Clay Mineralogy

The clay mineral composition of soils and clays is providing an understanding of their properties.

Ralph E. Grim

Clay materials are generally considered to be natural, fine-grain, earthy materials which have the property of plasticity when they contain moderate amounts of water. Most soils can be classed as such materials, along with clays and shales. Clay materials have been studied for centuries because of their importance in agriculture, in ceramics, and in many industries. It was recognized from the start that the properties of clay materials varied widely—for example, some soils produced good crops whereas others in the same area with the same climatic conditions did not; some clays produced good ceramic products and others did not.

The primary objective in studies of clay materials was, and indeed still is today, the determination of the fundamental factors that control their properties. Early studies showed that some of the properties of clay materials are related to the size distribution of their component particles, and also that this is not the sole causative factor, although for some properties it may be a very important one. With the advent of precise chemical analyses it was learned that clay materials are generally composed of alumina, silica, and water, frequently with moderate-to-minor amounts of iron, alkalis, and alkaline earths. The relative abundance of these chemical components varies widely in clay materials, and it was shown early that the properties may vary with the chemical composition but, again, that the chemical composition, alone or in conjunction with particle-size distribution, is not adequate to explain the variation in properties of all clay materials.

Early chemical investigations emphasized that an understanding of the properties of clay materials demanded an understanding of the nature of the fundamental material in which the alumina, silica, and so on were present—that is, whether they were in amorphous or in crystalline state, what the type of the compound was, and so on. Many concepts of the character of the fundamental matter that composes clay materials are presented in the literature. However, there was no agreement regarding these concepts, since prior to the 1920's no adequate analytical techniques were available for determining the true nature of materials in particles as small as those that make up clay materials.

The advent of x-ray diffraction techniques resolved the problem of the nature of the fundamental components of clay materials. It was shown by Hadding in 1923 (*1*) and by Rinne in 1924 (*2*), quite independently, that clay materials are generally composed of crystalline particles of a small number of minerals. Within a few years x-ray diffraction techniques were supplemented by other analytical tools that were applicable to the analysis of extremely small particles; these tools included improved optical microscopic procedures and differential thermal methods. Still later, electron microscopy and diffraction, infrared absorption, and other methods were applied to the study of clay materials. All these procedures have shown that clay materials are essentially composed of extremely small particles, generally less than several microns in maximum diameter, of a few crystalline compounds which have come to be known as the clay minerals. A given clay material may be composed of particles of a single clay mineral or of a mixture of them. Chemically the clay minerals are composed of alumina, silica, and water and sometimes, in addition, of iron or magnesium, or both. Some of them also contain alkalis and alkaline earths. Clay materials also may contain varying amounts of such non-clay-mineral particles as quartz and calcite, and, as I will show presently, such components may influence the physical properties of clay materials.

Early x-ray diffraction studies suggested that clay materials were entirely composed of crystalline compounds—that is, they contained no amorphous material. It is now recognized that some clays and soils contain a component that is amorphous as revealed by x-ray diffraction, and that such material may influence physical properties. It appears that such material sometimes has a low degree of ordering and at other times is well organized but on too small a scale for the order to be revealed by x-ray diffraction. Thus, in some cases electron diffraction has revealed order in material that is amorphous as revealed by x-rays. Such so-called amorphous material does not appear to be common in clay materials and cannot be universally cited to explain all the properties of clays and soils.

The new techniques opened vast new possibilities for clay research, and beginning about 1930, there was a renaissance of effort in this direction. Mineralogists, geologists, chemists, physicists, agronomists, engineers, ceramists, and others began active investigations of clay materials, using the new procedures. Since that time there has been a flood of literature reporting researches which have greatly extended our knowledge of these materials (see *3*). Here, I review briefly some of the advances that have been made and some important current areas of research.

Structural Studies

X-ray and electron diffraction procedures not only provide identification of the crystalline components of clay materials but also permit investigation of the organization of atoms in the components—that is, of their atomic structures. Knowledge of the structure is fundamental to an understanding of the properties of clay minerals and, in turn, of the properties of clay materials.

The general character of the atomic structure of most of the clay minerals was worked out in the 1930's on the basis of general structural relationships

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The author is research professor of geology at the University of Illinois, Urbana.

of layer silicate minerals, as determined by Pauling (*4*). Somewhat later, Bradley (*5*) proposed a structure for another type of clay mineral, attapulgite, which has an elongate fibrous character and is structurally similar to the amphibole minerals.

Recent investigations have shown that the structures first suggested for the clay minerals are correct in general outline. Modifications in detail have been proposed, and in general the structures are less regular than was originally suggested. Of particular significance is a recent finding of the widespread occurrence of so-called mixed-layer structures, which I will consider presently. In some cases structural studies are seriously hampered because of the absence in nature of pure samples of certain clay-mineral species. For example, clay-mineral chlorite seems always to be mixed with other clay minerals.

There are three general structural types among the clay minerals: layer structures of two types and one fibrous structure. One of the layer types is composed of unit layers, with each layer consisting of one silica tetrahedral sheet and one alumina octahedral sheet tied together in a common sheet with shared oxygens. There are few. if any, substitutions of cations within the structure, and it is balanced electrically. The units are stacked one above the other in the *c*-axis direction. Kaolinite (Fig. 1) is an example of this type of structure, and in well-crystallized kaolinite there is a regular stacking arrangement of the silicate units. Clays composed of kaolinite are essentially aggregations of booklike particles with hexagonal outlines (Fig. 2), each "page" of the book having the structure indicated. Halloysite has a similar structure, but successive silicate layers are shifted in a more or less random fashion, in both horizontal directions (the *a*- and *b*-axis directions), and a layer of water a single molecule thick may separate the silicate layers. Further, the layers may be curled or rolled up into tubes (Fig. 3). Still other clay minerals of this structural type are intermediate between kaolinite and halloysite in that they show some random stacking, with shifts in only the *b*-axis direction. Such material is generally designated poorly ordered kaolinite.

The other layer structural type is composed of two silica tetrahedral sheets with a central octahedral unit

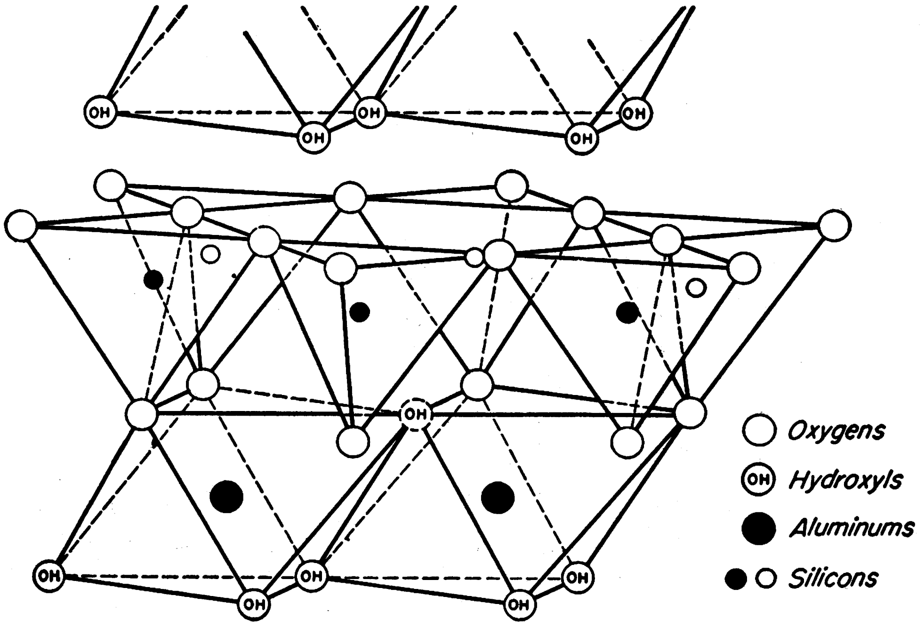

Fig. 1. Structure of kaolinite. [After Gruner (*12*)]

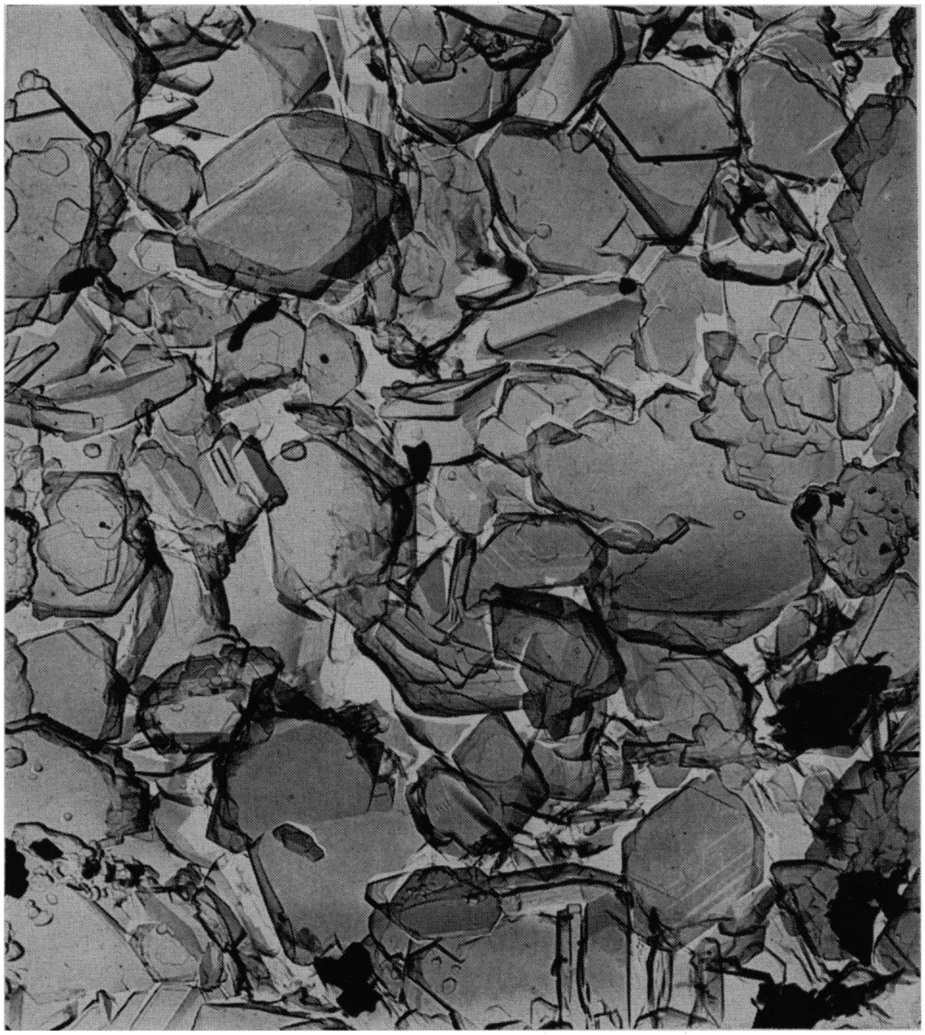

Fig. 2. Electron micrograph of kaolin composed of well-ordered units of kaolinite. (About × 29,120) [From K. M. Towe (*7*)]

held together by two common sheets, with shared oxygens. The layers are stacked one above the other in the *c*-axis direction. In this type of structure there may be substantial substitution of alumina for silicon in tetrahedral positions and the population of the octahedral positions may be either aluminum, iron, or magnesium, alone or in combination. All the octahedral positions may be filled (the trioctahedral structure) or only two-thirds of them may be filled (the dioctahedral structure). The population of cation positions is such that the layers, in the case of the clay minerals, are unbalanced electrically, with a positive-charge deficiency which is satisfied largely by cations between the silicate layers. This situation does not prevail for some other layer silicates, such as talc and pyrophyllite, in which the silicate layers are balanced and there are no interlayer cations.

Specific clay minerals belonging to this second structural category differ from each other in the population of cation positions, in the charge on the lattice, in the nature of the balancing interlayer cations, and in the stacking arrangement. Thus in illite, similar to muscovite (Fig. 4) and biotite, there is some substitution (±15 percent) of

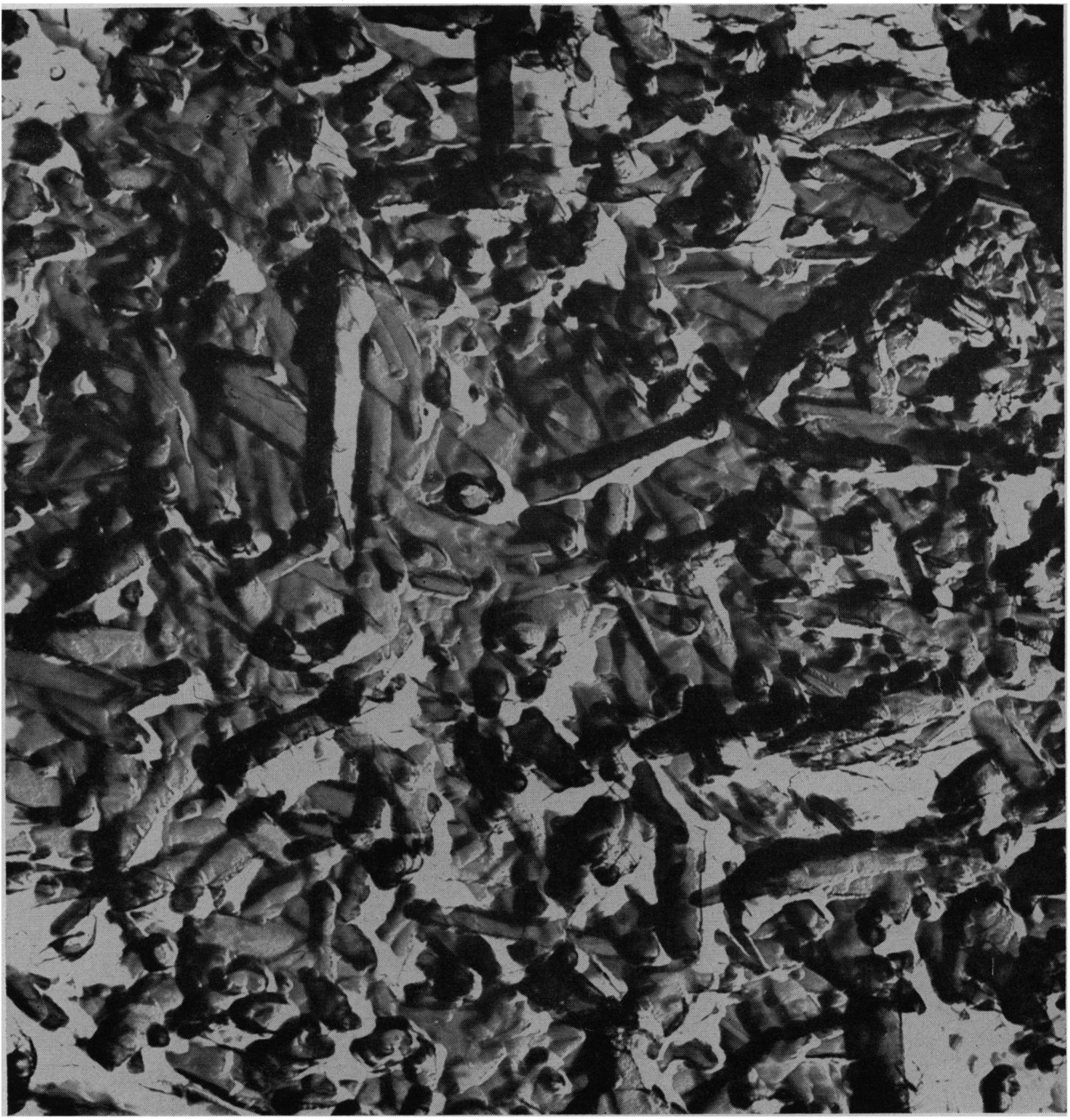

Fig. 3. Electron micrograph of clay composed of tubular units of halloysite. (About × 43,680) [From K. M. Towe (7)]

aluminum for silica and the balancing interlayer cation is potassium. Aluminum is the dominant octahedral cation, but magnesium and iron are also present and the mineral may be dioctahedral or trioctahedral. Commonly, illite occurs in such small particles so intimately mixed with other clay minerals that the stacking arrangement of successive layers cannot be determined and the trioctahedral or dioctahedral character is likewise not determinable. *Illite*, thus, is a general name for such material. Where, because of purity, particle size, and so on, more precise analytical data can be obtained, a more specific mineral name should be used.

Chlorite also belongs to the second structural category. In chlorite there is considerable substitution of aluminum for silica, which is balanced by interlayer magnesium surrounded by hydroxyls in octahedral coordination in a brucite structure. The magnesium is partly replaced by aluminum or ferric iron to provide the excess positive charge necessary to balance the substitutions in the silicate layer. The population of the octahedral positions in the silicate layer may be quite variable, and the mineral may be either trioctahedral or dioctahedral.

Montmorillonite (Fig. 5), another member of the second structural category, has substitutions largely in the octahedral positions which are balanced by a variety of interlayer cations which are rather loosely held and which are exchangeable. Successive silicate layers are loosely held together, and layers of water or other polar molecules of variable thickness may enter between the silicate layers, separating them. The thickness of the interlayer zone varies with the nature of the interlayer cation and the amount of available water or other polar molecules. Montmorillonite, unlike illite or chlorite, in which the interlayer cations tie successive silicate layers together firmly, has an expanding lattice with a variable *c*-axis dimension. The population of octahedral positions is quite variable, and the mineral may be either dioctahedral or trioctahedral. Montmorillonite clays are composed of extremely small units of indefinite shape (Fig. 6), which disperse in water into very thin flakes.

It was suggested by Edelman and Favejee in 1940 (*6*) that some of the tetrahedrons of the silica sheet might be inverted. This suggestion at first met with disfavor, but recent work in my

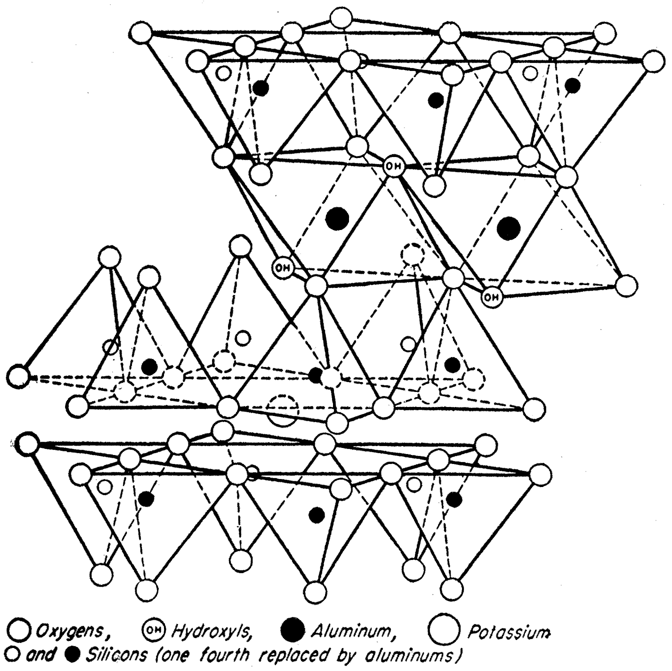

Fig. 4. Structure of muscovite. [After Jackson and West (*13*)]

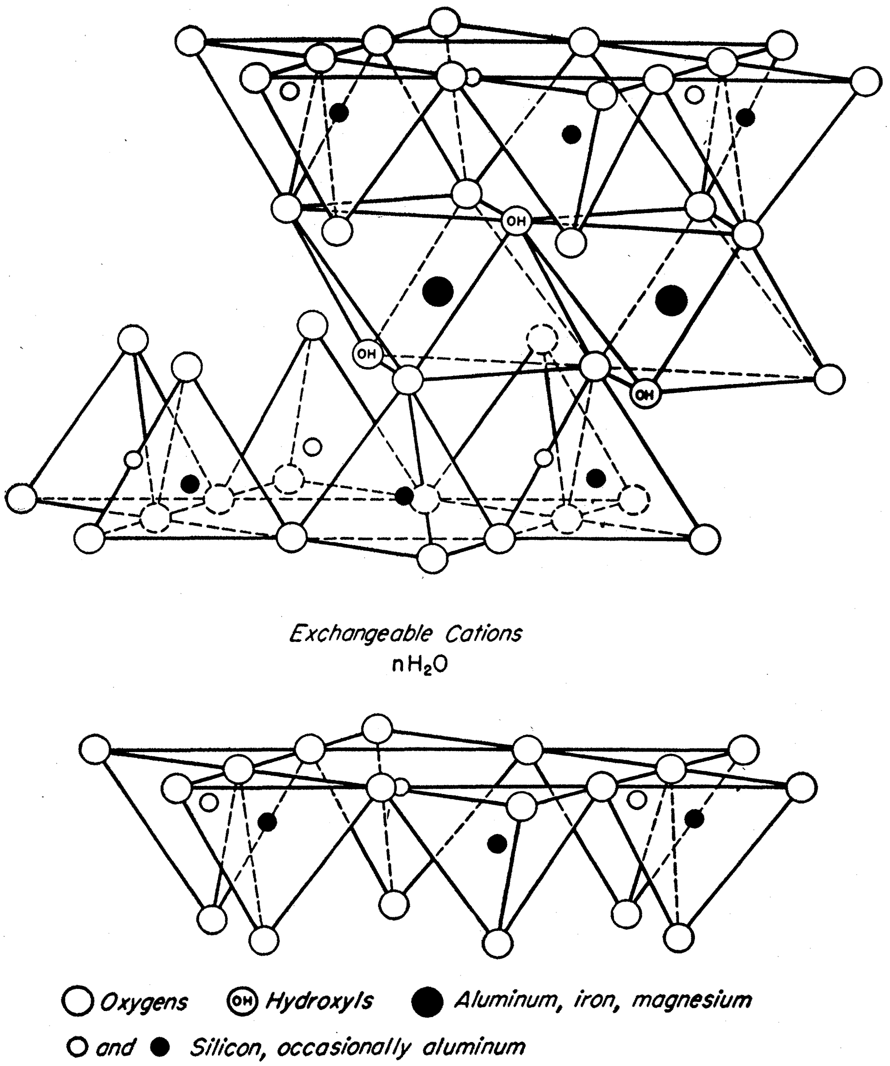

Fig. 5. Structure of montmorillonite. [After Hofmann, Endell, and Wilm (*14*), Marshall (*15*), and Hendricks (*16*)]

laboratory indicates that a small amount of inversion of tetrahedrons in some montmorillonites is likely.

Vermiculite, still another member of this second structural category, is similar to both chlorite and montmorillonite. The unbalancing substitutions are largely in the tetrahedral part of the structure, and the interlayer balancing cation is largely magnesium, which, however, is hydrated rather than encased in hydroxyls in octahedral coordination. As indicated, interlayer water is present, and the mineral expands—that is, the amount of interlayer water or other polar material is variable. In vermiculite, unlike montmorillonite, the expansion is limited.

Recent careful x-ray diffraction studies have shown that minerals of this second structural category commonly occur in nature in complex units in which layers of variable thickness of one type—for example, montmorillonite—are interlayered with units of variable thickness of another type—for example, illite. In other words, a given minute particle may be composed of successive layers of montmorillonite and illite. The successive layers may be arranged in a regular or random fashion. In most cases this means that in such mixed-layer structures the population of interlayer balancing cations is not the same from the top to the bottom of a unit of many successive silicate layers. Where the stacking mixing is regular and determinable, the material has distinct diffraction characteristics and is classed as a specific mineral. In the case of random assemblages, which can be extremely complex, the matter of nomenclature becomes very difficult and it seems best to describe the complex in terms of the structure of the units mixed, insofar as they can be determined, and not to apply the name of a specific mineral.

Many discredited mineral names applied to components of clays in the early literature are now known to have stood for such mixed-layer material. The origin of mixed-layer structures often poses difficult problems. They are sometimes formed during the weathering of illite and chlorite, and essentially this means that there is a definite pattern to the removal of interlayer potassium or magnesium cations rather than gradual removal from the edge inward in a given particle. Possibly the original illite or chlorite particle possessed structural variations which determined the removal pattern of the interlayer cation.

Attapulgite is representative of the fibrous type of clay minerals (Fig. 7). According to Bradley (*5*) it is composed of ribbonlike layers of two silica tetrahedral units tied together by a central octahedral unit, through common oxygens. The ribbons are tied together at their long edges, through common oxygens, to provide a gutter-and-channel-type structure. Magnesium is the dominant component of the octahedral positions, but there is some replacement by aluminum and possibly by iron. The structure is essentially balanced electrically. It appears that there can be considerable variation in the population of octahedral positions in this type of structure, and such names as palygorskite, paramontmorillonite, and parasepiolite have been applied for various compositions. Much remains to be learned about this type of clay mineral. The problem is complicated, because attapulgite clays seem always to contain montmorillonite so intimately mixed that pure attapulgite cannot be isolated.

Clay Mineralogy in Geology

Until recently geologists in their studies of the petrography of sediments have largely ignored clays. The particle size, particle shape, and mineral identity of the sand and silt fractions of sediments were studied in detail, but the fine clay material was frequently discarded and listed as so much clay, without any attempt being made to characterize it. It is now realized that clays may reflect the history of the sediment better than any other component because the characteristics of the clay minerals are, at least to some extent, subject to changes depending on the environment in which they are found. The clay-mineral composition of the sediment should provide, therefore, information on the character of the source area, on the environment of accumulation, and perhaps on postdepositional changes. Currently, a vast amount of work is being reported on the clay-mineral composition of recent and ancient sediments, with the foregoing considerations in mind.

Soil scientists are providing a point of departure for such studies by revealing the changes in clay minerals from various parent materials that take place during weathering under various conditions of climate, topography, and vegetation. This is an area too vast to be considered in a brief review; it is sufficient to say that the types of clay mineral that tend to develop from various parent materials under various conditions of weathering are now reasonably well established.

So long as the weathered debris remains in fresh water there appears to be no further alteration beyond that developed by the weathering processes. When the weathered material is carried from fresh to saline water, significant changes *may* take place. There is a tendency for micas which have been degraded in the weathering process by the partial removal of the interlayer cations to be regraded into better-crystallized illite and chlorite. There may be some development of illite and chlorite from montmorillonite. Kaolinite appears to be unchanged, except in some instances where it seems to disappear in favor of the micaceous clay minerals.

As I have just stated, significant changes *may* take place in an argillaceous material when it is carried from fresh into saline water, and therein lies a huge puzzle. There is definite evidence that clay minerals do originate or significantly change in the marine environment in some cases; glauconite is a case in point. There are other sediments in which there is little or no evidence of significant change. Why is there response to environment of the clay minerals in some instances and not in others? The answer is not yet available, but the following factors must be pertinent. One might expect such changes to be relatively more important when the sediment is deposited very slowly. The character of the sediment supplied must be important in that some parent material is more susceptible to alteration than other material. Argillaceous material on coming in contact with saline water may experience differential flocculation—that is, some clay-mineral components may be flocculated and deposited immediately, whereas others may be carried farther out in the area of accumulation—thereby making it difficult to detect clay-mineral alterations.

Later, metamorphic changes may tend to conceal the original character of the clay minerals as they were in the environment of deposition. Thus, Paleozoic shales, over wide areas and extensive stratigraphic intervals, are often composed of well-crystallized illite and chlorite. Sometimes a detailed study of the clay mineralogy (*7*) reveals significant variations which have persisted through the probable metamorphic changes.

In my opinion a further factor is important: volcanic ash falling into an area of accumulation in relatively minor amounts may greatly influence the character of the accumulating terrigenous sediment even though the amount of the ash is too small to be detectable with certainty. The ash may act to "season" the environment of accumulation. The Eocene Porters Creek clay of the Gulf Coastal Plains and the Cretaceous Pierre shale of the High Plains may be cited as examples. Ross (*8*), years ago, pointed out the importance of volcanic debris in ancient sediments, but the significance does not seem to have been appreciated generally. Similarly, the entrance into an area of accumulation of waters of unusual chemical composition—for example, waters high in silica, iron, or magnesium from igneous activity or a peculiar source area yielding material of restricted com-

Fig. 6. Electron micrograph of bentonite composed of extremely small units of montmorillonite. (About × 21,390) [From K. M. Towe (*7*)]

position—may serve to direct the clay-mineral changes taking place. In such a manner the proper environment for the formation of glauconite may be provided, or, under other conditions, an environment for the formation of attapulgite.

Clay Mineralogy in Technology

The physical properties of clay materials are largely determined by their clay-mineral composition and fundamentally are derived from the atomic-structural attributes of the clay minerals (*9*). That is to say, an understanding of the properties depends on an understanding of the clay-mineral structures. In the case of some properties of clays, such as catalytic activity and adsorptive capacity and selectivity, the clay minerals are the sole determinants, and any nonclay minerals are merely dilutants. In the case of others, the moisture present in the clay is important, and fundamentally the properties depend on the character of the water held on the clay-mineral surfaces; this in turn is related to the nature of the clay-mineral surfaces and the nature of any adsorbed ions or polar molecules also held by the clay minerals. The properties of plasticity, sensitivity, shear strength, and consolidation are in this category, and nonclay minerals are largely dilutants unless they are present in major amounts, when they may exert control.

There are still other properties for which clay-mineral composition may or may not be a determining factor. Thus, in the case of the properties of fired ceramic bodies, kaolinite is refractory and illite is not, but relatively small amounts of some nonclay minerals may provide fluxing material that outweighs the other components, making up as much as 95 percent of the clay.

As a consequence of the foregoing considerations and because clay materials are of great importance in many technologies and industries, there is continuing intensive study in many laboratories of the properties of the clay minerals, based on their structural attributes in relation to the properties of clay materials determining their use. Let us consider a few pertinent examples of such studies. I recently summarized this "applied clay mineralogy," with references to the original work (*9*).

The clay minerals enter into cation-exchange reactions with organic as well as inorganic cations. The exchangeable cations occur on the surface of the clay-mineral units, and so, with proper selection of the size of the organic cation, the clay-mineral surface can be changed from hydrophyllic to oleophyllic. The clay minerals also react with polar organic molecules replacing water; such molecules are tied to the clay-mineral surfaces through hydrogen bonds. On the basis of this information, clays composed of organic-clad particles can be prepared. Many important uses have been found for such materials in paint, ink, plastics, and other compounds, because of their tendency to react with other organic ingredients of such compounds, forming integral units with them. Organic-clad kaolinite and montmorillonite clays are now tailor-made by clay producers for particular uses.

It has been known for a long time that certain clays catalyze certain organic reactions. Since World War II, catalysts prepared from montmorillonite, kaolinite, or halloysite clays have been used to produce about 50 percent of our gasoline (synthetic catalysts produce the other half). Such catalysts are made by treating the clay minerals with acid to produce proton-donating surfaces which are devoid of metallic cations and subsequently treating them with heat to modify but not destroy the structure of the clay-mineral particles. The fundamental explanation of the catalytic property remains a mystery, but somehow the property seems to be related to the similarity in structure of the clay-mineral surfaces and the hydrocarbon chains, and to the position of the aluminum molecules behind the surfaces.

The catalytic properties of the clay minerals interfere with the use of these minerals for some purposes. Thus, clay used in decolorizing oils should not change the oil in the decolorizing process. Similarly, clays are used extensively as carriers for pesticides, and the pesticide must not be altered by the carrier in such a way as to reduce its potency. In recent years there has been much research aimed at coating the active clay-mineral surfaces in order to conceal their catalytic activity when they are used for this purpose.

Clay-Water Systems

There are many instances in which the properties of clays with limited amounts of water are of great importance. Properties of plasticity, shrinkage, shear strength, and consolidation are examples. As a consequence, there has been intensive study of the character of the water adsorbed on the clay-mineral surfaces. It has been shown that such water has properties other than those of fluid water. The water molecules are believed to be organized in a definite structural pattern extending outward from the clay-mineral surfaces for variable distances depending on the clay mineral itself and the nature of any adsorbed ions. This concept has led to an understanding of many of the properties of clay-water systems which hitherto have not been explained satisfactorily. I will give one example.

The sensitivity of the soil is a measure of its strength in the natural state as compared to its strength after remolding with the same moisture content. In Canada, Norway, and elsewhere there are soils of extremely high sensitivity, called "quick clays," which have good strength if undisturbed and no strength if disturbed. They are, therefore, commonly the site of landslides. Rosenquist (*10*) has shown that in Norway such clays were deposited in a loose flocculated condition in marine waters and that they carried sodium as the adsorbed cation. Later, after elevation of the land, the sodium was leached away, without any change in the moisture content. The strength of the clay was due, to a considerable extent, to the rigid water on the particle surfaces. The rigidity of the water and the thickness of the rigid layers was largely due to the presence of the sodium ion. The leaching of the sodium ion, in effect, removed the cation which largely gave the water its strength properties, and the water was, therefore, in a state of nonequilibrium, so that a slight disturbance would liquefy it, resulting in a complete loss of strength.

High-Temperature Reactions

When the clay minerals are heated to 400° to 700°C they lose their hydroxyl water, and the loss is accompanied by some disruption or alteration of their structure, depending on the type of structure. At higher temperatures the structure disappears, and the disappearance is followed by the development of new crystalline phases or fusion, again depending on the nature of the clay mineral and also on the presence of small amounts of extraneous elements.

The transformation of clay minerals on heating has been the subject of much study, because such transformation provides a simple means of studying solid-state transformations of one crystal structure to another and because it is fundamental to an understanding of the firing of ceramic bodies.

From the vast literature on this subject which has appeared in recent years, the following general conclusions seem particularly important.

The structure of the original clay mineral, as well as its chemical composition, exerts a control on the new phase formed. Often a sequence of phases develops as the temperature is raised, and the clay-mineral structure is particularly important in the earlier phases. The new phases may appear at temperatures differing by several hundred degrees from those suggested by equilibrium diagrams for the elemental clay-mineral composition.

The foregoing statements apply to substantially pure clay mineral. The presence of small amounts (a few percent) of certain elements (especially, but not solely, elements considered to be fluxes) may either postpone the development of new phases, so that they occur at higher temperatures; lower the temperature at which they form; or block their formation entirely. For example, the presence of about 1 percent of potash may prevent the formation

Fig. 7. Electron micrograph of clay composed of fibrous units of attapulgite. (About × 30,720) [From K. M. Towe (7)]

of any high-temperature phase from montmorillonite.

Needless to say, such data have been of great importance in the ceramics industry, and ceramic products are now fired for only a small fraction of the time previously considered necessary, with satisfactory results.

Atomic-Waste Disposal

The disposal of radioactive-fission-product wastes from atomic-energy plants and laboratories is of very great importance and has been the subject of much study. From the start the possibility of adsorbing the "hot" elements on clay was considered, as well as the possibility of later firing the clay to fix the isotopes in an insoluble form. Several disposal methods are in operation utilizing the adsorptive capacity of pure clay minerals to decontaminate wastes of low- and intermediate-level activity.

To be used successfully, the clay minerals must have highly selective adsorptive capacity for isotopes with a long half-life—a category in which radioactive strontium and cesium are of great importance. Many of the results of studies of pertinent properties of the clay minerals have not been published, but some findings are now available. Thus, Tamura and Jacobs (*11*) have shown that illite has particularly high affinity for cesium and that the *c*-axis dimension of the three-layer clay minerals is important; this dimension should be about 10 angstroms. Other, similar clay minerals can be improved by treatment with potassium followed by moderate heating, which serves to induce and maintain the optimum *c*-axis dimension. Ion-exchange capacities and surface area are secondary to the *c*-axis dimension as factors in the cesium-adsorption behavior of the clay minerals.

Conclusions

The structures of the clay minerals are reasonably well known, but greater detail and more precision are needed if the properties of clays and soils are to be fully understood. For example, the selective adsorptive and catalytic properties and the reaction with organic materials vary with the character of the clay mineral, but the structural factors that control such properties are not well understood. Research is urgently needed on the structure of pure clay minerals and on the reactions of pure clay minerals with organic and inorganic materials. Much past research on clay-mineral reactions has little fundamental value because the clay that was used was composed of a mixture of minerals which were not well characterized. It is not a simple matter to find pure samples of many of the clay minerals, and to a considerable extent progress depends on finding such pure minerals or preparing them in the laboratory.

Recent research has shown that the clay minerals found in sediments to some extent reflect the conditions of formation of such sediments. This is a matter of intense interest to the geologist and a field of great promise for future research. Investigations are particularly needed on the composition of recent and ancient sediments where the conditions of deposition and the history of the sediment are well known. Such work requires the utmost in analytical detail. Cursory clay-mineral analyses are useless. The clay-mineral composition must be determined in detail, and many samples must be studied to eliminate fortuitous variations in isolated samples.

Clay-mineral research has an unusual fascination because of the wide range of problems that are encountered and because of the combination of fundamental problems and problems of application. On one day one is concerned with finding why a particular clay is suitable for atomic-waste disposal; on another day, with finding why only one particular kaolin is good for coating certain paper; and on still another day, with finding whether a particular soil may be detrimental in a problem of foundation engineering. The answers must be given, and one knows ultimately whether the answer is right or wrong. The answer can be given only if the structure and properties of the clay minerals are understood.

References

1. A. Hadding, *Z. Krist.* **58**, 108 (1923).
2. F. Rinne, *ibid.* **60**, 55 (1924).
3. R. E. Grim, *Clay Mineralogy* (McGraw-Hill, New York, 1953).
4. L. Pauling, *Proc. Natl. Acad. Sci. U.S.* **16**, 123 (1930).
5. W. F. Bradley, *Am. Mineralogist* **25**, 405 (1940).
6. C. H. Edelman and J. C. L. Favejee, *Z. Krist.* **102**, 417 (1940).
7. K. M. Towe, thesis, University of Illinois (1961).
8. C. S. Ross, *Bull. Geol. Soc. Am.* **66**, 427 (1955).
9. R. E. Grim, *Applied Clay Mineralogy* (McGraw-Hill, New York, 1962).
10. I. T. Rosenquist, *Geotechnique* **3**, 195 (1953).
11. T. Tamura and D. G. Jacobs, *Health Phys.* **2**, 391 (1960).
12. J. W. Gruner, *Z. Krist.* **83**, 75 (1932).
13. W. W. Jackson and J. West, *ibid.* **76**, 211 (1930).
14. V. Hofmann, K. Endell, D. Wilm, *ibid.* **86**, 340 (1933).
15. C. E. Marshall, *ibid.* **91**, 433 (1935).
16. S. B. Hendricks, *J. Geol.* **50**, 276 (1942).