the relative proportions of the three constituents dependent to some extent on the acidity of the extracting medium. In time, a goodly number of rock-forming silicates not particularly soluble may, where present in soil and subjected to solutions of suitable pH, decompose to form clay.

An alkaline environment which gives a sufficient supply of magnesium or ferric or ferrous iron in addition to silica and alumina, is apt to lead to the development of montmorillonite. In wet and warm climates, where weathering and oxidizing conditions are comparatively rapid, kaolinite and lateritic soil are more likely to form than montmorillonite.

Frederickson (1951) proposes, largely on theoretical grounds, that the mechanism of weathering is essentially a base-exchange process between two similar crystal structures with different degrees of order. The mechanism is visualized as a process whereby the hydrogen ions of crystalline water are base-exchanged for the sodium ions of albite (which is used as a model). The small size of the hydrogen ion and the fact that its introduction into a crystal system is an exothermic reaction makes the process possible. The mechanical effect of this base-exchange reaction is a net expansion in the reacting layer of the crystal which causes the rock to exfoliate and become more chemically reactive. The minerals will break down into colloids or small clumps of insoluble silica depending on the Al : Si ratio in the crystal lattice.

Wiklander (1950) has studied the fixation of potassium by clays saturated with different cations. A micaceous clay (Clarence soil, Illinois) was treated for 21 days with HCl, NaCl, KCl, NH₄Cl, and CaCl₂ in order to obtain maximum replacement of K⁺ by the other ions. The subsequent fixation of K by the K⁺-depleted clays was then studied by the use of radioactive K⁺; fixation was found to be low for H⁺-, K⁺-, and NH₄⁺-saturated clays but high for Ca⁺⁺-, and more especially, Na⁺-saturated clays. Similar experiments on ground biotite showed low fixation values for H⁺- and NH₄⁺-saturated biotite, but high values for Mg⁺⁺- and Ba⁺⁺-saturated biotite.

Marshall (1948) has reported on ionization of calcium from soil colloids. Dilute suspensions of beidellite, montmorillonite, and kaolinite have been titrated with NaOH and with Ca(OH)₂ and the activities of H⁺, Na⁺, and Ca⁺⁺ in the solution (pH, pNa, and pCa) determined at frequent intervals during the titration. Kaolinite, which probably binds the bases on the surface of the particles only, gives highly ionized "salts," whereas much of the sodium or calcium taken up by beidellite or montmorillonite is held in an un-ionized state. This effect is more marked with calcium than with sodium.

It was Nutting's (1945) conclusion that montmorillonite, given sufficient time, will go into solution in slightly acid water, but that only the bases will be removed in strong acids, and that only free silica will be removed in pure water.

Kelley (1939) has pointed out that the most conspicuous effect produced on clays and argillaceous sediments by base exchange is reflected in their permeability. Generally speaking, calcium-saturated clays tend to be granular and comparatively pervious, whereas sodium clays are highly dispersed and relatively impervious.

Kelley indicates that the pH of a clay may be influenced significantly by base exchange. Calcium clays, if free from calcium carbonate, are approximately neutral, whereas sodium clays may be highly alkaline, a result of the hydrolytic property of sodium clay by which sodium ions are replaced by hydrogen ions. Ordinary water always contains a low concentration of hydrogen ions and rain water is commonly acidic because of dissolved carbon dioxide, which substantially increases its hydrogen ion concentration. The hydrogen ions, having strong replacing power, tend to replace sodium, with the consequent formation of dilute solutions of sodium bicarbonate, sodium carbonate, or sodium hydroxide, resulting in increased alkalinity of the sodium clays. If sodium clay is mixed with calcium carbonate, it may be-

come highly alkaline upon leaching, owing to the fact that calcium ions, furnished by calcium carbonate, will replace significant amounts of sodium from the clay with the consequent formation of corresponding amounts of sodium carbonate.

According to Kelley, magnesium, although present in sea water in lower concentration than sodium, takes a more active part in the base exchange of sediments with which it comes in contact. Consequently, sediments in contact with sea water will inevitably contain practically as much replaceable magnesium as replaceable sodium.

The decomposition of biotite in soil has been discussed by Walker (1949) with special reference to soils in northeastern Scotland. The weathering of biotite causes an increase in the optic axial angle, a decrease in refractive indices, a decrease in specific gravity, the disappearance of pleochroism, and a marked color change. This is accompanied by a loss of iron, preceded by oxidation of ferrous to ferric, loss of magnesium, potassium, and sodium, and a gain in water. The products of the weathering are hydrobiotite, chlorite, a vermiculite, and ultimately kaolinite.

In biotite at Glen Buchat, weathered biotite flakes alter to a vermiculite, the alteration proceeding through the crystal layer by layer. The properties of the vermiculite differ somewhat from those of the hydrothermal vermiculite previously described.

In a study of Australian soils derived from granitic and basaltic parent material, Hosking (1940) has separated colloidal fractions from the subsoils and has identified the clay minerals present by X-ray diffraction. Kaolinitic clay was found in several granitic soils of different conditions of origin. In basaltic soils, however, the type of clay mineral present is a reflection of the soil moisture conditions: kaolin-group clays alone characterize the red loams, montmorillonite-group clays prevail, together with a little kaolin, in the red-brown earth, and the montmorillonite group alone is typical of the black earths. Montmorillonite may form in areas of restricted drainage over basaltic rocks, where climatic conditions would lead to the formation of kaolinite if the area were readily drained.

Graham (1941) looks upon an acid clay as an agent in chemical weathering. He believes that hydrogen clay may become an active agent in mineral and rock weathering processes. His conclusion, however, is based upon limited data on the transport of calcium from anorthite, a not too common feldspar, to colloidal clay.

Grim et al. (1939) conclude, on the basis of data relating to the climatic conditions under which various clay minerals in Illinois sediments are formed, that the joint presence of illite and kaolinite in a formation indicates a source area, some parts of which had a warm climate and other parts a cool climate.

Studies of the clay minerals contained in the fine fraction of the insoluble residues from 35 Illinois limestone and dolomite samples representing the major stratigraphic units of the Illinois geologic column reveal the presence of illite in all samples, kaolinite in twenty samples, and beidellite (?) in three samples. Much of the illite may be authigenic and probably was derived from beidellite; the kaolinite is probably detrital. Kaolinite characterizes all the Pennsylvanian and Silurian samples studied. Some Mississippian and some Devonian samples contain kaolinite, others do not. The Ordovician samples contained only illite.

Transportation and Accumulation. Deposits of clay minerals resulting from transportation and deposition probably constitute some of the most extensive clay-mineral deposits. The minerals most frequently encountered among these clays are illite (hydromica), kaolinite, montmorillonite, and attapulgite.

In some basin areas of the earth's surface, the clay-mineral constituents of sediments derived from widely separated areas appear to be remarkably similar. This formation of similar products from widely divergent original materials is a matter of considerable interest. Such convergence in clay sedimentation, although entirely supergene, finds a parallel in the clay-mineral convergence in hydrothermal metamorphism where various rock types alter to the same clay sequence.

In a study of flint clays, Galpin (1912) reported a mixture of kaolinite and hydromica, probably essentially the same as illite. These clays were formed by the recrystallization of fine sediments purified by the action of carbon dioxide in the waters transporting them, and by leaching action caused by plant roots. The increase in hydromica is thought to be a result of heat and pressure.

According to Bates (1947) illite (hydromica) forms the bulk of the fine micaceous material in the slates from the Lehigh-Northampton district of northeastern Pennsylvania. Although similar to the type illite from Fithian, Illinois, in all other respects, the mineral in the slate, studied under the electron-microscope, is seen to occur in flakes which morphologically are larger and much better defined than the fuzzy aggregates of minute shreds or fibers which characterize electron micrographs of illite obtained from shales. X-ray studies show that the flakes are arranged in parallel orientation in the slate and that the amount of alignment is related to the degree of metamorphism. In the specimens studied, the development and alignment of illite plates by metamorphic processes was thought to be the cause of slaty cleavage.

The illite of the underclays of Illinois described by Grim and Bradley (1939) is presumably of sedimentary origin. The source of the illite-bearing clay is presumably the weathered surface material from the area enclosing the region of accumulation. The clay was evidently transported and deposited as illite.

Grim (1933) has identified the constituents of the so-called fuller's earth from the Eocene Porter's Creek formation near Olmstead, Illinois. Montmorillonite is the most abundant mineral present and the only clay mineral listed. Grim ascribes near-shore marine origin to the Olmstead deposits. Porter (1907) states that clays that contain montmorillonite originated in basic rocks where augite and hornblende were prevalent. Rocks high in magnesia probably constitute the source of sedimentary accumulations of montmorillonite.

Grim and Allen (1938) record the alteration of feldspar in gumbotil in situ to montmorillonite. This has been confirmed in the case of the subtropical turfs, sometimes called black turf soils, of the Bushveld igneous complex.

The sedimentary kaolinite of Georgia was derived (Henry and Vaughan, 1937) from the feldspathic rocks

of the Piedmont Plateau. Prior to the Cretaceous, these rocks were weathered to great depths, and clay was formed. At the beginning of the Cretaceous, tilting of the land surface and the rearrangement of the drainage system allowed the clay to be eroded and to be carried along with other sediments to the sea. The deposits of clay accumulated in fan-like freshwater deltas. That some recrystallization took place after deposition is indicated by the presence of fragile vermicular growths of kaolinite which can be observed with the microscope.

Kaolinite from Mesa Alta, New Mexico (Main, 1950), represents a sedimentary accumulation, probably having been subject to transportation more than once. Microscopic study of the textures in the clay indicates that in parts of the deposit clay pellet conglomerates exist which suggest kaolinitic alteration, both before and after final deposition.

Diagenesis in Saline Waters

It is believed by some that clay minerals may form under conditions of marine diagenesis. If this theory be correct, small flakes of mica, kaolinite, or other minerals deposited on the ocean floor undergo progressive change to illite and montmorillonite. Clay deposited as kaolinite in brackish water or near shore may disintegrate if deposited at depth. It is even suggested that, in a general way, the clay-mineral assemblage and textures of crystallization may indicate the depth at which the sediments were deposited.

According to Dietz (1941), montmorillonite may be the original clay mineral deposited in some places on the ocean floor, and subsequently alter to illite.

Grim et al. (1949) in their discussin of recent sediments of the Pacific Ocean near California and in the Gulf of California attribute broad-range depth characteristics to kaolinite, montmorillonite, and illite. Kaolinite is thought to be gradually eliminated by a diagenetic process with increase in depth. The samples studied cover a depth range from near shore to 13,386 feet. While the process suggested is of considerable interest, too little data are available for precise application.

Glass (1951) has applied diagenesis in the interpretation of the conditions of origin of the clay minerals in the Cretaceous and Tertiary sediments of New Jersey. The minerals involved are kaolinite, montmorillonite, hydromuscovite, illite, a chloritic mineral, and glauconite. Transitions may be traced, using differential thermal curves from light brown to dark brown montmorillonite, from light green dispersed glauconite, through light green glauconite grains, to dark green glauconite grains.

Well-crystallized kaolinite in the New Jersey sediments is attributed to a fresh-water lake in Triassic shale hollows. The kaolinite in coastal sediments shows a decrease in crystallinity because the waters are not entirely fresh, and brackish water deposits show a decrease in crystallinity of kaolinite and hydromuscovite, and an increase in the amount of chlorite formed largely at the expense of hydromuscovite. In marine sediments, illite is formed. When marine conditions are nonreducing, an increase in salinity is considered to bring about a decrease in the amount of kaolinite and chlorite formed, and an increase in the amount of illite formed.

Alteration Aided by Organic Acids

Bog Deposits. Clay deposits have been reported a number of times from bog or swamp accumulations, either of present-day or more ancient origin. The clays formed in this way may owe their purity to the leaching action of waters containing carbonic and various humic or organic acids that are derived from the decay of organic matter and organic processes, as a result of the leaching action of living plants.

A residual kaolinite deposit formed by the decomposition in situ of granodiorite, probably as a result of the corrosive action of organic acids acting in old peat bogs, has been described by Kerr (1930). The deposit was encountered in a subway tunnel excavated in Brooklyn, New York.

Laterite. Such a close relationship exists between the formation of clay minerals and laterite or bauxite that discussion of the origin of clay minerals would be incomplete without at least a brief consideration of these frequently associated materials.

The essential mineralogical constituents of laterite are such aluminian minerals as cliachite, gibbsite, boehmite, or diaspore, and such ferrian minerals as limonite, goethite, or lepidocrocite. These hydrous aluminian or ferrian oxides are ordinarily impure, and the extent of their development is an index of the amount of lateritization involved. The tropical weathering of magnesian and ferrian rocks in certain areas suggests that perhaps secondary serpentine or other hydrous magnesian minerals may form in a similar manner.

Many divergent solutions have been proposed for the problem of the nature and mode of origin of laterite (Robinson, 1949). More than a hundred years ago, H. Buchanan (1807) proposed the name laterite for a type of red soil frequently found in southern India. The term has since been applied to red soils both in tropical regions and elsewhere.

Martin and Doyne (1927), on the basis of chemical analysis, consider laterite a material in which the molecular ratio of silica to alumina is less than 1.33:1, while in lateritic soils the ratio is 1.35 to 2.0:1. This definition is inadequate as it neglects iron as a clay mineral constituent and groups together soils of different profile characteristics and history.

Pendleton (1936) restricted the term laterite to specific soil layers rich in sesquioxides of iron and aluminum. Many such layers are characterized by the presence of pisolitic material and colloform crusts overlying mottled or vesicular zones. Campbell (1917) considers laterite of western Australia and Africa to have been developed by ground-water. Pendleton (1936) considers laterites to result from pseudo-illuvial deposits in the zone of a fluctuating water table under peneplanic conditions. Later uplift may cause these ground-water conditions to disappear, inducing the development of a new profile. Profiles which may be explained in this way occur in many parts of the world.

Harrassowitz (1926) lists four horizons for a typical lateritic profile: (1) the parent rock at the base; (2) the horizon representing the material of initial weathering, which appears to be kaolinitic; (3) the lateritic horizon; and (4) a surface horizon with ferruginous incrustations or pisolites. The physical characteristics are fairly well

recognized. The lateritic horizon is colorful, consisting of red material mottled with yellow or violet, and is generally argillaceous. When derived from quartzose rocks, it may be granular in texture, vesicular or cellular, with pores frequently filled with white or grayish material. When moist, the laterite can be dug, but it hardens on drying and can be used as a building material. The surface crust may develop to such an extent that it prevents the growth of vegetation.

Pendleton (1936) considers laterites in Siam to be a result of ground-water action. He distinguishes laterite occurring in deep horizons, where parent rocks are saturated with water and iron compounds go into solution, from laterite formed near the surface where the pores are filled with air and the ferrous compounds become oxidized to ferric.

The typical lateritic profile exhibits concretionary or crust-like material underlain by mottled clay, but there are profiles in which, although concretionary material occurs, the mottled horizons are absent. Hardy and Follett-Smith (1931) describe variations in the lateritic profile. The source material apparently influences the development of laterite. Hardy and Follett-Smith state that acidic rocks such as granite do not yield laterites. This may be because of the substitution of a kaolinitic weathering product formed from the potash and potash-soda feldspars occurring in such rocks.

Various opinions have been given concerning the mechanism of laterite formation. Harrison (1934) considers that two main processes are involved: (1) primary lateritic formation; and (2) resilicification of the lateritic product by deposition of silica from ascending solutions. The latter process occurs in localities affected by a high water-table.

Campbell (1917) considers Australian and African laterites to have been formed by changes which occur in the zones of permanent and intermittent saturation in the vicinity of the water-table. Oxygen required for the oxidation of ferrous to ferric iron implies a near surface formation.

Hydrated sesquioxides are a result of hydrolysis of silicate minerals. Alkaline ground-water solutions convert the iron silicates to ferrous hydrogen carbonate and the alumina silicates to alkaline aluminates. During periods of drought, dissolved material from the water table migrates upward; the ferrous hydrogen carbonate is oxidized to amorphous hydrated ferric oxide, and the aluminates to amorphous hydrargillate $Al_2O_3 \cdot 3H_2O$. Campbell (1917) considers further changes to involve the formation of something he called "turgite" $2Fe_2O_3 \cdot 3H_2O$, and possibly hematite, Fe_2O_3, from amorphous ferric oxide hydrate, and crystalline gibbsite $Al_2O_3 \cdot 3H_2O$ from hydrargillite. The greater mobility of ferric oxide in colloidal solution causes lateritic horizons to become progressively more aluminous as laterization continues.

Woolnough (1918), in his studies of western Australia, concurs with Campbell. He limits laterization to those situations in which free drainage does not exist, as in a peneplain near sea level. Laterites at higher elevations are products of processes which took place prior to uplift, and of a change in hydrological conditions.

Whether alluvial deposition of sesquioxidic material may or may not have occurred in the presence of a high ground-water table, it seems likely that the principal climatic circumstances are high temperature and the alternation of aerobic and anaerobic conditions in the soil profile.

The mobility of sesquioxidic constituents in the soil profile has been attributed by Campbell (1917) to the alkalinity of the ground-water, by Harrassowitz (1926) to the protective effect of silicic acid soils. Each of these explanations may be applicable in the wide range of lateritic profiles which exists.

Kaolinite is an intermediate product in the formation of Arkansas bauxite. Gordon, Tracey, and Ellis (1949) have recognized residual and colluvial bauxite deposits as the chief source for commercial production. Kaolinitic clay separates the residual bauxite from fresh nepheline syenite, the initial source of the alumina. The colluvial deposits grade into a surrounding kaolinite envelope.

Harder (1949) agrees with other students of the subject that bauxite may originate directly by the alteration of primary aluminum-bearing rocks. He also points out that both field and microscopic evidence show that kaolinite may be an intermediate product in the formation of bauxite. He does not think that kaolinite found in association with bauxite represents resilication of the bauxite.

Bauxite deposits (Harder, 1949) may consist mainly of the trihydrate, gibbsite, or the monohydrate, boehmite, mixed locally with diaspore. Pressure and possibly heat first change the gibbsite to boehmite, and eventually change the boehmite to diaspore.

According to Harder (1949), the weathering of any one of many rock types or their weathered derivatives may produce bauxite or laterite, although more than normal alumina content and the presence of soluble constituents accelerate the process. The rock type, composition of ground-water, topographic relief, temperature, and rainfall are all significant factors in bauxite formation or lateritization. A warm humid climate with alternating wet and dry seasons hastens the process. A land surface of low relief, permitting rainfall to penetrate the ground, is considered essential. The chemical composition of the ground-water and the solvents present are important. In many cases, the original constituents of the rock determine whether bauxite, iron ore, or manganese ore results.

Rankama (1950) emphasized the role of carbonated waters in the formation of aluminum hydroxide from basic igneous rocks. He also attributes the formation of some calcareous bauxite to the action of carbon dioxide-bearing waters in a warm climate. The argillaceous constituents of limestone are converted into bauxite and the calcium carbonate is removed as bicarbonate.

Goldman (1949), in a detailed petrographic study of specimens from Arkansas, has described the alteration of feldspars to finely crystalline gibbsite, thence to seemingly amorphous pisolitic bauxite, followed by kaolinization of the aluminous hydrates by silica derived from the unaltered core. It is not clear how often this process may take place.

Allen (1948) describes three processes in the formation of bauxite: (1) desilication; (2) migration; and (3) resilication. Desilication of the original rock and the migration of the clay and aluminous material have long been recognized. Resilication, or the union of silica with

gibbsite to form clay, however, has not been generally recognized. Allen states that the occurrence of cellular kaolin in Georgia suggests formation by addition of silica to gibbsite, rather than by migration of kaolinite. This conclusion he strongly supports in a more recent publication (Allen, 1952).

Bates (1942, 1945) has described a kaolinitic clay, the Edwin clay, from near Ione, California. Field work, microscopic study, and evidence secured from firing tests show that the Edwin clay is residual, derived directly from laterite. Transitions observed in the field, similar textures, and other evidence suggest that the laterite is intimately connected with greenstone (Jurassic meta-andesite), common in the foothills of the Sierra Nevada.

Goldich (1948) concludes that in regions favorable for the formation of laterite and bauxite, the position of the water table may determine whether "transitional" clay will form, or bauxite will be produced directly. Below the water table, clay minerals are most likely to be the end product of weathering; but above the water table, the alteration product will be bauxite or laterite. Below the water table in tropical regions, endellite, halloysite, and kaolinite develop. Why halloysite 2H$_2$O and halloysite 4H$_2$O both develop below the water table is not clear.

Lapparent (1936) reports that the bauxitic clays of Ayrshire contain boehmite, diaspore, and kaolinite formed from basaltic rock. He believes that the alteration began as an alumina-silica gel, resulting from the hydrolysis of silicates in a tropical climate.

The evolution of the gel first took place in the presence of humic waters that favor the crystallization of boehmite; subsequently, it evolved at a lower depth, where higher temperature favored the crystallization of diaspore. Kaolinite was formed later than the hydroxides of aluminum.

CONCLUSION

In view of the complex chemical conditions involved and the wide variety of possible origins, it is remarkable that the clay minerals fall into a comparatively small number of groups.

Although great improvement in the nomenclature of clay minerals has been made in recent years, there is still considerable progress to be made. It is hoped that a more general agreement on the nomenclature of several important groups may be possible before long. Such clarification would facilitate discussion.

Major contributions remain to be made, particularly in accumulating experimental data on clay-forming processes. Further, a closer correlation of field and laboratory studies and studies of supergene and hypogene clay deposits on the part of workers in this field is to be encouraged. Much laboratory work is to be checked in the light of field conditions.

DISCUSSION

R. A. Rowland:

Professor Kerr mentioned some of Dr. Grim's work in the Gulf of California which indicated the disappearance of kaolinite and the presence of degraded illite. It has been noted that flakes of mica larger than most clay particles are common in the soils in the United States. S. B. Hendricks refers to these as "stripped micas" because most of the potash has been removed. Below the *upper soil zone where the stripped micas are found, there is often* a gumbotil composed largely of a clay mineral which has been

called either beidellite or montmorillonite. The material from the gumbo horizon is similar to that in the shales of the Gulf Coast region. It is a stripped illite which now behaves like montmorillonite. These shales also contain larger flakes of potash micas which could be called illite, and a variety of chlorites. It is thought that the soil material has been thoroughly weathered and broken down so that only montmorillonite remains to be transported to the Gulf of Mexico. Once in the Gulf the montmorillonite may change to either illite or chlorite. What is this process of diagenesis in clays? Is there any evidence to indicate that isomorphous substitution takes place in the process of diagenesis or whether the substitution takes place long before the material has become a mineral? In other words, do these clays undergo diagenesis by high-energy-level processes or do they undergo diagenesis by low-energy-level solution processes?

R. E. Grim:

The American Petroleum Institute is investigating recent sediments in the Gulf of Mexico and a number of samples have been collected off the south part of the Texas coast in deep water. These samples are being studied in my laboratory. The water-soluble salts have been washed out of the samples and the amounts of calcium, sodium, potassium, and magnesium determined. The determinations did not yield absolute values but ratios of sodium to each of the elements. It was found that material deposited on the Gulf floor is largely montmorillonite, with a little illite and kaolinite. A plot of the ratio of sodium to potassium in the soluble salts against distance from shore shows a relative decrease in potassium close to shore. There is a correlative increase in the proportion of illite-like material close to shore. The sodium-magnesium ratios remain constant until some distance from shore, where the magnesium seems to disappear.

P. F. Kerr:

I referred to the large accumulation of clay minerals in the Gulf Coast region which has been derived from the erosion of a very heterogeneous assemblage of material. Dr. Grim has pointed out that many of these materials come from a variety of sources in a basin at least 1,000 miles across, and yet ultimately are reduced chiefly to montmorillonite. There is a parallel to this in connection with hydrothermal alteration. At Marysvale, Utah, similar clay-mineral assemblages are produced in surprisingly different rock types.

Isaac Barshad:

In order to answer Dr. Rowland's question as to the possible diagenesis of the clay minerals upon being deposited in the Gulf by the rivers, it is first necessary to consider the changes which the mica minerals undergo during the course of weathering into the hydrous mica minerals—or if you like—the "stripped micas." Two of these changes are significant in the present discussion: (1) the replacement, through exchange, of the interlayer K$^+$ by H$^+$, Ca^{++}, Mg^{++}, and possibly Na$^+$; and (2) the resultant hydration and interlayer expansion of the crystal lattice. Both of these changes bring about a reduction in the density of the weathered mica. It is also important to remember that the changes indicated are readily reversible. With these facts in mind, the process of diagenesis may be pictured to involve (1) a replacement of the readily exchangeable cation with K$^+$, particularly in those mica clay minerals which have undergone the smallest degree of change; (2) a dehydration and contraction of the crystal lattice; and (3) an increase in density of the crystal lattice. The increase in density is important because it causes this fraction of clay to settle out first; that may be the explanation of the fact that the clay material nearest the shore line contains the most mica minerals. The fraction of the clay which does not undergo the changes described will settle farther from the shore line and change into a chlorite-like mineral.

As to whether isomorphous substitution plays a role in diagenesis—I would say that it probably does not. It is unnecessary to postulate isomorphous changes to explain the results.

W. F. Bradley:

One difference between kaolin minerals and montmorillonite minerals is that those of the montmorillonite group are stable in extremely minute flakes, while those of the kaolin group have a large inherent particle size. Alteration resulting in kaolinite usually ends at that point. When alteration products pass through a degraded mica or montmorillonite stage they are highly mobile. They lose alkalis and magnesium and the particles are then rela-

tively barren during transportation to the sea. The pH of the ocean is higher than that of river water. Through increased pH, cations and protons are extracted from the sea water, which is essentially a process of precipitation of brucite. The magnesium content of the ocean water is such that it may actually represent a concentration equal to the solubility of the brucite attached to chlorite at the pH which obtains. When the clay comes into salt water it immediately picks up some potash and magnesium by ordinary exchange mechanism. It becomes illite or magnesium-saturated montmorillonite. As pH increases with distance from shore brucite layers are synthesized and the montmorillonite changes to sedimentary chlorite. They need not become trioctahedral and ordinarily the chlorite of sediments does not appear to be trioctahedral. The diagenesis takes place between the layers but the layer structure need not be affected.

T. F. Bates:

There is an interesting analogy between this situation and that for the Ordovician metabentonites, or potassium bentonites, which occur in abundance in the Appalachian region. C. E. Weaver has established that potassium bentonite found in Pennsylvania is a mixed layer complex (Weaver and Bates, 1952). By using Brown and MacEwan's (1951) curves, 80 percent of the layers were found to be saturated with potassium and were non-expanding, and 20 percent of the layers were saturated with calcium and a little sodium and were or could be expanded. Chemical analyses on the same material by Dr. Goldich of the University of Minnesota were calculated by the Ross and Hendricks method to determine the location of the various cations. The X-ray data were corroborated, for, of the total exchangeable cations, 80 percent were potassium, and the remaining 20 percent largely calcium and sodium, and some magnesium. The bentonite beds were very high in chlorite near the edges. Farther from the bentonite the clay mineral was illite, apparently washed in.

The material probably originated as a volcanic ash that was later altered to montmorillonite. Still later, because potassium was available, 80 percent of the layers were saturated with potassium ions in the base-exchange position and became non-expanding. The distribution of the chlorite may reflect low permeability which prevented the penetration of magnesium into the inner parts of the bed.

The 2-1 layers in the expanded portion of the mixed layer minerals are the same in composition as the non-expanded portion, suggesting that the layers have retained the composition derived from the original alteration of the volcanic ash. This provides additional evidence that commonly the external cations only must be changed to make a non-expanding clay from an expanding clay.

E. A. Hauser:

When there is no change in the basic structure all the properties result from two factors—the surface condition of the clay-mineral particles, and the ions which are available to be adsorbed as a result of the free energy located in that surface. With reference to swelling bear in mind the degree of hydration of the ions that are adsorbed on the clay particle. It is not the clay-particle micelle as such which does the swelling, it is the outer layer which we may not consider specifically as water because those water molecules are all dipolarly oriented and can be considered as a solid.

C. S. Ross:

We have collected a number of good analyses of the Appalachian potassium bentonites, which show a strong tendency for the potash to come out approximately half, or less frequently three-quarters the amount found in a true mica.

W. D. Keller:

I have worked on the clay mineral prominent in the Missouri River mud. It has a very indistinct X-ray pattern which is somewhat similar to that of montmorillonite, and it gives a very weak response in differential thermal analysis. It comes from soils pauperized in potassium. It looks as though it started as illite, and the potassium was then stripped out. This is similar to what happens when montmorillonite is treated with a little HCl to cause a breakdown into aluminum hydroxide and silica. Silicate and alumina wreckage may be present here, so poorly organized that it gives little X-ray response and so poorly bonded that it gives no good energy response. Mortland and Geiseking (1951) have recently shown that potassium is fixed more readily from potassium silicate than from other potassium salts. On entering water with silica and potassium in solution, as happens when the Mississippi River flows into the Gulf of Mexico, the stage is set for a better, quicker,

or stronger fixation of potash. Alumina wreckage and high polymerized silica may get together and illite may be formed. The clay particles carried by the Missouri and Mississippi Rivers are not as flaky as those found in shales. It seems that the crystals are developed during or after deposition. It would seem to be that diagenesis is a slow reversal of the weathering, or stripping, process.

W. J. Weiss:

Is the potassium bond in illite or hydrous mica strong enough to resist breakage by mechanical shearing, and could the bond be disrupted without disintegrating the resulting fragments?

Isaac Barshad:

The answer to the first part of your question is "yes". The evidence which supports this answer is based on the finding that only small variations in the cation exchange-capacity exist in illite fractions of varying particle size. Thus, in an illite from Fithian, Vermilion County, Illinois, the exchange capacity of the fraction consisting of particles less than 0.3 micron was found to be about 28 me. per 100 g. whereas that of the fraction consisting of particles ranging in size from 1.0 micron to 0.5 micron was about 22 me. per 100 g. Such a small difference in exchange capacity, in spite of the large difference in particle size, would indicate that the breakage of the coarse illite particles into the finer ones must have occurred across the plates rather than parallel to the plates. This kind of breakage indicates therefore that the potassium bond is strong enough to resist the glacial grinding action which these illite particles underwent.

The answer to the second part of your question is also "yes". Evidence for this is found in grinding experiments in which the mica particles were broken in a direction parallel to the plates and also in cation exchange experiments in which the K^+ was replaced with a cation such as Mg^{++}. In both cases the cation exchange capacity of the finer particles goes up markedly but the particles when resaturated with K^+ are as true a mica as before the grinding or removal of the K^+ by exchange.

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