RESEARCH ON EVOLUTION OF CLAY MINERALS AND ARGILLACEOUS AND SILICEOUS NEOFORMATION

by

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ABSTRACT

The following recent work is reviewed.

In the Triassic basin of the Jura detrital illite changes into chlorite (chlorite and chloritic mixed layers) toward the middle of the basin.

In the profiles of podzolic soils and podzols, illite and chlorite change, through illite–vermiculite and chlorite–vermiculite stages, into vermiculite.

In Cambrian sandstones of the Sahara two successive diagenetic changes have taken place: early postdepositional kaolinization, and illitization by salt waters.

Neoformation of aluminomagnesian clays in the alkaline sediments of the Eocene basins in Africa produces a sedimentary and geochemical sequence of montmorillonite, attapulgite and sepiolite.

When siliceous neoformation is produced by crystal growth, the growth is regular in the production of quartz, and irregular or hindered in the formation of chalcedony or opal–cristobalite.

Kaolinite has been synthesized at low temperatures in dilute solutions.

Transformations of triphormic clay minerals in the hydrosphere consist of a progressive expansion of layers. Environment controls the equilibrium between interlayer cations and adjacent layers. Siliceous and argillaceous neoformation consists of organization of silica tetrahedrons; this organization depends on the environment and especially on the environmental cations. Transformation by diagenesis is more intense and allows direct passage from illite to kaolinite.

STUDIES OF TRANSFORMATIONS

Transformations of Clay Minerals in the Triassic Sedimentary Basin of Jura (Lucas and Bronner, 1961)

Triassic formations of the French Jura are of the German Trias type. Three principal levels may be distinguished: (1) The lowest level, the Buntsandstein, is chiefly gritty and not clearly distinguishable from the Permian. Bundsandstein and Permian rocks are combined in the term "Permo-Trias". (2) The intermediate level, the Muschelkalk, consists of limestones, dolomites, clays, and commonly evaporites. (3) The highest level, the Keuper, consists essentially of clays and evaporites.

Statistical study of samples taken from boreholes shows appreciable differences in the clay composition; these differences are related to the facies and the position of the borehole in the basin (Fig. 1).

Relations between clay minerals and facies.—The data are summarized in Table 1, which shows the following relationships: Micaceous minerals of the
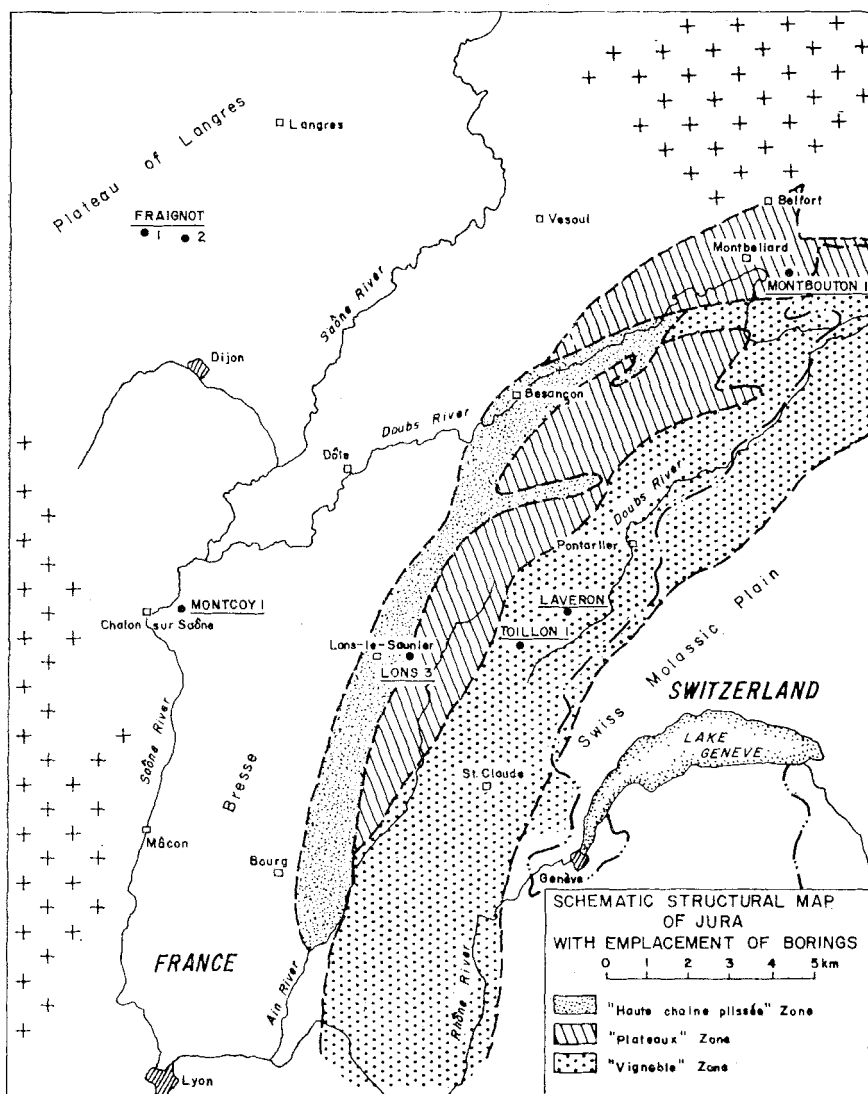

FIGURE 1.—Schematic structural map of Jura showing emplacement of borings.

TABLE 1.—RELATION BETWEEN CLAY MINERALS AND FACIES IN THE
TRIASSIC SEDIMENTARY BASIN OF JURA

Facies	Clay composition*
sandstone, clay, *limestone, dolomite*, gypsum, salt	I > C + different mixed-layers
Sandstone, *clay*, limestone, gypsum, **salt**	C + Corrensite + I
Sandstone, **clay**	C + I
Sandstone	I
Conglomerate, **sandstone**	I(+ K + C)
Conglomerate, Sandstone	I > K

* I, illite; C, chlorite; K, kaolinite.

illite type are found most often in detrital and coarse sediments; chlorite in fine sediments; and illite and irregular mixed layers in chemical sediments. Clay composition appears thus to be bound partly to the facies. This is especially clear in the borehole of Laveron (Fig. 2), in which the alternation of the clay and salt zones of Muschelkalk and lower Keuper is directly related to the alternation of the clay mineral composition: chlorite and illite in clays; corrensite and illite in salt.

Relation between clay minerals and their disposition in the basin.—The nature of the clays that are deposited at any one time changes proportionally to the distance from the basin edges. In the formations that are deposited near the borders, illite remains predominant, regardless of the constitution of the facies. At a greater distance from the edge, regular mixed layers appear in the formations. The percentage of chlorite, however, remains relatively constant. Chlorite becomes predominant only where the formation presents its greatest thickness.

Interpretation.—The abundance of chlorite and mixed-layer chlorite clays in the Triassic belonging to the type German Triassic is well known (Honeyborne, 1951; Jeannette and Lucas, 1955; Lippmann, 1956; Martin Vivaldi and MacEwan, 1957).

A problem is presented concerning the origin of these minerals, which are relatively abundant in the whole Triassic; study of the Triassic basin of Jura suggests a possible explanation: The argillaceous and detrital minerals, which are carried to the basin by flowing water, are composed chiefly of illite, which is more or less degraded by weathering and which is accompanied by small amounts of chlorite and kaolinite. The slight variations in composition of the clays, which were situated near the coast during the entire Triassic, permit us to presume that the supply did not change greatly during this period. At greater distances from the edges, the inherited illites were subjected to the basin influences and were imperceptibly changed, first into random mixed layers, then into regular mixed layers of the corrensite type, and finally into well-crystallized chlorite. The "chlorite" phase is reached only where subsidence is strongest, i.e. in the middle of the basin. The influence of the

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LAVERON

I II III IV

Keuper		sup.	Sandstone – clay
			motley clay with gypsum and anhydrite
		m.	Dolomite of Beaumont, clay, sandstone
	inferior		Thick banks of halite with intercalations of argillaceous sandstone
			Thin banks of halite with clay and gypsum
			clay with anhydrite
			halite
			clay with banks of halite
			halite
			clay, halite, anhydrite

I   ILLITE

II   CHLORITE + ILLITE

III   CORRENSITE + CHLORITE + ILLITE

IV   VARIOUS MIXED-LAYERS+CHLORITE + ILLITE

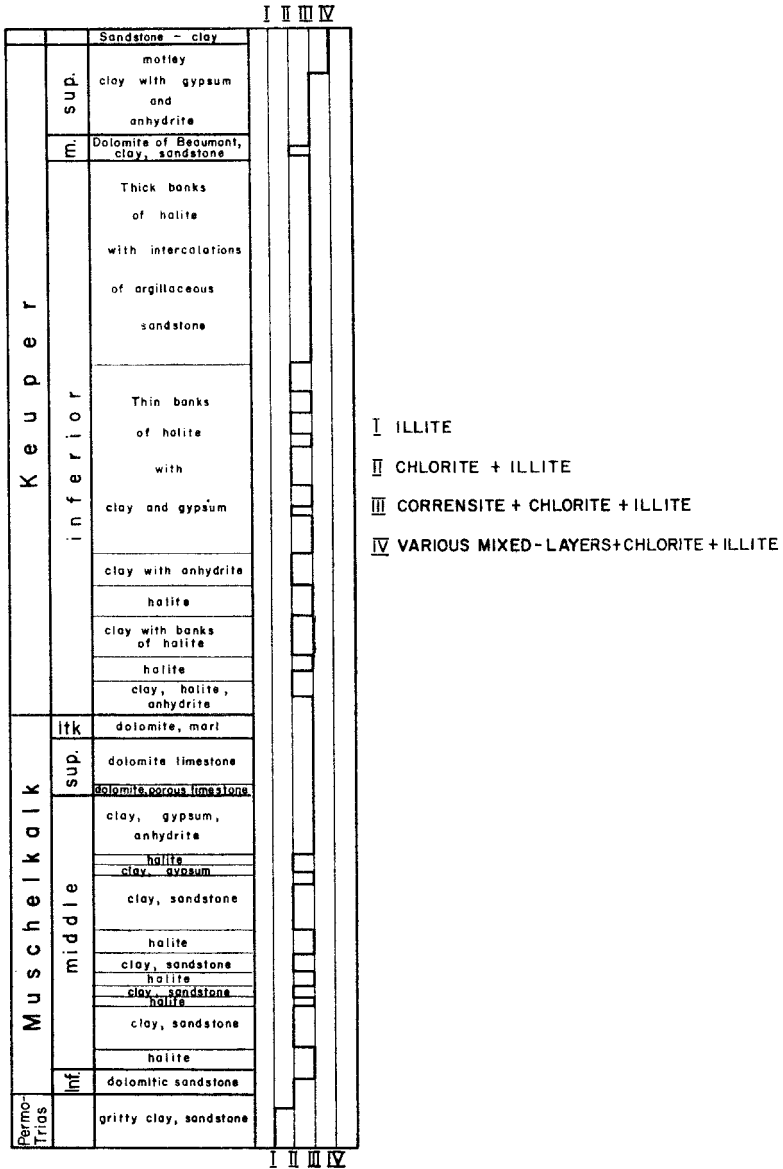| Muschelkalk | | ltk | dolomite, marl |
	sup.		dolomite limestone
			dolomite, porous limestone
	middle		clay, gypsum, anhydrite
			halite
			clay, gypsum
			clay, sandstone
			halite
			clay, sandstone
			halite
			clay, sandstone
			halite
			clay, sandstone
			halite
	Inf.		dolomitic sandstone
Permo-Trias			gritty clay, sandstone

I II III IV

FIGURE 2.—Stratigraphic section, Laveron, showing clay-mineral distribution.

conditions, which are special to each facies, is added to this scheme. Thus, in the middle of the basin, salt was precipitated and stopped the transformation at the "corrensite" stage, whereas deposition of clay allowed formation of chlorite.

These clay mineral differences between clay and salt zones are hardly due to differences in supply, but are readily explained by the transformation of the minerals. Thus we conclude that the corrensite and chlorite formed by transformation in a saline environment. This confirms the hypotheses of Fuechtbauer and Goldschmidt (1959) concerning the German Zechstein and those of Grim, Droste and Bradley (1960) regarding the Permian salt series in New Mexico.

Transformations of Clay Minerals in Temperate and Podzolic Soils (Camez, Franc de Ferrière, Lucas and Millot, 1960)

Clay minerals and especially the most common weathering minerals, illite and chlorite, change in the course of pedogenesis in temperate and wet climates. These transformations were noted by several research workers some ten years ago.

In the symposium on vermiculite, Millot and Camez (this Volume) presented results concerning podzols and podzolic soils, which supported those found in Scotland, North America and Scandinavia, but the transformations do not reach the montmorillonite stage. Only the following transformations are to be found: Illite changes into illite–vermiculite, then into vermiculite and chlorite changes into chlorite–vermiculite and finally also into vermiculite. These transformations consist especially of a leaching action and exchange of interlayer ions.

The effects on the crystal chemistry of the layers themselves are not well known. The stronger the alterations, the more important are the transformations in the octahedral and tetrahedral layers. But it is well known that discrimination between vermiculite and montmorillonite in soils differs only in nomenclature, based on entry of one or two glycerol sheets between the layers. The important factor in these transformations is not the discontinuous vocabulary that is employed, but the progressive expansion of the micaceous type layers (illite–chlorite) as they are subjected to the influence of continual weathering. This progressive expansion is reversible and of geologic significance (Weaver, 1958).

Transformations of Clay Minerals in Diagenesis (Kulbicki and Millot, 1960)

The term "diagenesis" is taken here in the strict sense used in France. It indicates transformations that take place within the sediments after sedimentation but before low-grade metamorphism. In the symposium on industrial applications, Kulbicki and Millot (this Volume) described the transformations that occur during diagenesis in the oil-bearing sandstones of the Sahara. Microscopic and X-ray studies suggest two successive diagenetic changes: (1) The Cambrian sandstones of the Sahara contained feldspar, mica,

some illite and a small amount of kaolinite. Early postdepositional diagenesis changed feldspar, mica and illite into kaolinite showing "fan" and "accordion" facies. These facies are preserved intact in the sandstones that are saturated with oil. (2) In the sandstones that are saturated with native salt waters, a second diagenesis occurs: kaolinite with "fan" and "accordion" facies is changed into illite.

This example seems to indicate that diagenetic transformations take place under the influence of salt waters and that a micaceous lattice can develop from a kaolinite arrangement. This example shows also that successive diagenetic changes are possible and finally that there is a relation between clay minerals, oil, and salt water migrations.

STUDIES OF NEOFORMATION

Neoformation of Aluminomagnesian Clays (Millot, Elouard, Lucas and Slansky, 1960)

Conditions of sedimentation.—The authigenic sediments of the Eocene in Africa have been studied intensively for the last few years. They are of an exclusively chemical origin and were formed in alkaline environments: carbonates, silica, phosphates and aluminomagnesian clays (montmorillonite, attapulgite and sepiolite). Millot, Radier and Bonifas (1957) and Slansky, Camez and Millot (1959) have demonstrated that these clays are not detrital but authigenic. Recent observations by Elouard (1959) and Slansky (1959) show that the distribution of these neo-formed clays in the previously existing basin of sedimentation is somewhat haphazard.

Elouard (1959) studied Eocene sediments in the Senegalese basin, south of Mauritania. These sediments present a sandy and kaolinitic aspect. Toward the open sea, the detrital supplies disappear, clay, constituted by montmorillonite and attapulgite, becomes authigenic and presents a papyraceous or lamellar aspect. But Elouard observes that the attapulgite content increases away from the shore of the previous basin. Distances to the present shore, very near the previous shores, are from 24 to 65 km. Montmorillonite decreases in proportion to the other clays (Fig. 3).

Slansky (1959) found the same results in the Eocene of the littoral sedimentary basin of Dahomey, but in the Ypresian strata. This gives to the sequence a more general significance. On the other hand, quite interesting reports are given regarding the Ypresian strata of Senegal. In the previously uplifted region of Thiès, the formations are rather thin and contain attapulgite with or without montmorillonite (Capdecome and Kulbicki, 1954; Visse, 1954). On the contrary, in the Sangalcam borehole, in the very heart of the basin, in a subsident and thick series, the Ypresian strata contain a mixture of attapulgite and sepiolite with proportions ranging from 10 to 90 percent sepiolite (Slansky, 1959). This magnesian mineral seemingly completes the argillaceous sequence and should be studied in future boreholes in order to confirm this extension.

In the most favorable case, the authigenic sedimentary sequence of Slansky is as follows: Kaolinite, montmorillonite, attapulgite, sepiolite, with all the intermediate mixtures. This is a positive sequence in the sense used by Lombard (1953), in which there is at the same time detrital sedimentation occurring on the littoral side with kaolinite, and chemical sedimentation represented by the series of aluminomagnesian clays. Moreover, the fields characterized by the different minerals broadly overlap one another. Finally, the succession thus described on a horizontal plane is to be found again vertically, in the boreholes. When, in a sedimentary series, facies with kaolinite, montmorillonite, attapulgite and possibly sepiolite are seen following one another, from bottom to top, we shall characterize it as a transgression, since, in the vertical sequence, facies are deposited which are more and more distant from shore. The reverse succession characterizes a regression. This is
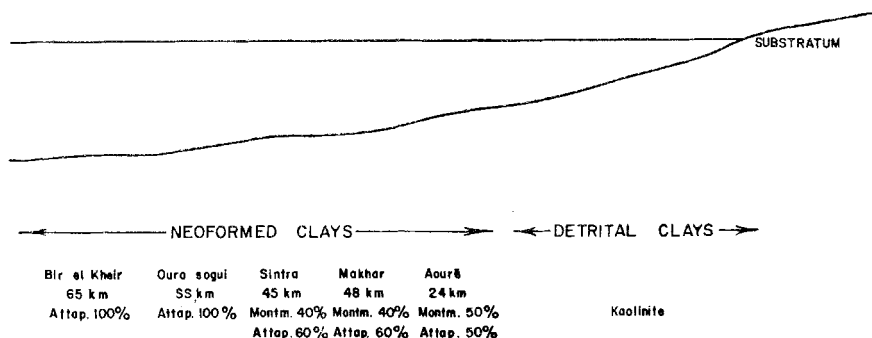

FIGURE 3.—Clay-mineral distribution in lower Lutetian strata of the Senegalese Basin (Elouard, 1959).

an interesting guide for the reconstruction of paleogeography; it is based on clay minerals and mainly on neoformed clay minerals.

Such are the facts. It is necessary to compare them with our present mineralogical knowledge about these clay minerals.

Mineralogy of aluminomagnesian clays.—Structural schemes for attapulgites have been suggested by Bradley (1940), and for sepiolite by Nagy and Bradley (1955) and Brauner and Preisinger (1956). More recently, Martin Vivaldi and Cano Ruiz (1956) and Kulbicki (1959) have discussed the relations between structure, chemical composition and fibrous facies. They have observed that the Al/Mg ratio changes: e.g. montmorillonite, Al/Mg high; attapulgite, Al/Mg slightly greater than 1; and sepiolite, Al/Mg low. Also, dioctahedral montmorillonite and trioctahedral stevensite and saponite are lamellar. Attapulgite and sepiolite are intermediate, and this results in hindering planar expansion of the lattice and leads to the "hollow brick" structural scheme of fibrous minerals. The variations in chemical composition involve structure and facies modifications in the minerals of these series.

Interpretation of sedimentary sequence.—A montmorillonite, attapulgite, sepiolite sequence is found in natural environments, and concurrently a high, $\geqslant 1$, and low Al/Mg sequence. The mineral which contains the greatest amount of alumina is in the most littoral facies, and that which contains the greatest quantity of magnesium is at the greatest distance from shore. The aluminum percentage decreases proportionally as the distance increases. Discontinuous series of neoformations correspond to this continuous variation of the environment. In this respect, a preferential combination of silica with alumina and only later with magnesium should be noticed; authigenic minerals are strongly subjected, or related, to environment.

Siliceous Neoformation (Millot, 1960)

Climatic silicification.—The intense silicification of the surface of the outcropping rocks in the Sahara is attributed to climatic weathering. We can infer a general rule from observations by many workers (Millot, Radier,
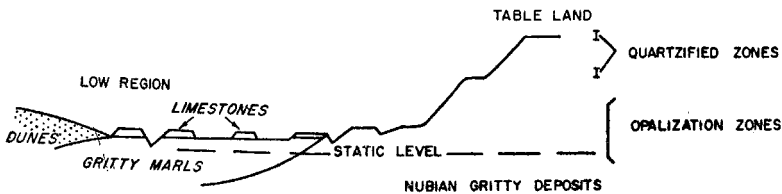

FIGURE 4.—Distribution of silicification in the Cherguya (Fezzan) according to Muller-Feuga (1952).

Muller-Feuga, Defossez and Wey, 1959). On the surfaces of well-drained plateaux, rocks, and especially sandstones, are transformed into quartzites by the development of overgrowths. At the foot of slopes, in depressions and at water-table level, rocks are silicified into chalcedony and opal. In the first case, the percolating waters are pure; in the second case, they are more concentrated and charged with mineral ions (Fig. 4).

Sedimentary silicification.—Sedimentation can be accompanied or immediately followed by silicification. Many authors have made observations on sedimentary quartzites, cherts, gaizes, etc. A comprehensive study was made by Cayeux (1929), but numerous reports have since been published. In all cases, silicification is attained by substitution or epigenesis of preexistent minerals which can be most diverse, but the main ones are carbonates and clays. The products of silicification are not haphazard as concerns the substituted minerals. In siliceous sandstone, overgrowths form on the quartz grains and the rock becomes a quartzite. In limestone, substitution leads mainly to chalcedony, sometimes retaining the previous structures, as shells or fragments of organisms, oolites, etc. Finally, clays seem to be transformed more easily into opal. A particularly striking example has been presented by

Elouard (1959). A sandy formation containing calcareous nodules from the Eocene has been silicified. It has been proved that this silicification took place immediately after deposition, since silicified shingle is found in the strata directly above.

After silicification, the sand became a quartzite, with quartz overgrowths, while the calcareous nodules containing fragments of organisms became chalcedonic chert in which organic traces are recognizable. Here we can see the various results of silicification, according to the nature of the local environment.

Old interpretations.—Studies made in the latter part of the nineteenth century and beginning of the twentieth century on the genesis of siliceous masses and silicification, and concerning amorphous silica in general, have greatly influenced our concepts of silicification. Consequently, silicification commonly is explained by the flocculation of amorphous silica, developing progressively toward still better crystallized silica. It is possible that this mechanism could be used to explain the formation of certain volcanic or hydrothermal deposits: veins, geysers, etc.; but it cannot be used to explain the phenomena of climatic and sedimentary silicification. Modern works on the chemistry of silica in water prohibit this explanation, and recent studies of chalcedony and opal allow quite another interpretation.

Chemical point of view.—The solubility of silica in water is now well known, as a result of the work of Alexander, Heston and Iler (1954), Krauskopf (1956, 1959), and Okamoto, Okura and Goto (1957). This solubility is controlled by laws of polymerization and depolymerization. As long as the total content of silica in water is below 100–140 ppm at 25°C, silica is dispersed in a state of balance, in the form of molecules of monosilicic acid, $Si(OH)_4$; it is a true solution. This solubility is practically independent of pH, as long as the latter remains below 9. Beyond pH 9, $Si(OH)_4$ is dissociated and the true solubility of silica increases. If the content of silica exceeds 140 ppm at 25°C and below pH 9, molecules of $Si(OH)_4$ are polymerized and colloidal solutions of silica are obtained. All this concerns solutions in equilibrium and one must insist on the fact that this equilibrium is reached slowly.

The geological consequences of this new knowledge are considerable.

(*a*) First, silica is usually present in natural waters in amounts less than the limit of true solubility (100–140 ppm) of the monomer $Si(OH)_4$. Consequently the normal state of silica in natural waters is that of a true molecular solution; in sea water and river water as well as the water confined within the sediments or soils. Colloidal solutions are exceptional and occur in hydrothermal water only. Therefore natural solutions of silica cannot flocculate, since they are true solutions.

(*b*) Secondly, the amount of silica retained in solution does not depend on the pH between pH 2 and pH 9, which are the two extremes in the scale of pH as it occurs in nature. No variation of pH can ever lead to precipitation.

(*c*) Lastly, it is useful to examine the behavior of quartz in water. Solutions kept in long contact with quartz have a content of 7–10 ppm monomolecular silica, $Si(OH)_4$. This is important in geochemistry, for any solution that is

undersaturated in regard to amorphous silica, within the range 10–140 ppm, will be supersaturated in regard to quartz.

In conclusion, it is impossible to refer to the flocculation of colloidal silica in order to explain silicification at the surface of the earth's crust. Let us examine the known mineralogical data on chalcedony and opal before we propose another hypothesis.

Mineralogical point of view.—Chalcedony is composed of very small crystals of quartz (Washburn and Navias, 1922; Rinne, 1924; Sosman, 1927). Correns and Nagelschmidt (1933) have described chalcedony as formed of alternating fibers of quartz and thin layers of opal. Midgley (1951) and Folk and Weaver (1952) could not confirm the presence of opal in the interstices. Pelto (1956) applied to chalcedony the hypothesis used to explain the structures at the boundaries of the grains in metals. The boundaries between quartz fibers are made of a transitional structure, formed by dislocations and islands of poor adjustment. In places where the point of contact is not exact, adjustment is achieved by impurities, foreign ions and water; part of this water can be bound to silica. Chalcedony appears thus as quartz fibers which are separated by disordered joints, including some water and foreign ions. The silica and water in disordered arrangement may represent the opal of Correns and Nagelschmidt (1933).

The crystallinity of opal has been confirmed by Levin and Ott (1932). Some of the most recent work is that of Flörke (1955, 1961), who reports that opal is composed of small crystallites of cristobalite and tridymite, which are disordered by variations in the stacking arrangement perpendicular to the SiO_4 layers. Crystallites are of such minute dimensions that the superficial and disturbed zone forms an important percentage of their volume. The foreign cations block these disordered structures, preventing their evolution toward the stable state of quartz.

Genesis of silicification by way of crystalline growth.—It is impossible today to explain the genesis of natural surface silicification by flocculation of colloidal silica from supersaturated solution. I propose, therefore, the hypothesis of the growth of crystals. Three cases will be studied successively.

(a) Quartzification: Quartzification is common on the high Saharian surfaces where the surface water has a brief existence and is pure. The amount of silica remains small. We often meet solutions that are undersaturated in regard to amorphous silica but supersaturated in regard to quartz. The growth of crystals starts around the quartz grains, which act as nuclei. The optical orientation of the growth halo is the same as that of the grain. The quartzite is formed by "feeding" of the grain. Likewise in sandy sediments, solutions that are slightly siliceous but poor in foreign ions assure the growth of the grains and lead to sedimentary quartzite. *We are here in the domain of the regular growth of macrocrystals.*

(b) Silicification into chalcedony: Numerous chert deposits as well as numerous silicifications of Saharian depressions or subterranean water tables are constituted by fibrous chalcedony as shown by microscopic observation. Let us start with solutions containing a moderate amount of silica. These

solutions are common in nature—40, 60, 80 ppm at 25°C (Bonifas, 1958; Dapples, 1959). These solutions, which are richer in silica, are also charged with foreign ions of all sorts furnished by the rock in the process of silicification, or gathered in solutions. The growth of crystals starts but is less orderly. The quartz, hindered in its growth, becomes arranged in long spiral fibers separated by disordered regions where the water and foreign ions enter. That is the situation which leads to the numerous varieties of chalcedony. All the intermediate forms exist, from the previous example, through chert with microcrystalline quartz, to chalcedonic chert. *We are here in the domain of hindered microcrystalline growth.*

(c) Silicification into opal: Numerous sedimentary rocks give evidence of their epigenesis to opal. In the Sahara also, sandstones, limestones or clays are silicified into opal by water in depressions or at the water table. Modern knowledge of opal shows that here we are in the presence of a still more disorderly development. The network of low-temperature cristobalite tends to form, but it does so in a very imperfect way and encloses foreign ions and water. By 1929 Cayeux had already noted that opal is the most common form of silicification of clays. It is possible to consider the siliceous layers of clay sheets as playing a pilot role in this organization. Here we approach the limit of the crystalline state, but all the intermediate states exist from chalcedony through chalcedonic opal and fibrous opal (lussatite) to isotropic opal. *We are here in the domain of cryptocrystalline growth, which is greatly hindered and very imperfect.*

It is interesting to consider the influence of solutions on neoformations in the process of growth. In pure, barely siliceous water, the growth is assured in a regular fashion; but where the waters are mineralized, the growth of crystals is hindered. In the case of chalcedony, fibers of quartz develop. In the case of opal, islands of cristobalite have much difficulty in developing. Once more, a discontinuous petrographic sequence is obtained by arrangement of a unique and simple constituent—silica.

Synthesis of Kaolinite at Low Temperatures
(Siffert and Wey, 1961)

Siffert and Wey (1961) synthesized kaolinite at low temperatures in the Physicochemical Soil Laboratory at the University of Strasbourg. They noted that colloidal gels were obtained when solutions saturated with silica and containing Al^{3+} were made alkaline. The same result was attained when solutions saturated with silica and containing $(Al(OH)_4)^-$ were made alkaline. This proved the tendency of Al^{3+} and $(Al(OH)_4)^-$ to enter into fourfold coordination rather than sixfold coordination. Consequently, Siffert and Wey were able to substitute the complex anion $(Al(C_2O_4)_3)^{3-}$ in place of the preceding Al ions. By eliminating a part of the oxalate ions, in the form of calcium oxalate, the pH decreases and Al ions having sixfold coordination were released and, with the silica of the solution, formed kaolinite.

This synthetic kaolinite was studied and identified by X-ray diffraction and

thermal analysis. Chemical analysis showed it to be low in silica; hence the tetrahedral layer was not complete.

It appears that the "alumino-oxalic complex anion" acts as a mineralizer in the formation of kaolinite, as constituents of humus act in nature.

CONCLUSIONS

The Triassic basin of sedimentation provides an example of the transformation of clay minerals, with typical development of chlorite in this environment and in this period. On the other hand, pedological weathering determines the relative release of mica and chlorite layers toward more or less expansible structures. We conventionally call these structures vermiculite or montmorillonite, but with reservations. The evolution of triphormic and original continental minerals in the hydrosphere is thus a sort of "breathing" of clay minerals.

In a well-drained and leaching continental environment, the interlayer cations, held by electrostatic attraction, are progressively released, allowing the separation of the corresponding layers through a progressive series of stages. In a saline environment, in marine or supersaline sediments, the layers contract and tend to resume their original dimensions.

Neoformation of silicates in sediments is definitely different in that there is no alteration of a pre-existing lattice but formation of new structures. The environment is determinative for the growth of neoformations; the cations play a "pilot" role.

Siliceous neoformations consist of an arrangement of silica tetrahedrons in successive ascending layers. This arrangement is regular in pure waters (quartzification); it is irregular in waters containing ions and particles, particularly in the building of chalcedony and opal.

Argillaceous neoformations consist of a combination of silica tetrahedrons with such ions as Al and Mg. In an alkaline environment, series of authigenic minerals can occur: these are triphormic minerals—montmorillonite, attapulgite, sepiolite, with preferential utilization of alumina and magnesium. In an acid environment, synthesis of kaolinite in the laboratory shows that it is necessary to have Al ions in sixfold coordination in the silica tetrahedrons.

Heritage, transformation, neoformations, postdepositional diagenesis—all add their effects and determine the associations of clay minerals in sediments. The work of the geologist consists chiefly in discerning these four mechanisms.

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