CLAY MINERALOGY

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The present volume attempts to summarize available data on the structure, composition, properties, occurrence, and mode of origin of the various clay minerals whose identities have been reasonably well established. The distribution of the clay minerals in rocks of various lithologic types, geologic age, and condition of formation is considered, and an attempt is made to analyze the environmental conditions under which the individual clay-mineral groups are formed and are stable. Because of the scantiness of available data, the general conclusions resulting from such analyses must be considered as tentative and preliminary. Future researches may show that some major revisions are necessary.

The aluminum and ferric iron hydrate minerals found in some clay materials are not considered herein. Generally such minerals have not been classed with the clay minerals, and their structure, properties, occurrence, and modes of origin have already been reported in detail in monographic form in the literature.

The specific properties of the individual clay minerals are discussed, but no attempt is made to consider the larger rock properties of clay materials except incidentally as they are related to specific mineral properties. For example, the changes taking place when the individual clay minerals are heated are discussed at some length, and the relation to the refractoriness of clays is indicated. A detailed discussion of the refractoriness of clays, which is influenced by other factors than the clay-mineral composition, is not, however, included.

The clay minerals are the major factor controlling the larger rock properties of clay materials, such as plasticity, strength, sensitivity, etc. Other factors also influence these properties, and an adequate discussion of them would require the presentation of much additional fundamental data. Further, an analysis of such rock properties, even if restricted to the clay-mineral viewpoint, would require a volume at least the size of the present one.

A brief discussion is presented of the various concepts of the composition of clay materials that have been advanced in the past, as well as a brief history of the development of the present clay-mineral concept. Such discussion is necessary as a background for the consideration of the clay minerals themselves.

Clay materials have been studied by scientists for a great many years, but within the last 30 years there has been a tremendous expansion of
clay investigations. Many investigators approaching the subject from different disciplines have devoted all or most of their attention to clay materials. As a consequence of this enlarged effort, fundamental information on all aspects of clay materials has been greatly extended since about 1920. The reason for this great expansion of interest in clays has been twofold. In the first place, new research tools, such as X-ray-diffraction analysis, became available for studying extremely small particles. In the second place, the economic importance of clay materials was more generally appreciated. A long list of important commercial applications of clay-mineral studies could be given, but the following will suffice to illustrate the application of clay mineralogy in diverse fields.

In the ceramic industry, only certain clays with peculiar properties can be used to manufacture certain products. Thus, only certain clays of particular clay-mineral composition will withstand high temperatures and, therefore, can be used for the making of refractory brick. Studies of the changes taking place when clay minerals are heated to elevated temperatures have greatly enhanced the understanding of exactly what happens when clay products are burned. A consequence of such clay-mineral data has been to improve the quality of some ceramic products and to reduce the time necessary to fire them.

In the oil industry certain types of bentonite clay are essential for the preparation of the muds required for the drilling of many oil wells, and other types of bentonite clay form the basis for many of the catalysts used in the refining of petroleum products. Detailed clay-mineral studies have been and are being made of the particular bentonites needed for each of these uses. The result of this work has vastly aided drilling-mud practice and the refining operation. It has also been of great value in the search for adequate supplies of the particular type of bentonite needed for each of these uses.

The most important outlet for certain types of kaolinite clays is in the paper industry, where they are used for fillers and coating materials. Researches into the structure and properties of kaolinite have permitted improvements in the clays produced for the paper trade; these have resulted in improvements of such paper properties as acceptance to ink, rate of drying, etc.

Construction engineers are frequently faced with the problem of building a structure through a clay material, as in the case of a tunnel, on clay material, as in the foundation of a building, or with a clay material, as in the subgrade of a highway or an earth-filled dam. The method of procedure, of necessity, is to obtain samples of the material which must be used or is available, and to test them in the laboratory under conditions representing field conditions as nearly as possible. On the basis of the empirical laboratory data, the engineer arrives at the structural design
and, in so doing, frequently must predict how the soil material will act when it is placed under different conditions, as, for example, when the water table is changed, after a base-exchange reaction has taken place in the clay, etc. Obviously the likelihood of the accuracy of such predictions is increased if the fundamental factors controlling the properties in question are understood. Much progress remains to be made on this subject, but currently it is possible to warn the engineer on the basis of simple clay-mineral determinations when he is facing materials that are likely to give some misleading empirical test data.

In the field of agriculture the tilth of a soil, its content of plant nutrients, and its treatment possibilities with fertilizers are all to a very large extent contingent on the clay-mineral composition of the soil. It is not difficult to understand, therefore, why soil investigators have been in the forefront of those carrying on clay-mineral investigations.

Geologists have been interested in clay-mineral researches for a variety of reasons, but two of them are particularly important from an economic standpoint. It seems likely that the clay-mineral composition of a sediment will ultimately prove to be an important clue in unraveling the conditions under which it was deposited. Also it seems likely that the clay minerals may have played an important role in the origin of petroleum by acting as catalysts in the alteration of the original buried organic material to hydrocarbon compounds. Clay-mineral researches should therefore provide significant information on the origin of petroleum and important criteria for the location of source beds of petroleum. In short such researches should be of great aid in the search for petroleum by geologists.

The author wishes to express his thanks to the persons who have permitted the reproduction of data from their published reports. Professor Thomas A. Bates of Pennsylvania State College kindly obtained special electron micrographs for this volume. Professor Paul F. Kerr of Columbia University, and the American Petroleum Institute have graciously allowed the reproduction of some electron micrographs and other data from their reports of work done on their Project 49. Professor G. W. Brindley and the Mineralogical Society of Great Britain have permitted the use of data from the recent monograph “X-ray Identification and Structure of the Clay Minerals.” Doctor S. B. Hendricks has very willingly allowed the author to follow his plan of illustrating the clay-mineral structures. All these and other sources of information in the volume are, of course, acknowledged specifically at the proper place.

The author wishes to express his great indebtedness to Dr. W. F. Bradley of the Illinois State Geological Survey, with whom he has been associated in clay-mineral researches for 20 years. Many of the subjects in the present volume have been discussed many times through the years
Preface

with Dr. Bradley, and his thoughts and work have contributed immensely to many of the conclusions presented herein. Doctor Bradley has read much of the manuscript and offered many significant comments. Any omissions or errors in the data presented are, however, solely those of the author.

The author began his studies of the clay minerals as a member of the Illinois State Geological Survey. These studies were continued in that organization for twenty years always with the enthusiastic support of Dr. M. M. Leighton, Chief of the Survey. The author wishes to acknowledge this support and the encouragement which came from Dr. Leighton's appreciation of the importance of clay mineralogy.

Great difficulty was experienced in presenting the X-ray-diffraction data, since it is recorded in both angstrom and kX units, and it was not feasible to translate all the essential data into either one of these units. The volume, therefore, contains both kX and angstrom units. In general, X-ray-diffraction data are given in kX units and dimensional data of lattices, ions, etc., in angstrom units. This point is discussed in some detail on page 84, and the factor for translating one unit to the other is given there. As shown in that discussion, the difference between the two units is very small, and for all intents and purposes the values are substantially equivalent for much of the clay-mineral data.

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CHAPTER 1

Introduction

DEFINITIONS

Clay is used as a rock term and also as a particle-size term in the mechanical analysis of sedimentary rocks, soils, etc. As a rock term it is difficult to define precisely, because of the wide variety of materials that have been called clays. In general the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water. By plasticity is meant the property of the moistened material to be deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed. Chemical analyses of clays show them to be essentially silica, alumina, and water, frequently with appreciable quantities of iron, alkalies, and alkaline earths.

The difficulty is that some material called clay does not meet all the above specifications. Thus, so-called flint clay has substantially no plasticity when mixed with water. It does, however, have the other attributes of clay.

The term clay has no genetic significance. It is used for material that is the product of weathering, has formed by hydrothermal action, or has been deposited as a sediment.

As a particle-size term, the clay fraction is that size fraction composed of the smallest particles. The maximum size of particles in the clay size grade is defined differently in different disciplines. In geology the tendency has been to follow the Wentworth¹ scale and to define the clay grade as material finer than about 4 microns. In soil investigations, the tendency is to use 2 microns as the upper limit of the clay size grade. Although there is no sharp universal boundary between the particle size of the clay minerals and nonclay minerals in argillaceous sediments, a large number of analyses have shown that there is a general tendency for the clay minerals to be concentrated in a size less than about 2 microns, or that naturally occurring larger clay-mineral particles break down easily to this size when the clay is slaked in water. Also such analyses have

¹ Wentworth, C. K., A Scale of Grade and Class Terms for Clastic Sediments, J. Geol., 30, 377-392 (1922).
shown that the nonclay minerals usually are not present in particles much smaller than about 1 to 2 microns. A separation at 2 microns is frequently about the optimum size for the best split of the clay-mineral and nonclay-mineral components of natural materials. There is, therefore, a fundamental reason for placing the upper limit of the clay size grade at 2 microns.

Clays contain varying percentages of clay-grade material and therefore, varying relative amounts of nonclay-mineral and clay-mineral components. The writer knows of no clay which does not contain some nonclay-mineral material coarser than the clay grade, although the amount in some hydrothermal clays is extremely small (less than 5 per cent). Many materials are called clays in which the clay-grade and clay-mineral component make up considerably less than half the total rock. In such materials the nonclay is frequently not much coarser than the maximum for the clay grade, and the clay-mineral fraction may be particularly potent in causing plasticity. In general fine-grained materials have been called clay so long as they had distinct plasticity and insufficient amounts of coarser material to warrant the appellations silt or sand. If particle-size analyses are made, the term clay would be reserved for a material in which the clay grade dominates. However, names have been and are applied most frequently solely on the basis of the appearance and bulk properties (e.g., plasticity) of the sample.

Shale is a fine-grained, earthy, sedimentary rock with a distinct laminated, or layered, character. The layering may be due to a general parallel arrangement of flake-shaped or elongate particles or to an alternation of beds of somewhat different composition. The lamination is parallel to the bedding and has not been developed by postdepositional metamorphic action. The requirements of composition are substantially the same for a shale as for a clay. Occasionally, however, natural materials are called shale with little regard to composition. Thus, thinly layered rocks composed essentially of quartz and/or carbonate with little clay-mineral component have been called shale. Sometimes, although by no means always, shales are more indurated and harder than clays. The term shale is sometimes used by engineers for any hard, indurated, argillaceous rock regardless of any lamination.

Argillite is a fine-grained argillaceous material that is massive and somewhat indurated and hard. It differs from shale in being massive rather than laminated and from clay by being harder.

The term soil is likely to have a considerably different meaning when used by a geologist, by an agronomist, and by a civil engineer. Soil to a geologist is the weathered regolith at the earth's surface that supports vegetation. It is thought of generally as being loose, argillaceous, and with some organic content. To the agronomist it is the loose regolith
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at the earth's surface. It need not be weathered nor contain any vegetation; it may be gravel, for example. Also according to agronomists, a soil is likely to be composed of a series of horizons and have properties quite independent of the underlying parent bedrock. The civil engineer tends to divide the material at the earth's crust into two categories (1) rock and (2) soils. Rock is defined as something that is hard and consolidated. Soil, according to Terzaghi and Peck, is a natural aggregate of mineral grains that can be separated by such gentle means as agitation in water. Substantially any loose material at the earth's crust, regardless of particle-size distribution, composition, or organic content, is soil to the engineer. It may or may not be weathered. Similarly soil to the engineer can extend to any depth below the surface so long as the material is not indurated substantially. Shale to the engineer is similar to soil except that the term is applied to material that is slightly harder and is definitely argillaceous. The term clay is primarily a particle-size term to the engineer.

The author has found it convenient to use the expression clay material for any fine-grained, natural, earthy, argillaceous material. Clay material includes clays, shales, and argillites of the geologist. It would also include soils, if such materials were argillaceous and had appreciable contents of clay-size-grade material.

No attempt will be made herein to consider the definitions of relatively minor types of argillaceous materials with somewhat specific properties, such as loam, gumbo, etc. Description of such materials can be obtained from standard textbooks on soils and sedimentary rocks.

FACTORS CONTROLLING THE PROPERTIES OF CLAY MATERIALS

The factors which control the properties of clay materials or the attributes which must be known to characterize completely a clay material may be classified as follows:

a. Clay-mineral Composition. This refers to the identity and relative abundance of all the clay-mineral components. Since certain clay minerals which may be present in very small amounts may exert a tremendous influence on the attributes of a clay material, it is not adequate to determine only the major clay-mineral components. Thus a small amount (5% ±) of montmorillonite in a clay is likely to provide a material very different from another clay with the same composition in all ways except for the absence of montmorillonite. In order to make complete clay-mineral determinations, it is frequently necessary to

fractionate the clay grade to concentrate minor constituents so that adequate analytical data can be obtained. Fortunately such a concentration can often be attained, because the various clay minerals frequently occur in particles of different sizes or break down easily in water to particles of different size. Also the clay minerals must be determined in their natural state. For example, care must be taken that the analysis will reveal the natural hydration state of the minerals and their ion-exchange composition. Clays composed of halloysite have very different physical properties depending on whether the mineral is in the $4H_2O$ form, the $2H_2O$ form, or an intermediate state. Montmorillonite clays have very different properties when $Na^+$ is the exchange cation and when $Ca^{++}$ is the cation.

In clay materials containing a considerable amount of nonclay-mineral material, it is frequently necessary to remove the nonclay-mineral material before the clay minerals can be identified completely. Frequently this involves merely a particle-size separation. Sometimes, as in the presence of pigmentary iron oxide or hydroxides, extremely fine carbonate, and pigmentary organic material, other methods must be attempted. Considerable caution is necessary to avoid significant change in the clay-mineral components in such separations. For example, the use of acids to remove the iron or carbonate, even if very dilute, may dissolve certain of the clay minerals if they are present (see Chap. 12). In the case of iron oxide or hydroxide, recent biological methods of removal appear to be quite satisfactory. Strong oxidizing agents to eliminate the organic material are likely to alter the clay minerals significantly.

b. Nonclay-mineral Composition. This refers to the identity of the nonclay minerals, their relative abundance, and the particle-size distribution of the individual species. Calcite, dolomite, large flakes of mica, pyrite, feldspar, gibbsite, and other minerals are very abundant in some clay materials.

Obviously, it is impossible or unjustifiably time-consuming to get all the data concerning the nonclay minerals in most investigations of clay materials. The lengths to which one can and must go depend largely on the problem at hand and the purpose of the investigation. It is frequently adequate to determine the identity of only the more abundant nonclay minerals and their sorting and particle-size distribution in a general way. Thus the "heavy minerals" may be of no significance in

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relation to the physical properties of a clay but may be of important
diagnostic value in determining whether or not a clay has formed by the
alteration of volcanic ash. As another example, the study of a soil from
the point of view of soil mechanics demands that sorting within the silt
size range be studied in considerable detail, since the presence of some
silt materials may yield a material of unique physical properties of great
importance to the construction engineer. The analysis of a clay material
must be tailor-made to the material being studied and to the purpose of
the investigation and must provide comparable results from one sample
to another. One cannot blindly use a set analytical procedure for all
materials and all problems and still get adequate data without a tremen­
dous waste of time and effort.

The nonclay minerals in clay materials tend generally to be concen­
trated in particles coarser than about 2 microns. There are, however,
materials in which they are much finer grained. In some Wyoming
bentonites, for example, a considerable amount of cristobalite is
present in particles considerably less than 1 micron in diameter intimately
mixed with the clay mineral montmorillonite. Many clay materials con­
tain extremely fine iron oxide or hydroxide, which acts as a pigment.
The identification of the coarser nonclay minerals can be made with the
petrographic microscope. The determination of those occurring in
extremely fine particles requires X-ray techniques. Neither of these
methods permits very precise quantitative determinations. In the case
of extremely fine silica, the maximum accuracy by X-ray diffraction is
about ± 2% if the quantity is small and somewhat less if the quantity is
large (4% ± ). Numerous attempts have been made to determine the
amount of nonclay minerals chemically, e.g., the amount of free and
combined silica in a clay material. Such methods are based on a differ­
ence in solubility of the constituents. Unfortunately variations of
solubility with particle size cause the results to have questionable value.
The absence of accurate quantitative methods for determining the non­
clay-mineral components of clay materials frequently makes it impossible
to obtain exact data on the chemical composition of the clay minerals
themselves in such materials.

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6 Roth, R. S., The Structure of Montmorillonite in Relation to the Occurrence and
7 Trostel, L. J., and D. J. Wynne, Determination of Quartz (Free Silica) in Refrac­
8 Sauseat, H., Can Free Quartz Be Determined in a Rock, Rev. ind. minérale, 529,
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c. Organic Material. This refers to the kind and amount of organic material contained in the clay material. In general the organic material occurs in clay materials in two ways: it may be present as discrete particles of wood, leaf matter, spores, etc., or it may be present as organic molecules adsorbed on the surface of the clay-mineral particles (see Chap. 10). The discrete particles may be present in any size from large chunks easily visible to the naked eye to particles of colloidal size which act as a pigment in the clay-mineral material.

The total amount of organic material can be determined simply by readily available standard analytical procedures. Values may be obtained from the difference between total loss on ignition and determination of loss of water, sulfur, and other inorganic volatiles. Such values are not precise but are usually adequate. Differential thermal analyses provide a crude determination of amount of organic material. Fine pigmentary organic material gives a dark gray or black color to a clay material, but there is no direct relationship between the color and organic content. A very small amount of organic material may have a very large pigmenting effect.

Determination of the kind of organic material is a more difficult problem. Sometimes, if the discrete particles are relatively large, they can be identified visually or microscopically. By means of X-ray-diffraction technique, the presence of adsorbed organic molecules may usually be determined. At the present stage of our knowledge it is usually impossible to go further and identify the organic components present in small amounts and of extremely fine size, either discrete or adsorbed. A large amount of fundamental work, applying modern methods, such as infrared absorption, must be done on the organic material in clay materials to provide basic data before any more or less routine procedures can be devised for such analyses.

The study of the organic content of clay minerals is a problem worthy of intensive research for a variety of reasons. For example, the organic content often is important in determining the properties of a clay material, and also a knowledge of clay-mineral–organic relations might throw much light on some important geologic processes. It might improve our understanding of the origin of petroleum, since the clay minerals may well have acted as catalysts in the transformation of the parent organic matter into hydrocarbons.

d. Exchangeable Ions and Soluble Salts. Some clay materials contain water-soluble salts which may have been entrained in the clay at the

time of accumulation or may have developed subsequently as a consequence of weathering or alteration processes, as in the oxidation of pyrite to produce sulfates. It is frequently necessary to wash out the soluble salts before other attributes of the material are studied. Some salts may act to flocculate the clay, so that it cannot be dispersed for particle-size analysis or for fractionation preliminary to clay-mineral analysis until the salts are washed out. Common water-soluble salts found in clay materials are chlorides, sulfates, and carbonates of alkalies, alkaline earths, aluminum, and iron.

The clay minerals and some of the organic material found in clay materials have significant ion-exchange capacity. The ion-exchange capacity of the clay minerals and the organic components, as well as the identity and relative abundance of the exchangeable ions which are present, are extremely important attributes of clay materials. It is difficult to distinguish sometimes between exchangeable ions and those present in a moderately soluble compound, so that determinations of ion-exchange characteristics are difficult in a material containing appreciable water-soluble salts. This whole matter, together with analytical procedures, is discussed in detail in Chap. 7.

e. Texture. The textural factor refers to the particle-size distribution of the constituent particles, the shape of the particles, the orientation of the particles in space and with respect to each other, and the forces tending to bind the particles together.

Some knowledge of the particle-size distribution of the coarser grains can be obtained quickly by microscopic examinations, and detailed determinations can be made by sieving and/or wet sedimentation methods. Fine-grained particles require wet methods, and this applies to the clay-mineral fraction. It must be remembered that wet methods are likely to reflect only the degree to which clay-mineral units or aggregates have been cleaved or broken down in the process of making the analysis rather than any inherent attribute of the natural material. In dispersing clays in water for analysis, the material is usually agitated, which splits and cleaves natural particles. The particle-size distribution records the amount of agitation applied. There are clay-mineral materials from which literally any particle-size distribution can be obtained by relatively slight variations of the preparation procedure. In general the particle-size distribution of clay materials composed of montmorillonite, vermiculite, and the attapulgite-sepiolite clay minerals would be more affected by analytical procedures than clay materials composed of the other clay minerals.

The use of chemical dispersing agents almost certainly will alter the base-exchange composition of the material, and consequently such agents must not be used or at least used only with great caution, if
exchangeable ions are to be determined. It is generally essential to
determine the exchangeable ions on the "as received" material, since any
mixing in water or washing is likely to cause a significant change. Also
such chemicals are likely to yield salts in the resulting fractions which
complicate the identification of any clay minerals therein.

The dewatering of the fine clay grades may well yield a material in a
different hydration state than the original material, and such dehydra­
tion, if it is complete, may tend to conceal some of the clay-mineral
components. Thus, completely collapsed montmorillonite from which
all adsorbed water has been removed is easily mistakable for illite. If
clay-mineral determinations are to be made on clay fractionations, it is
essential they be only air-dried, not oven-dried.

It is obvious that the particle-size-grade analysis of clay materials is
difficult, and care must be taken to devise a tailor-made procedure best
suited to the material at hand and to the objectives of the investigation
if pertinent, reproducible, and comparable data are to be obtained.

The shape of the finest particles is revealed best by electron-microscope
studies. Such investigations have shown the hexagonal outline of the
flake-shaped units of kaolinite, the elongate tubular shape of the halloysite
minerals, the irregular flake shape of the illite, chlorite, vermiculite,
and most montmorillonite mineral particles, and the elongate lath or
fiber shape of some of the montmorillonite minerals and of attapulgite­
sepiolite-palygorskite. Information on the thickness as well as areal
dimensions can frequently be obtained from electron micrographs;
kaolinite particles that have been studied show a ratio of areal diameter
to thickness of 2-25:1, whereas for montmorillonite it is 100-300:1.
In the application of the electron beam in electron microscopy, consider­
able heat is developed in the specimen so that some concern has been felt
as to whether or not some of the observed results are due to this heat and
the possible resulting dehydration rather than to the natural mineral.

The microscope using ordinary light can, of course, be used to study
the coarser particles. The lower limit for the study of the shape of
particles by ordinary microscopic methods is about 5 microns.

Some information regarding the orientation of extremely fine particles
can sometimes be obtained from the study of thin sections. In the
absence of appreciable amounts of nonclay-mineral components, aggre­
gate parallel orientation of the anisotropic clay-mineral particles as
compared to random orientation is shown by uniform extinction and bire­
fringence characteristics. Thin-section studies appear to have distinct
limitations. The thickness of the sections is many times that of the
individual clay-mineral components, so that many individuals lie on top
of each other. The presence of even small amounts of organic material
or free ferric iron oxide or hydroxide will mask the individual components
and distort the optical values. Also the clay material must be dried in preparation for the cutting of the section, so that the texture observed may be not quite that of the original material. Even with these deficiencies of thin-section study, it is usually worth while to cut sections and study them in any clay-material investigation. Such studies,\textsuperscript{12} for example, have revealed particularly pertinent data on the paragenesis of hydrothermal clay minerals in wall-rock alteration associated with ore bodies.

Some few attempts have been made to devise new methods of studying the texture of clays in their natural state, such as the replica electronmicrograph methods, the relation of preferred aggregate orientation to certain physical properties, and the cutting and study of thin sections of frozen clay materials. It appears that work with such methods has not reached the point where general results are available. The texture of clay materials is an important and promising field for research that should attract able investigators.

So little is known in detail about the forces binding the particles together in clay materials that the possible types of binding forces can merely be enumerated.

1. Forces due to the attraction of the mass of one clay-mineral particle for the mass of another particle.

2. Intermolecular forces resulting from the nearness of one particle to another with the overlap of fields of force of molecules in the surface layers of adjacent particles.

3. Electrostatic forces due to charges on the lattice resulting from unbalanced substitution within the lattice, broken bonds on edges of the lattice, and the attractive force of certain ions adsorbed on clay-mineral surfaces. Examples are to be found in the bonding action of \( K^+ \) between mica layers and of multivalent ions with one valence tied to one particle and another valence tied to a second particle.

4. The bonding action of adsorbed polar molecules. Oriented water molecules (see Chap. 8) between two clay-mineral surfaces may form a bridge of considerable strength if only a few molecules thick and of no strength if more than a few molecules thick. Similarly, adsorbed polar organic molecules could serve as a bond between clay-mineral particles.

In any given clay material all the bond forces probably are at work, and they are interrelated. Thus the nature of the adsorbed ion will itself influence bonding and also affect the development of oriented adsorbed water, which in turn is related to bonding.

since it largely determines the sensitivity and strength of soil materials. Construction failures have occurred because the strength properties of a soil that developed during construction could not be predicted adequately from empirical laboratory testing data. Without fundamental data on how and why clay materials are held together, it is impossible always to predict safely from any empirical data how a clay material will act when load is applied, when the water table is altered, or when other conditions are changed.

ADDITIONAL REFERENCES

CHAPTER 2

Concepts of the Composition of Clay Materials

OLD CONCEPTS

Because of the importance of clay materials in ceramics and other industries, in agriculture, in geology, and elsewhere, their investigation goes back far into antiquity. Many people have devoted most of their lives to the study of clay materials. From the first, investigators learned that clays and soils had widely varying properties. Even soils and clays which had the same color and general appearance and the same texture were found to differ widely in other characteristics. As soon as procedures for the ultimate analysis of clay materials were worked out, it was learned that clay materials differed widely in their chemical composition. The finest fractions of clay materials, which were thought to be the essence of the material, showed wide variations in the amounts of alumina, silica, alkalies, and alkali earths that they contained. It was also found that clays of the same ultimate chemical composition frequently had very different physical attributes, and that clays with substantially the same physical properties might have very different chemical compositions.

It is obvious from the foregoing statements that there must be variations not only in the amounts of the ultimate chemical constituents, but also in the way in which they are combined, or in the manner in which they are present in various clay materials. A review of the older literature shows that a considerable number of concepts were suggested to portray the fundamental and essential components of all clay materials and to explain their variation in properties. These concepts essentially present ideas of the nature of the way in which the alumina, silica, etc., are made up into the fundamental building blocks of clay materials.

Until very recent years there have been no adequate analytical tools to determine with any degree of certainty the exact nature of the fundamental building blocks of most clay materials. It is understandable, therefore, that many different concepts were suggested and that there was no general agreement among the workers in this field.

It is desired to present here very brief statements of the older concepts to serve as a background for the later consideration of the development of the present, generally accepted clay-mineral concept. For a more detailed discussion of these early ideas of the nature of clays and soils,
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Reference should be made to the works of Blanck,1 Stremme,2,3 Oden,4 Bradfield,5 Marshall,6 and Kelley.7 There is no definite sequence in the development of these older concepts; in general they existed contemporaneously in the minds of various investigators.

A very old idea is that there is a single pure clay substance and that this pure clay substance is the mineral kaolinite or something substantially similar to it. Clay materials, according to this concept, are composed of kaolinite, frequently with varying amounts of other materials considered to be impurities. Differences in the chemical composition between kaolinite and natural clays are explained by the presence of these impurities. Kaolinite, however, was thought to be the essence of clays.

This concept of the general prevalence of kaolinite was held widely by geologists and, indeed, unfortunately persists in the thinking and writings of some present-day members of this profession. Also the concept has persisted to some extent in many other quarters. The Webster’s New International Dictionary, 1934 edition, in the definition of clay states “the essential constituent of pure clay, or kaolin, is the mineral kaolinite . . . Most clays, however, contain other hydrous aluminous minerals with more or less finely comminuted quartz, feldspar, mica, etc."

Some clays are composed almost wholly of kaolinite, and in some of such clays, the particles of kaolinite are large enough to be seen and identified positively by the microscope with relatively low magnification. Such clays are the rare exceptions in which the fundamental building blocks could be identified definitely in the years prior to the development of modern research tools for studying extremely small particles. Also such kaolinite clays are of particular importance in the ceramic art and to geologists; hence they were among the first to be studied in detail. It was a simple matter to extend the findings of the study of these kaolinite clays to all clay materials. It is now established, of course, that there are many clay materials in which there is no kaolinite present. Merrill8 and

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Ries early emphasized the error of considering that kaolinite was the base of all clays, but the error tended to persist.

Another concept very widely held, particularly by soil investigators, was that the essential component of all clay materials was a colloid complex. Particularly in early days, all colloidal material was thought to be amorphous, and the colloidal complex in clays was thought to be amorphous. The complex was thought to be partly inorganic and partly organic when the clay material contained some organic material.

In general there were two more or less clearly defined ideas concerning the character of the colloidal complex. One of the ideas, with which the names of Van Bemmelen and Stremme are particularly associated, regarded the complex not as a definite compound but as a loose mixture of the oxides of silicon, aluminum, and iron. In later years, the researches of Thugutt, Bradfield, and many others showed that clay materials generally did not contain a colloidal mixture of oxides. The other idea regarded the complex as a compound or a mixture of compounds. The compounds were generally thought of as salts of weak ferroalumino-siliceous acids. In some cases these compounds were considered definitely to be amorphous, but mostly there was no real concept of the structure of the colloidal complex.

Way in his early work on the exchange reaction in soils concluded that the exchange complex in soils was a hydrous aluminum silicate quite similar to artificial precipitates produced in the laboratory.

Van Bemmelen and later Stremme divided their colloidal fraction into two parts. One part, which was soluble in hydrochloric acid, they called allophaneton, and a second part not soluble in hydrochloric acid but soluble in hot concentrated sulfuric acid came to be called kaolinton. The allophaneton was thought to be highly colloidal of very varying composition and largely responsible for the plastic and adsorptive properties of clay materials. Kaolinton was thought to be largely amorphous but at times containing also some crystalline material. Its composition showed relatively little variation and usually approached that of the

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12 Thugutt, H., Are Allophane, Montmorillonite, and Halloysite Units or Are They Mixtures of Alumina and Silica Gels?, Centr. Mineral Geol., pp. 97–103 (1911).
mineral kaolinite. Attempts were made to classify clay materials on the basis of their kaolinton and allophaneton content.

Mellor\textsuperscript{15} and Searle\textsuperscript{16} also developed the idea that there were two essential components of clay. One, which was called "clayite," was thought to be the true clay substance in kaolins and was considered to be an amorphous substance with about the same chemical composition as the mineral kaolinite. The other, for which the name "pelinite" was suggested, was the true clay substance in clay materials other than the kaolins. The latter was thought of as an amorphous material of varying composition but of generally higher silica content than "clayite" and also with appreciable alkalies and/or alkaline earths.

Wiegner\textsuperscript{17} in his extensive studies of cation exchange viewed the exchange material as made up of three parts: (1) a kernel, (2) a layer of adsorbed anions external to the kernel but lying in contact with it, (3) exchangeable cations attracted to the particle by the adsorbed anions. The kernel was considered to be a hydrous compound chiefly of alumina and silica of variable composition and of unknown structural attributes.

In the extensive studies of cation exchange in soils by Gedroiz,\textsuperscript{18} this investigator considered the complex as zeolitic material, but not as zeolitic in the mineralogical sense. In other words the complexes had certain of the properties of zeolites but were not considered to have their precise composition or structure. The nature of their structure was not known.

Another slight variation of this same concept, which has been carried down to the present in the work of Mattson,\textsuperscript{19,20} is that the colloid complex is made up of a relatively inert framework of silica, iron, and aluminous materials encased in an active amorphous envelope of a varying compound of silica, alumina, and iron with alkalies and alkaline earths. Mattson considers this latter compound to be an amorphous isoelectric precipitate of hydrated sesquioxides and silicic acid. In the light of advances in clay mineralogy and the finding of the general crystalline nature of the components of clay materials, Mattson\textsuperscript{21} has somewhat


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modified his concept by postulating the colloidal complex as a crystalline kernel covered with an amorphous heterogeneous coating which lacks a definite composition and is not identical with the nucleus. According to Mattson, X-ray-diffraction analysis would reveal only the character of the crystalline nucleus and not of the heterogeneous coating which is the essence of the complex. Mattson concepts have been criticized by Kelley and Marshall, and there is no doubt that in many clay materials, X-ray analyses have shown that substantially all the components are definite crystalline compounds.

In a very recent work, Puri has considered soils to be composed essentially of ferroaluminosilicates of varying composition but all composed of the same framework. According to him, when soils from different localities are subject to treatment by mild acids, a framework residue is obtained which in every case behaves in the same manner. Studies of the structures of the clay minerals have, of course, shown that there are important and significant differences in the structure of the various components of the finest fractions of soils.

Asch and Byers and his colleagues in the U.S. Department of Agriculture considered that the essential components of soils were a number of substances rather than a single compound. They viewed these substances as aluminosilicic acids or salts of such acids with definite compositions and with definite structures. This concept approaches the present clay-mineral concept, and, in fact, Byers et al. suggested clay-mineral names, e.g., montmorillonitic, halloysitic, for their postulated acids.

It has long been known by mineralogists that the zeolite minerals are silicate compounds that possess the property of cation exchange. When Way and his successors showed that soil materials had cation-exchange capacity and that it resided in the silicate complex, an understandable step was to postulate that soil materials contained zeolites. Lemberg in 1876 particularly developed the concept of the presence of zeolites in soil materials. Later, when the general idea was that the colloidal complex was amorphous, it was postulated, notably by Gans, that the complex was zeolitic. That is, the complex was an amorphous counter-

part of the crystalline zeolite minerals. Even in relatively recent work the colloidal complex is sometimes referred to as zeolitic, although the work of Gedroiz\textsuperscript{28} and many others has shown wide differences between the properties of mineral zeolites and the finest fractions of clay materials and indicated that the exchange complex can be considered zeolitic only in the sense that it possesses cation-exchange capacity. Modern X-ray analyses have revealed one or two instances when zeolites do occur in bentonite clays, but such minerals are not general and significant components of clay materials.

It is generally recognized that the small size of the particles in clay materials is one of the reasons for their special attributes. It was suggested, notably by Oden\textsuperscript{4}, that particle size is the major factor and that, in fact, clays can be composed of almost any minerals if they are fine enough—about 1 micron was considered the upper size limit. According to Oden, clays are composed of a heterogeneous array of extremely small particles of crystalline and amorphous components. Some clays, especially those of glacial origin, may contain an unusually large variety of minerals in extremely small particle sizes. Present data indicate that certain minerals, i.e., the clay minerals, must be present in appreciable amounts if the clays are to have the plastic properties associated with the term clay. The shape of such particles, their adsorptive and surface properties, in addition to their small size, are essential if a material is to have the characteristics of clay.

**CLAY-MINERAL CONCEPT**

For many years some students of clay materials have suggested that such materials are composed of extremely small particles of a limited number of crystalline minerals. For example, Le Châtelier\textsuperscript{29} and Lowenstein\textsuperscript{30} arrived at this conclusion in 1887 and 1909, respectively. This is the clay-mineral concept, but prior to about 1920 to 1925 there were no adequate research tools to provide positive evidence for it. The clay-mineral concept, therefore, is not new; rather it has been well established and generally accepted in recent years.

In 1923, Hadding\textsuperscript{31} in Sweden and in 1924 Rinne\textsuperscript{32} in Germany, working

\begin{itemize}
  \item Le Châtelier, H., De l'action de la chaleur sur les argiles, *Bull. soc. franc. minéral*, 10, 204–211 (1887).
\end{itemize}
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quite independently, published the first X-ray-diffraction analyses of clay materials. Both these investigators found crystalline material in the finest fractions of a series of clays and also found that all the samples studied seemed to be composed of particles of the same small group of minerals. They did not find a large heterogeneous array of minerals of a wide variety of types in the fine fractions of the samples studied.

In the early years of the present century, careful researches by some soil scientists were leading many of them to the idea that soils generally were composed essentially of definite compounds and that there were a limited number of such compounds in soils. Previous mention has been made of the work of Byers and his colleagues of the U.S. Department of Agriculture which led them to postulate a few definite compounds, such as halloysitic acid, montmorillonitic acid, or their salts, as the essential constituents of all soils. Another example of this trend on the part of students of soils is the chemical work of Bradfield on the fine fractions of the Putnam soil from Missouri, which showed that the clay fractions below a certain size resembled each other very strongly but that none of them behaved like mixed gels of hydrous oxides.

About 1924, Ross and some colleagues of the U.S. Geological Survey began a study of the mineral composition of clays that led to a series of monumental papers on the subject. Working particularly with bentonites at first, but within a few years with a variety of clays used in industry and a variety of soils, it was shown, on the basis of extremely careful and painstaking optical work with the petrographic microscope supplemented by excellent chemical data, that the components of clay materials were largely essentially crystalline and that there was a limited number of such crystalline components, to which the name clay minerals was applied. A classification of the clay minerals was suggested. Ross's work corrected the erroneous notion, still held in some quarters, that microscopic studies are of no value in clay researches. Ross and his colleagues later added X-ray analysis to their investigations; in general it substantiated their earlier findings.

About 1926, Marshall\textsuperscript{39,40} began a study of the optical characteristics of clay-water suspensions when they were placed in an electrical field. He devised a quantitative method for measuring the birefringence resulting from the aggregate orientation that developed in the electrical field. Marshall's work showed the crystalline nature of the finest fraction of the soils which he studied. Marshall also showed that the birefringence exhibited a measurable variation with a variation in the nature of the exchange cation, indicating, at least in the soils studied, that the sites of the exchange cations were internal and related to the anisotropy of the crystal in some definite way. This latter finding did not hold for kaolinite clays, whose ionic exchanges could then be ascribed to external surfaces only.

Hendricks and Fry\textsuperscript{41} in 1930 and Kelley, Dore, and Brown\textsuperscript{42} in 1931, presented separate papers from independent work showing, chiefly on the basis of X-ray-diffraction analyses, that soil materials, even in their finest size fractions, are composed of crystalline particles and that the number of different crystalline minerals likely to be found is limited.

By the early 1930's what has come to be known as the clay-mineral concept became firmly established in the minds of a great many people actively studying clay materials. Ross and Kerr\textsuperscript{43} in 1931, Endell, Hofmann, and Wilm\textsuperscript{44} in 1933, and Correns\textsuperscript{45} in 1936 published particularly concise statements of this concept. At the present time it has come to be accepted by almost all students of clays. There are a few\textsuperscript{5} investigators, notably Mattson\textsuperscript{21} who have clung to the notion that the essence of substantially all clays is an amorphous, extremely variable material which cannot be revealed by X-ray-diffraction analyses.

According to the clay-mineral concept, clays generally are essentially composed of extremely small crystalline particles of one or more members of a small group of minerals which have come to be known as the clay minerals. The clay minerals are essentially hydrous aluminum silicates, with magnesium or iron proxying wholly or in part for the aluminum in


some minerals and with alkalies or alkaline earths present as essential constituents in some of them. Some clays are composed of a single clay mineral, but in many there is a mixture of them. In addition to the clay minerals, some clay materials contain varying amounts of so-called nonclay minerals, of which quartz, calcite, feldspar, and pyrite are important examples. Also many clay materials contain organic matter and water-soluble salts (see page 6).

According to the clay-mineral concept, the crystalline clay minerals are the essential constituents of nearly all clays and, therefore, the components which largely determine their properties. As noted before, the nonclay minerals and some other factors (see page 3) will also influence properties if they are present in appreciable amounts. In the early years of the acceptance of the clay-mineral concept, it was thought that amorphous material was substantially completely absent in almost all clay materials. Some amorphous material had been found, but it was thought to be limited to a few unique clays, e.g., in association with the halloysite in the so-called *indanaitie* from Indiana. Recent work indicates that extremely poorly crystalline material that appears in some cases to be actually amorphous to X-ray diffraction is not so rare as it was believed to be earlier. It does not, however, appear to be a very common component, and the great majority of clay materials appear to be entirely crystalline. Certainly amorphous material is not present in all or even in most clay materials, and it cannot be considered a universal constituent responsible for clay properties. The presence of poorly crystalline material is revealed by X-ray-diffraction data, but the presence of definitely amorphous material is usually hard to establish. Its presence is usually suggested when the analytical data do not indicate the crystalline constituents to be present in sufficient quantities to add up to 100 per cent.

Since about 1930 and the general acceptance of the clay-mineral concept, there has been intense interest in the study of clay materials, and a very voluminous literature has developed. Workers have approached the study of clay mineralogy from many different fields—mineralogy, geology, chemistry, physics, agronomy, etc. Also a tremendous amount of work has been done on applied clay mineralogy by ceramists, engineers, etc., in a host of university, commercial, and other laboratories. The clay-mineral literature appears in an extremely wide variety of publications—in chemical, physical, mineralogical, ceramic, and other journals—as is to be expected because of the wide range of backgrounds and approaches of the persons working in the field.

In the following statements an attempt will be made to indicate some of the more important contributions which have appeared in the development of clay mineralogy. It is impossible to mention all or even most of those who have contributed significantly, and an attempt can be made merely to list some of those who pioneered in the study of the clay minerals.

Reference has already been made to the monumental work of Ross and his colleagues, which did much to establish the clay-mineral concept. The work of Ross and Kerr on kaolinite and halloysite and later of Ross and Hendricks on montmorillonite provided fundamental data on the properties of these clay minerals essential to their determination in clay materials. Hendricks, working alone and with a series of colleagues from the U.S. Department of Agriculture, has produced a series of outstanding papers on the structure of the clay minerals and on many of their physical attributes. Among the many contributions of Hendricks of particular importance, in addition to his structural studies, are his works on cation exchange, on the reaction of organic ions and the clay minerals, on the hydration characteristics of certain of the clay minerals, and on the nature of the water adsorbed on the surface of the clay-mineral particle.

Since about 1930, Kelley and his colleagues at the University of California have contributed immensely to our knowledge of the distribution of the clay minerals in various soil types and the soil-forming condi-

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... under which various clay minerals form and are stable. Jenny\(^{58}\) of this school has made outstanding contributions to concepts of cation exchange, and recently Barshad,\(^{49}\) also of this school, has published valuable data on the vermiculite and chlorite clay minerals.

Beginning about 1931, Grim, Bradley, and their colleagues\(^{60-62}\) at the Illinois State Geological Survey and the University of Illinois have studied the illite clay minerals and the composition of many clays and shales. They have been particularly interested in the relation of the clay-mineral composition to the plastic, burning, strength, and other properties of clay materials which determine their utility in ceramics, soil mechanics, oil-well drilling, and other applied fields. They have also worked with the development of the differential thermal procedure\(^{63}\) for the analysis of clay materials and have studied the composition of recent marine sediments.\(^{64}\) Bradley,\(^{65}\) working independently, determined the structure of attapulgite, which provided for the first time an insight into the structure of some of the fibrous clay minerals.

The classical investigation of the structure of the layer silicates by Pauling\(^{66}\) provided the basic ideas permitting the elaboration of the structure of the layer clay minerals. Following Pauling's original ideas, Gruner worked out a structure for kaolinite\(^{67}\) and vermiculite.\(^{68}\) The structural concepts of the latter mineral largely led the way to an understanding of interlayered mixtures of clay minerals. Hendricks and Teller\(^{69}\)


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later worked out the theory of X-ray diffraction for such interlayered mixtures, which has permitted their detailed study and evaluation.

Contributions by Gieseking\textsuperscript{70} greatly enhanced our knowledge of the adsorption of organic ions and their influence on the structure of montmorillonite. Bradley\textsuperscript{71} pointed out that certain nonionic polar organic molecules are also adsorbed and indicated the nature of the bond between such molecules and the clay-mineral surfaces. Later Jordan\textsuperscript{72} in some extremely interesting and important work showed that multiple adsorption of organic molecules by montmorillonite was possible and described organophilic montmorillonite-organic complexes which formed gels in organic liquids.

At Pennsylvania State College, a group led by Henry\textsuperscript{73} and Bates\textsuperscript{74} have made notable contributions to clay mineralogy. Bates in recent years has contributed particularly to the knowledge of the halloysite minerals.

In Germany beginning about 1931 several schools of investigators began to study the clay minerals. At the Technische Hochschule in Berlin, Hofmann, Endell, and Wilm\textsuperscript{75} began a study of montmorillonite which resulted in a suggested structure for this mineral which is now widely accepted in its broader outlines. This same team of workers\textsuperscript{76,77} investigated many German clays and were among the first to show the relationship between the properties of the individual clay minerals and the larger ceramic and other properties of the clays themselves.

Correns\textsuperscript{78} and his associates at the University of Rostock published valuable data on the X-ray, optical, and chemical specifications of the various clay minerals. Mehmel\textsuperscript{79} of this group was the first to indicate

\textsuperscript{76} Hofmann, U., K. Endell, and D. Wilm, Röntgenographische und kolloidchemische Untersuchungen über Ton, \textit{Angew. Chem.}, 47, 530–547 (1934).
\textsuperscript{79} Mehmel, M., Ueber die Struktur von Halloysit und Metahalloysit, \textit{Z. Krist.}, 90, 85–93 (1935).
clearly the two forms of halloysite and to show their relations to each other. They also showed that the indices of refraction of some of the clay minerals may vary with the nature of the index liquid used to measure them. Correns, studying the marine-bottom samples collected by the Meteor, was among the first to investigate recent marine sediments by modern analytical techniques.

At Hanover in Germany, Noll began about 1933 the study of the laboratory synthesis of the clay minerals and produced the best data yet available on this subject.

In the Netherlands at the Agricultural College in Wageningen, Edelman and his colleagues began an active study of clay mineralogy in the early 1930's. They developed a structural concept of montmorillonite and halloysite, somewhat different from that suggested by Hofmann et al., which still claims considerable attention. They also determined the clay-mineral composition of many types of soil.

In 1927, Orcel in Paris first applied the differential thermal procedure in its modern form to the study of clay minerals, and its general use today is due in no small part to Orcel’s efforts. In association with Orcel at first and later independently, Henin and Caillere have actively pursued a variety of clay-mineral investigations. They have contributed particularly to our knowledge of the sepiolite-palygorskite clay minerals. Other French investigators, notably Longchambon and De Lapparent, have contributed to the study of clay materials.
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also have contributed important information regarding this group of clay minerals.

More recently a second group of French students of clays, led by Mering\textsuperscript{91,92} at the National Chemical Laboratory in Paris, has produced extremely important contributions to the subject. Mering\textsuperscript{93} contributed to the X-ray analysis of the interlayer mixtures of clay minerals, extending the earlier work of Hendricks and Teller.\textsuperscript{89} He has also enhanced our knowledge of the hydration of montmorillonite and of the catalytic activity of the same mineral. His colleagues\textsuperscript{94,95} have recently contributed to the adsorption phenomena of the clay minerals and their texture as revealed by the electron microscope.

Among the early contributors to clay mineralogy in Great Britain were Nagelschmidt and Brammall. Nagelschmidt\textsuperscript{96,97} published clay-mineral analyses of a variety of soils and was among the first to suggest that some of the clay minerals had an elongate fibrous form. Brammall\textsuperscript{98,99} contributed particularly to the illite clay minerals and to the possible variations in the composition of some of the other clay minerals.

More recently a very great interest in clay mineralogy has developed in Great Britain. MacEwan\textsuperscript{100} of the Rothampsted Agricultural Experiment Station has studied in detail the reaction of the clay minerals and organic compounds. He has presented the analyses of many soil materials\textsuperscript{101} and has contributed to X-ray techniques\textsuperscript{102} and the structure of

\textsuperscript{91} MacEwan, D. M. C., Les Minéraux argileux de quelques sols écossais, \textit{Verre silicates ind.}, \textbf{12}, 3–7 (1947).
\textsuperscript{92} MacEwan, D. M. C., Some Notes on the Recording and Interpretation of X-ray Diagrams of Soil Clays, \textit{J. Soil Sci.}, \textbf{1}, 90–105 (1949).
the clay minerals. Brindley\textsuperscript{103,104} at the University of Leeds has studied the kaolinite minerals in detail and has shown the possible variations in the degree of crystallinity of these minerals. At the Macauley Agricultural Research Institute in Aberdeen, Scotland, Walker\textsuperscript{105} and Mackenzie\textsuperscript{106} have studied the composition of Scottish soils and contributed to our knowledge of the biotite-like and vermiculite-like clay minerals.

Considerable investigation of clay minerals has been made in the U.S.S.R. by Belyankin,\textsuperscript{107} Sedletsky,\textsuperscript{108} and others.\textsuperscript{109} Unfortunately much of the work of the Russian investigators is not available outside of that country, so that neither the magnitude nor the worth of it can be adequately evaluated.

In other countries, notably in Sweden with the work of Forslind,\textsuperscript{110} in Australia with the work of Hosking\textsuperscript{111} and others,\textsuperscript{112} in India with the work of Mukherjee,\textsuperscript{113} Chatterjee,\textsuperscript{114} and others, in Italy with the work of Gallitelli,\textsuperscript{115} and in Spain with the work of Hoyos,\textsuperscript{116} notable contributions to the knowledge of clay mineralogy have been and are being made.

\textsuperscript{108} Sedletsky, I., Mineralogy of Dispersed Colloids, \textit{Acad. sci. URSS}, 114 pp. (1945).
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ADDITIONAL REFERENCES

Old Concepts


Clay-mineral Concept


CHAPTER 3

Classification and Nomenclature of the Clay Minerals

CLASSIFICATION OF THE CLAY MINERALS

The following classification of the clay minerals is suggested on the basis of currently available data on the structure and composition of the various clay minerals. Because such data are far from complete, the classification can only be tentative, and future investigations may show that major revisions are necessary. Some classification, however, is required as a basis for a discussion of the clay minerals.

Table 1. Classification of the Clay Minerals

<table>
<thead>
<tr>
<th>I. Amorphous</th>
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<td>Allophane group</td>
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<table>
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<tr>
<th>II. Crystalline</th>
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<tbody>
<tr>
<td>A. Two-layer type</td>
</tr>
<tr>
<td>(sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)</td>
</tr>
<tr>
<td>1. Equidimensional</td>
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<tr>
<td>Kaolinite group</td>
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<tr>
<td>Kaolinite, nacrite, etc.</td>
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<tr>
<td>2. Elongate</td>
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<tr>
<td>Halloysite group</td>
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<tr>
<td>B. Three-layer types</td>
</tr>
<tr>
<td>(sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)</td>
</tr>
<tr>
<td>1. Expanding lattice</td>
</tr>
<tr>
<td>a. Equidimensional</td>
</tr>
<tr>
<td>Montmorillonite group</td>
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<tr>
<td>Montmorillonite, sauconite, etc.</td>
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<tr>
<td>Vermiculite</td>
</tr>
<tr>
<td>b. Elongate</td>
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<tr>
<td>Montmorillonite group</td>
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<tr>
<td>Nontronite, saponite, hectorite</td>
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<tr>
<td>2. Nonexpanding lattice</td>
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<tr>
<td>Illite group</td>
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<tr>
<td>C. Regular mixed-layer types (ordered stacking of alternate layers of different types)</td>
</tr>
<tr>
<td>Chlorite group</td>
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<tr>
<td>D. Chain-structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)</td>
</tr>
<tr>
<td>Attapulgite</td>
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<tr>
<td>Sepiolite</td>
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<tr>
<td>Palygorskite</td>
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The suggested classification is based on structural attributes of the clay minerals. The major subdivision into amorphous and crystalline groups seems to be necessary, even though the amorphous clay minerals are relatively rare and of little importance.

The separation of the three-layer minerals into expanding and non-expanding types may ultimately prove unwise, since there may be a continuous gradation between some nonexpanding and expanding clay minerals, and some interlayered complexes are difficult to place in either category. However, the expanding attribute is usually a readily determinable diagnostic criterion, and it imparts generally more or less unique physical properties to clay materials composed of such minerals.

Also the separation of the expanding minerals into equidimensional and elongate divisions may ultimately prove to be undesirable, because there may be a complete gradation between them. At the present time no separate name has been applied to the elongate varieties; montmorillonite has been used as a group to include both varieties. The division is made because the shape is a readily recognizable characteristic that probably reflects important structural attributes.

No attempt has been made to create new separate categories on the basis of the population of the octahedral layer, i.e., whether the mineral is dioctahedral or trioctahedral. Future work may show this to be desirable and feasible. Examples of both kinds of three-layer types are known, but their relation to each other and their prevalence are not known. It is not established, for example, whether there can be complete gradations between them or only limited variations from the exact dioctahedral and trioctahedral populations. Further, it is frequently impossible at the present time to determine whether a given clay mineral which may occur intimately mixed with another mineral is dioctahedral or trioctahedral. A classification based on this attribute is, therefore, now unworkable.

At the present time the chlorite minerals are the only known examples of clay minerals with a regular ordered interstratification of different types of layers. Future researches may well show that there are other examples.

No separate category is made for random interlayer mixtures, since their character varies with the mixing. They must, therefore, be designated as mixtures of the layers involved.

The clay minerals with the hornblende-like structures are particularly poorly known. Almost certainly future investigations of these minerals will make some sort of subdivision of them possible. All that can be done at this time is to list examples that appear to belong together in this category.

Other reasons for suggesting the classification given in Table 1 will
Classification and Nomenclature of the Clay Minerals

appear in the discussion to follow and in the consideration of the structures of the various clay-mineral groups. Details of the classification will also be presented at that time.

NOMENCLATURE OF THE CLAY MINERALS

The name allophane was first applied by Stromeyer and Hausmann in 1816 to material lining cavities in marl. The term is derived from Greek words meaning “to appear” and “other,” in allusion to its frequent change on standing from a glassy material to one with an earthy appearance because of the loss of water. Since the work of Stromeyer and Hausmann a considerable number of materials have been described as allophane or classed with it. In general all such material was thought to be amorphous, and hence the name allophane came to be associated with amorphous constituents of clay. The study of much of this material, particularly by Ross and Kerr, showed that some of it was actually crystalline but that much of it was really amorphous to X-ray diffraction. They suggest that the term be used for all amorphous clay-mineral materials regardless of their composition. These investigators point out that the known examples of amorphous material in clays and soils show considerable variation in composition.

As has been indicated (page 13), the word allophaneton has been used for the portion of a clay soluble in hydrochloric acid. At the time the term was suggested such material was thought to be amorphous. It is now known that some of the crystalline clay minerals, e.g., montmorillonite, are fairly soluble in this acid and that others are somewhat soluble if present in extremely small particles. The term allophaneton has about disappeared from usage.

Ross and Kerr discuss in detail the nomenclature of the kaolin minerals, and their usage has been generally accepted. According to them, ... by kaolin is understood the rock mass which is composed essentially of a clay material that is low in iron and usually white or nearly white in color. The kaolin-forming clays are hydrous aluminum silicates of approximately the composition $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and it is believed that other bases if present represent impurities or adsorbed materials. Kaolinite is the mineral that characterizes most kaolins.

The name kaolin is a corruption of the Chinese “kauling” meaning “high ridge,” the name of a hill near Jaucahau Fu, China, where the material was obtained centuries ago. Occurrences in many parts of the world are

1 Stromeyer, F., and J. F. L. Hausmann, Göttingische Gelehrte Anzeigen, 2, 125 (1816).
well known today. Johnson and Blake in 1867 appear to have first clearly intended the name kaolinite for the "mineral of kaolin." Ross and Kerr have shown that the kaolin minerals cannot be assigned to a single species; i.e., clays of this character are not composed of a single mineral species, and minerals of that composition also are not all the same species. They concluded that three distinct species are represented, namely, kaolinite, nacrite, and dickite. Nacrite was proposed by Brongniart in 1807. Later Des Cloizeaux, and much later Dick, described a mineral called nacrite from mines in Saxony with sufficient analytical data to differentiate it from the "Dick mineral" but not from the "mineral of kaolin." Mellor accepted nacrite as a distinct mineral, and Ross and Kerr finally established its identity.

Dick in 1908 described a mineral from the island of Anglesey in Wales, without giving it any specific name, which was referred to with other clay minerals as a "mineral of kaolin." Ross and Kerr showed that the "Dick mineral" was a distinct species and first applied the name dickite.

Anauxite was proposed as a mineral name by Breithaupt in 1838 for a mineral from Bilin, Czechoslovakia. Smirnoff in 1907 gave a detailed description of it and showed photomicrographs of characteristic "worm-like" structures resembling those of kaolinite. The mineral from Bilin had a higher silica-to-alumina ratio than that usually found in the "mineral of kaolin," and Ross and Kerr proposed that anauxite be defined as a mineral with essentially the same attributes as kaolinite but with a higher silica-alumina molecular ratio, frequently approaching 3.

Anauxite is believed to be an interlayer mixture of a double silica layer and a two-layer type of sheet (see pages 51, 52). The mixing of the layers is not regular, and therefore it should not be placed in category C in Table 1. Further, the dimensions of both layers are substantially the same, so that it yields X-ray and optical data similar to kaolinite. It seems desirable to include it in the same category as kaolinite.

Very recently it has been shown, particularly by Brindley and Robin-
son,\textsuperscript{10} that there is considerable variation in the perfection of stacking and possibly also in the precise positions of the aluminums in the octahedral sheet of members of the kaolinite group. In the usual mineral the stacking is regular, whereas in some specimens random variations in certain directions are to be found. Brindley\textsuperscript{11} at first suggested the name mellorite for the less well crystallized material, thinking that there was a specific degree of such disorder. More recent work by Brindley\textsuperscript{12} himself suggests that there is a considerable range of disorder in the poorly crystallized kaolinites and that no new specific mineral name is warranted at this time.

The name halloysite was given by Berthier\textsuperscript{13} in 1826 for material found in pockets in Carboniferous limestone near Liége, Belgium, in a district of old zinc and iron mines. It was named in honor of Omalius d’Halloy, who had observed the mineral several years previously. In the years prior to the development of X-ray-diffraction techniques many materials were described as halloysite. Dana\textsuperscript{14} lists under halloysite 16 mineral names that he considers to be synonymous with it. Ross and Kerr\textsuperscript{15} studied much of this material by modern methods and in addition obtained samples from the mineralogical collections of the University of Liége which are probably as nearly representative of the type material as can be obtained at the present time. They show that halloysite is crystalline and state that it is closely related to but distinct from kaolinite. It is now generally accepted that halloysite is distinct from kaolinite and warrants a separate specific name.

Ross and Kerr\textsuperscript{15} in 1934 pointed out that “there are two types of halloysite—one that is usually white or light-colored, porous, friable, or almost cottony in texture; and another that is dense, nonporous and porcelainlike.” In the same year Hofmann, Endell, and Wilm\textsuperscript{16} pointed out that there were two forms of the mineral and also that one form was more hydrous than the other. They found that the more hydrous form had a larger $c$-axis spacing than kaolinite and, when dried at 105°C, experienced a structural change accompanying the dehydration to a

\textsuperscript{13} Berthier, P., Analyse de l'halloysite, \textit{Ann. chim. et phys.}, \textbf{32}, 332–335 (1826).
\textsuperscript{16} Hofmann, U., K. Endell, and D. Wilm, Röntgenographische und kolloidechemische Untersuchungen über Ton, \textit{Angew. Chem.}, \textbf{47}, 539–547, (1934).
material similar to kaolinite. Mehmel in 1935 and Correns and Mehmel clearly distinguished two forms of halloysite: one with the same chemical composition as kaolinite, and the other, more hydrated form differing from that of kaolinite by having an added $2\text{H}_2\text{O}$. They showed that the transition from the higher hydrated form to the lower hydrated form was not reversible, that it could take place at temperatures at least as low as $60^\circ\text{C}$, and that the lower hydrated form resembled but was not identical with kaolinite. Mehmel suggested the name halloysite for the highly hydrated form and metahalloysite for the lower hydration form.

Alexander et al. in 1943 suggested that the name halloysite be applied to the lower hydration form and the new name endellite be given to the higher hydration form. They made this suggestion because of their belief that the original material described by Berthier was the lower hydration form. MacEwan has disputed this point, claiming that the original material was the higher hydration form. MacEwan suggests that halloysite be used as a general term for all naturally occurring specimens of the mineral regardless of their state of hydration. He points out that natural materials may be in an intermediate state of hydration, and he would use the adjectives hydrated, nonhydrated, and intermediate, when the state of hydration is known and when it is important to describe it.

Unfortunately there is no agreement among clay mineralogists at the present time regarding the proper nomenclature for the halloysite mineral. The original locality is no longer accessible, and it seems impossible to establish to the satisfaction of everyone, the state of hydration of the original material described by Berthier. This is particularly true because of the fact that the transition and dehydration may take place at room temperature over long periods of time.

At the International Congress of Soil Science held in Amsterdam in 1950 a special meeting was held of those present interested in clay mineralogy to discuss the nomenclature of the clay minerals, particularly the problem of the halloysites. It was the general feeling of the meeting that great simplification and clarification would result if the word halloysite were employed for all forms of the mineral and, when necessary, additional self-explanatory qualifications be used, such as fully hydrated, nonhydrated, and intermediate.

hydrated, partially hydrated, dehydrated, halloysite-7-A, etc. It seems that this usage is the only one with any reasonable chance of wide acceptance, and it will be followed in the present volume.

Damour and Salvetat proposed the name montmorillonite in 1847 for a mineral from Montmorillon, France, which is a hydrous aluminum silicate with a silica-to-R₂O₃ ratio equal to about 4 and with a small content of alkalies and alkali earths. Le Châtelier later studied the material and presented the formula 4SiO₂·Al₂O₃·H₂O + aq. for montmorillonite; this was accepted by Dana. Dana listed a considerable number of names of minerals thought to be similar to montmorillonite wholly or in part.

Ross and his colleagues in a series of classical studies published from about 1926 to 1945 established the identity of montmorillonite as a valid clay-mineral group. They also indicate the variations in composition that are to be found in members of this group. For example, they showed the possible variation in the ratio of silica to R₂O₃ and the possible complete replacement of aluminum by iron and magnesium. They also emphasized the very frequent presence of magnesium in relatively small amounts in many specimens apparently as an essential ingredient.

Hofmann, Endell, and Wilm in 1933 published a structure for montmorillonite showing the expanding-lattice characteristics of the mineral, and this attribute is now generally considered to be an essential characteristic of the group. Gruner in 1935 and Marshall in 1935 pointed out possible replacements within the montmorillonite structure and emphasized their importance.

Cronstedt in 1788 described a material called "smectis" which seems
to be the same as montmorillonite. Kerr in 1932 showed that certain clay materials which have been described as smectite are actually montmorillonite. The name smectite, therefore, is earlier than montmorillonite. However, the name montmorillonite has been commonly used, while smectite has fallen into disuse or has been used for a fuller’s earth rather than for a definite mineral. As Kerr points out, “in view of the large amount of modern literature on montmorillonite it seems in the best interests of science to continue the use of montmorillonite and drop that of smectite.”

The earliest usage of the name saponite is difficult to establish. The name, derived from “sapo,” meaning soap, was used by Svanberg in 1840, and in 1842 he published chemical analyses showing the material to be essentially a hydrous magnesium silicate. As in the case of many of the other clay minerals, prior to the development of modern analytical techniques, the mineral could not be well characterized, and the early literature includes a considerable variety of materials under this name. Ross and Kerr in 1931 identified saponite as a member of the montmorillonite group with a high content of MgO. Ross and Hendricks in 1945 defined saponite as a member of the montmorillonite group in which the replacement of Al by Mg is essentially complete and with some replacement of Si by Al.

The name montmorillonite is used currently both as a group name for all clay minerals with an expanding lattice except vermiculite and also as a specific mineral name. Specifically it indicates a high-alumina end member of the montmorillonite group with some slight replacement of Al by Mg and substantially no replacement of Si by Al.

Berthier proposed the name nontronite for a material associated with manganese ore in the Arrondissement of Nontron near the village of Saint Pardoux in France. A chemical analysis given by Berthier shows the mineral to be a hydrous ferric iron silicate. Collins in 1877 appears to

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have been the first to recognize the association between nontronite and montmorillonite. The similarity of nontronite and montmorillonite was established by Larsen and Steiger,\textsuperscript{37} Ross and Kerr,\textsuperscript{33} and Gruner.\textsuperscript{27} Nontronite is now the name generally applied to the iron-rich end member of the montmorillonite group.

The name vermiculite from the Latin "vermiculair, to breed worms," was first used by Webb\textsuperscript{38} in 1824 for some material from Milbury, Massachusetts. Vermiculites have been classed with the micas and have frequently been listed as alteration products, chiefly of biotite and phlogopite. They have also been considered as closely related to the micas and were stated to show a considerable range in chemical composition. Until the work on the structure of vermiculites by Gruner\textsuperscript{39} and later by Hendricks and Jefferson,\textsuperscript{40} it was not known whether or not vermiculite was a distinct mineral. Only very recently\textsuperscript{41} has the occurrence of vermiculite in small particles as a clay-mineral constituent of clay materials been recognized.

Vermiculites have an expanding lattice, differing from montmorillonite in that the expansion can take place only to a limited degree. The possible range of composition of vermiculites is not known, but the natural materials always seem to contain considerable magnesium and iron (some of it ferrous), and Mg\textsuperscript{2+} seems to be the characteristic exchangeable cation. Like the montmorillonites, the vermiculites have high cation-exchange capacity. The composition of vermiculites can be the same as that of some montmorillonites, in which case the only difference would be in the larger particle size of the vermiculites.

The term illite was proposed by Grim, Bray, and Bradley\textsuperscript{42} in 1937 as a general term, not as a specific clay-mineral name, for the mica-like clay minerals. The name was derived from the abbreviation for the state of Illinois. Prior to 1937 the widespread occurrence of a mica-like clay mineral had been recognized by many investigators, and many names had been suggested, e.g., potash-bearing clay mineral,\textsuperscript{43} sericite-like mineral,\textsuperscript{43}

\textsuperscript{37} Larsen, E. S., and G. Steiger, Dehydration and Optical Studies of Alunogen, Nontronite and Griffithite, \textit{Am. J. Sci.}, ser. 5, \textbf{15}, 1–19, (1928).
\textsuperscript{40} Hendricks, S. B., and M. E. Jefferson, Crystal Structure of Vermiculites and Mixed Vermiculite-chlorites, \textit{Am. Mineral.}, \textbf{23}, 851–862 (1938).
\textsuperscript{41} MacEwan, D. M. C., Chlorites and Vermiculites in Soil Clays, \textit{Verre silicates ind.}, \textbf{13}, 41–46 (1948).
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Grim et al.\textsuperscript{42} pointed out objections to these earlier names, and the term illite has now been widely accepted for a mica-type clay mineral with a 10-A c-axis spacing which shows substantially no expanding-lattice characteristics.

Grim, Bray, and Bradley\textsuperscript{42} gave the general formula for illites as \((\text{OH})_4K_y(Si_{8-y}Al_y)(Al_4Fe^2_3Mg^2_3Mg_6)O_{20}\). In muscovite \(y\) is equal to 2, whereas in illite \(y\) is less than 2 and frequently equal to 1 to 1.5. According to the formula, illites would include both trioctahedral and dioctahedral types, and no attempt was made to differentiate between biotite and muscovite types of crystallization. At the present time the name illite is generally used, and will be used herein, for clay-mineral micas of both dioctahedral and trioctahedral types and of muscovite and biotite crystallizations. It may well be that future clay-mineral studies will show it desirable to subdivide the group, or even to use some very different larger categories.

It has been suggested, chiefly by Ross\textsuperscript{25} and his colleagues, that the name illite should be replaced by bravaisite on the basis that bravaisite is an earlier name and is a clay-mineral mica. Actually type bravaisite is a mixture\textsuperscript{44} of montmorillonite and a clay-mineral mica and not a specific mineral and therefore has no standing as a mineral species. Sarospatite has also been suggested by Hofmann \textit{et al.}\textsuperscript{46} as a substitute for illite, but the same objection\textsuperscript{47} can be raised, namely, that the type material from Sárosapatk, Hungary, is a mixture of clay minerals. It is believed that experience has shown the desirability of using a new name for this clay-mineral group rather than attempting a redefinition of an old name, particularly if the old name originally described a mixture of minerals.

Werner\textsuperscript{48} appears to have first used the name chlorite about 1800. It has been used for a group of green hydrous silicates in which ferrous iron is prominent and which are closely related to the micas. A large variety of materials have been described as chlorites, and there has been much confusion regarding the identity and validity of species belonging to the group.


The work of Pauling\textsuperscript{40} and McMurchy\textsuperscript{41} showed the general structural attributes of the chlorites, and recent works by Barshad\textsuperscript{51} and Brindley\textsuperscript{52} have provided detailed information on the relation of the chlorites to other micas and on the specific variations in structure between members of the group. Structurally the chlorites are regular interstratifications of single biotite mica layers and brucite layers. The chlorites provided an early example of interlayering of units into more complex structures, a phenomenon which is now known to be fairly common in clay materials.

Only recently\textsuperscript{41} have chlorites been recognized as important constituents of many clay materials, and it is likely that this clay mineral is much more abundant in clay materials than is now recognized. It is frequently very difficult to detect small amounts of chlorite when it is mixed with other clay minerals. The identification of chlorite is particularly difficult when kaolinite is also a constituent of the clay material being studied.

Sepiolite and meerschaum have long been considered as synonymous by mineralogists. The name meerschaum appears to have been first applied by Werner\textsuperscript{53} in 1789 and is German for "sea froth," alluding to the lightness and color of the material. The term sepiolite was first applied in 1847 by Glocker\textsuperscript{54} and is derived from the Greek for "cuttlefish," the bone of which is light and porous. The material is reported by Dana\textsuperscript{14} to vary from compact with a smooth feel to earthy or fibrous. He gives the formula $2H_2O \cdot 2MgO \cdot 3SiO_2$ for the mineral. Later Schaller\textsuperscript{55} stated the formula to be $4H_2O \cdot 2MgO \cdot 3SiO_2$.

The name palygorskite was first applied by Fersman\textsuperscript{56} to a family of fibrous hydrous siliceous minerals forming an isomorphous series between two end members: an aluminum end member called paramontmorillonite because of its resemblance to montmorillonite in all ways except the

\begin{thebibliography}{9}
\bibitem{mcmurchy} McMurchy, R. C., Structure of Chlorites, \textit{Z. Krist.}, 88, 420–432 (1934).
\bibitem{glocker} Glocker, E. F., "Generum et Specierum Mineralium secundum Ordines Naturales digestorum Synopsis" Halle (1847).
\bibitem{schaller} Schaller, W. T., The Chemical Composition of Sepiolite (Meerschaum), \textit{Am. Mineral.}, 21, 202–210 (1936).
\end{thebibliography}
fibrous character, and a magnesium end member called sepiolite. Longchambon,\textsuperscript{57} Migeon,\textsuperscript{58} and De Lapparent\textsuperscript{59} have studied these materials in considerable detail, but much additional work is required before the minerals can be well understood. The term palygorskite has also been used in a more specific sense for specimens thought to be like sepiolite except for some replacement of magnesium by aluminum. Longchambon\textsuperscript{57} first suggested that the palygorskite-sepiolite minerals have an amphibole-like structure composed of double chains of silica tetrahedrons, whereas De Lapparent\textsuperscript{59} believed them to have micaceous similarities.

The term attapulgite was first applied by De Lapparent\textsuperscript{60} in 1935 to a clay mineral he encountered in fuller's earth from Attapulgus, Georgia, Quincy, Florida, and Mormoiron, France. Bradley\textsuperscript{61} has determined the structure of the mineral, showing silica chains similar to those in amphibole to be essential components of its structure. It would seem that attapulgite is to be classed with sepiolite and palygorskite and that the existence of clay minerals of this type is now definitely established. Bradley\textsuperscript{61} gives the ideal formula of attapulgite as \((\text{OH}_2)_4(\text{OH})_2\text{Mg}_5\text{Si}_8\text{O}_{20}4\text{H}_2\text{O}\), in which there is considerable replacement of magnesium by aluminum.

As in the case of chlorite, the sepiolite-attapulgite-palygorskite minerals may well be much more abundant and widespread than is now considered to be the case. These minerals are easily missed in clay-mineral analysis. They are very soluble in acids, and they frequently occur in calcareous material. They would be destroyed if solution of the carbonates by acids preceded attempts at clay-mineral identification.

\textbf{QUESTIONABLE AND DISCREDITED CLAY MINERALS}

The literature contains a vast number of mineral names applied to materials which were mainly hydrous silicates of aluminum and iron and had clay-like properties. These materials were originally believed to be specific minerals. Many of these names have now been discredited, because the type material was shown to be a mixture of specific minerals.


\textsuperscript{58} Migeon, G., Contribution à l'étude de la définition des sepiolites, \textit{Bull. soc. franç. minéral.}, \textbf{59}, 6–133 (1936).


\textsuperscript{60} De Lapparent, J., Formula and Structure of Attapulgite, \textit{Compt. rend.}, \textbf{202}, 1728–1731 (1936).

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or identical with another species whose name had priority. Most of the
discredited names were suggested prior to the development of X-ray-
diffraction and differential thermal techniques when there were no ade-
quate analytical methods for differentiating the very fine grained
minerals. These early names were suggested on the basis of optical and
chemical data, and recent work has shown that these data are likely to be
inadequate to differentiate and characterize the clay minerals (see
Chap. 11).

Recently Kerr and Hamilton\(^{62}\) published a “Glossary of Clay Mineral
Names” in which are listed most of the names that have been given to
minerals which can be classed as clay minerals, together with their
original description. Kerr and Hamilton also record the work which has
established or discredited these names. No attempt will be made here
to discuss all the suggested clay-mineral species found in the literature.
Consideration will be restricted to those which have received some atten-
tion and whose discredited or questionable status has not yet been
implanted in the thinking of mineralogists, geologists, agronomists, and
others.

*Leverrierite* was first described by Termier\(^{63}\) in 1890 from material in
black carbonaceous shales near St.-Etienne, France. It was named after
the mining engineer Le Verrier. Dana\(^{64}\) in 1892 recognized the identity
of leverrierite with kaolinite, as did Cayeux\(^{64}\) somewhat later (1916).
Ross and Kerr\(^{2}\) studied the original type material in 1931 and concluded
it was kaolinite. De Lapparent\(^{65}\) in 1934 restudied more of the type
material and found a mixture of alternating plates of kaolinite and
muscovite. There seems no doubt, therefore, that the name should be
discarded. However, the name still persists in some very recently
published textbooks on mineralogy—in one instance listed as a member
of the montmorillonite group.

*Beidellite* was first used by Larsen and Wherry\(^{66}\) in 1925 for a clay
mineral occurring in a gouge clay in a mine at Beidell, Colorado. These
authors\(^{67}\) first described this same material as leverrierite in 1917 but in
their later work suggested that it was a distinct species. The original


\(^{64}\) Cayeux, L., Introduction à la étude petrographique des roches sédimentaires,*

\(^{65}\) De Lapparent, J., Constitution et origine de la leverrierite, *Compt. rend.*, 198,
669–671 (1934).

\(^{66}\) Larsen, E. S., and E. T. Wherry, Beidellite—A New Mineral Name, *J. Wash.

\(^{67}\) Larsen, E. S., and E. T. Wherry, Leverrierite from Colorado, *J. Wash. Acad. Sci.*, 7,
208–217 (1917).
material was thought to be a member of the montmorillonite group which differed from the type montmorillonite in having a lower silica-to-
alumina molecular ratio (about 3 instead of 4) and somewhat higher indices of refraction.

Larsen and Wherry did their work before the development of X-ray and differential thermal techniques, and their identification was based on optical, chemical, and dehydration data. Grim and Rowland, on the basis of X-ray-diffraction and thermal data, concluded that the type material was a mixture of clay minerals and showed that the other samples listed as beidellite in the U.S. National Museum collections were also mixtures. For example, a sample from Namiquipa, Mexico, listed as beidellite, which had apparently the appropriate optical properties, proved to be composed of a mixture of halloysite, limonite, and a small amount of illite.

In early clay-mineral studies in the 1930's a large amount of material was identified as beidellite on the basis of analytical data now known to be inadequate. Many of these identifications were based on X-ray-diffraction patterns which did not include low-angle reflections, which are now known to be most critical, and/or on optical measurements, which are now also known to be inadequate. Also such identifications were made before the development of the glycol technique for the detection of small amounts of montmorillonite in mixtures with other clay minerals. Recent studies show that a very large amount of this early so-called beidellite is actually a mixture, in many cases an interlayered mixture of illite and montmorillonite. Many clay-mineral investigators feel, therefore, that the term beidellite should be dropped from clay-mineral terminology, and the author subscribes to their view. Recently, Ross and Hendricks have published a definition of beidellite as a member of the montmorillonite group in which there is substantially no magnesium or iron present and in which replacement of Si$^+$ by Al$^{3+}$ accounts for the cation-exchange capacity. This is substantially in accord with the original definition of Larsen and Wherry. However, because of the past usage of the term, it is believed desirable to drop it entirely in order to avoid confusion.

Monothermite was suggested by Belyankin in 1938 for a material from Chassov-Yar, U.S.S.R., that showed a single high-temperature thermal reaction at about 550°C and had a composition 2RO Al$_2$O$_3$ 3SiO$_2$ 1.5H$_2$O 0.5Ag. The name has not been used outside of the U.S.S.R. and only recently has come to be used in that country by others besides Belyankin. Sedletsky has recently stated that it occurs in the weathered products

of some slates from the Don Basin. It is impossible to determine positively from the published analytical data whether or not the mineral is a valid species and, if so, its proper classification. However, the data strongly suggest that the mineral is a mixture in which illite and kaolinite are important components.

*Gedroizite* was first suggested as a mineral name by Sedletsky[70] in 1939 and later[71] (1941) described in more detail for a material believed to be a specific mineral and characteristic of many alkali soils. The name is after Gedroiz, the famous Russian soil scientist. Sedletsky gives the formula \(6(K·Na)_2O \cdot 5Al_2O_3 \cdot 14SiO_2 \cdot 12H_2O\) for the mineral and states that it belongs to the vermiculite group. He considers it to be a vermiculite in which the magnesium is replaced by potassium and sodium. As in the case of monothermite, material called gedroizite has not been studied outside of the U.S.S.R., and the validity or possible classification of the mineral cannot be determined.

*Pkolverite* was originally used by Guillemin[72] in 1825 for a mineral from Rive-de-Gier in France. The original descriptions are somewhat vague, but the same material was described later in more detail by Des Cloizeaux[73] in 1862, and his descriptions apply to kaolinite. Ross and Kerr[75] in 1931 showed definitely that the mineral is identical with kaolinite, or one of the other kaolin minerals, and point out that the name should be abandoned.

*Morencite* was first described from Morenci, Arizona, by Lindgren and Hillebrand[74] in 1904 as a brownish-yellow hydrous silicate of ferric iron with magnesium, calcium, and aluminum. Gruner[76] has shown the mineral to be structurally the same as nontronite.

*Celadonite* was proposed in 1847 by Glocker[77] for a soft gray-green mineral that was a hydrous silicate of iron, magnesium, and potassium. The name, meaning “sea-green” in French, refers to the color of the mineral. Similar material appears to have been described earlier as *terra verti* by DeLish[78] in 1783 and as *grunerde* by Hofmann[79] in 1788. Hendricks and Ross[80] in 1941 showed that celadonite and glauconite have

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a very similar structure. The original celadonite came from amygdaloidal fillings, and Kerr and Hamilton\(^6\) have suggested that it may be desirable to retain the name celadonite because of its different origin from that of glauconite.

Faratsihite was first described by Lacroix\(^9\) in 1914 from Faratsiho, Madagascar. The original material was pale yellow in color and was described as a hydrous silicate of aluminum and iron. On the basis of X-ray-diffraction data Gruner\(^2\) showed that some specimens of the mineral were identical with nontronite, and Hendricks\(^8\) has shown that other specimens are mixtures of kaolinite and nontronite.

Sedletsky and Yusupova\(^8\) in 1940 described a mineral from Jurassic beds of Tashkent, U.S.S.R., as ablykite. The material was said to resemble halloysite in its dehydration characteristics but to differ from it in its X-ray-diffraction properties. Analytical data are insufficient to determine the validity or possible classification of the material.

Chloropal, meaning "green opal," was first described by Bernhardi and Brandes\(^8\) in 1822 for material from Unghvar, Hungary. Gruner\(^2\) and Ross and Hendricks\(^2\) have shown that chloropal and the montmorillonites rich in iron are the same. The name chloropal has priority over nontronite, but nontronite has come to be the accepted name for the mineral. Further, the name chloropal is unsatisfactory, since it erroneously implies that the mineral is an opal.


CHAPTER 4
Structure of the Clay Minerals

GENERAL STATEMENT

The atomic structures of the common clay minerals have been determined in considerable detail by numerous investigators based on the generalizations of Pauling\(^1\) for the structure of the micas and related layer minerals.

Two structural units are involved in the atomic lattices of most of the clay minerals. One unit consists of two sheets of closely packed oxygens or hydroxyls in which aluminum, iron, or magnesium atoms are embedded in octahedral coordination, so that they are equidistant from six oxygens or hydroxyls (Fig. 1). When aluminum is present, only two-thirds of the possible positions are filled to balance the structure, which is the gibbsite structure and has the formula Al\(_2\)(OH)\(_6\). When magnesium is present, all the positions are filled to balance the structure, which is the brucite structure and has the formula Mg\(_3\)(OH)\(_6\). The normal O-to-O distance is 2.60 Å, and a common OH-to-OH distance is about 3 Å, but in this structural unit the OH-to-OH distance is 2.94 Å, and the space available for the ion in octahedral coordination is about 0.61 Å. The thickness of the unit is 5.05 Å in clay-mineral structures.

The second unit is built of silica tetrahedrons. In each tetrahedron a silicon atom is equidistant from four oxygens, or hydroxyls if needed to balance the structure, arranged in the form of a tetrahedron with a silicon atom at the center. The silica tetrahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form a sheet of composition \( \text{Si}_4\text{O}_6(\text{OH})_4 \) (Fig. 2). The tetrahedrons are arranged so that the tips of all of them point in the same direction, and the bases of all tetrahedrons are in the same plane. The structure can be considered as made of a perforated plane of oxygens which is the plane of the base of the tetrahedral groups; a plane of silicon atoms with each silicon in the cavity at the junction of three oxygen atoms and therefore forming a hexagonal network; and a plane of hydroxyl atoms with each hydroxyl directly above the silicon at the tip of the tetrahedrons. The open hexagonal network can be considered as composed of three strings of oxygen atoms intersecting at angles of 120°. The O-O distance in the silica tetrahedral sheet is 2.55 Å, and the space available for the ion in tetrahedral coordination is about 0.55 Å. The thickness of the unit is 4.93 Å in clay-mineral structures. Each of these units presents a center-to-center height of about 2.1 Å.

Some of the clay minerals are fibrous and are composed of different structural units from those noted above. These minerals resemble the amphiboles in their structural characteristics, and the basic structural unit is composed of silica tetrahedrons arranged in a double chain of composition \( \text{Si}_4\text{O}_{11} \), as shown in Fig. 3. The structure is similar to that of the sheet of silica tetrahedrons in the layer minerals except that it is continuous in only one direction. In the other direction it is restricted to a width of about 11.5 Å.

The chains are bound together by atoms of aluminum and/or magnesium placed so that each such atom is surrounded by six “active”
oxygen atoms. The active oxygens are those with only one link to silicon and hence are those at the edges of the chains and at the tips of the tetrahedrons.

**Fig. 3.** Diagrammatic sketch of double chains of silica tetrahedrons, as in the amphibole structural type of clay minerals; (a) in perspective, (b) projected on the plane of the base of the tetrahedrons.

**ALLOPHANE MINERALS**

By definition the allophane clay minerals are amorphous to X-ray diffraction. It seems probable that allophanes are random arrangements of silicon in tetrahedral coordination and metallic ions in octahedral coordination without any symmetry. Such a random arrangement of silica tetrahedrons, alumina octahedrons, and occasional other units such as phosphate tetrahedrons appears more likely than a completely unorganized assembly.

Very little careful study has been made of allophanes, and their variation in composition is unknown. Their study is particularly difficult.

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because of the problem of separating them from intermixed crystalline material.

KAOLINITE MINERALS

The structure of kaolinite was first suggested in general outlines by Pauling. It was worked out in some detail by Gruner and later revised by Brindley and his colleagues. The structure is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer (Fig. 4). All the tips of the silica tetrahedrons point in the same direction and toward the center of the unit made of the silica and octahedral sheets. The dimensions of the sheets of tetrahedral units and of the octahedral units are closely similar in their $a$ and $b$ dimensions, and consequently composite octahedral-tetrahedral layers are readily formed. Only minor changes in interatomic distances are necessary, and there would seem to be little

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tendency for the unit to bend in the stacking arrangement of kaolinite, although large crystals would be unlikely.

In the layer common to the octahedral and tetrahedral groups, two-thirds of the atoms are shared by the silicon and aluminum, and then they become O instead of OH. Only two-thirds of the possible positions for aluminum in the octahedral sheet are filled, and there are three possible plans of regular population of the octahedral layer with aluminums. The aluminum atoms are considered to be so placed that two aluminums are separated by an OH above and below, thus making a hexagonal distribution in a single plane in the center of the octahedral sheet. The OH groups are placed so that each OH is directly below the perforation of the hexagonal net of oxygens in the tetrahedral sheet.

The charge distribution in the layers is as follows:

$$
\begin{align*}
6O^- & \quad 12- \\
4Si^{4+} & \quad 16+ \\
4O^- & \quad 2(OH)^- \quad 10- \quad \text{(Layer common to tetrahedral and octahedral sheets)} \\
4Al^{3+} & \quad 12+ \\
6(OH)^- & \quad 6- 
\end{align*}
$$

The charges within the structural unit are balanced. The structural formula is \((\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{10}\) and the theoretical composition expressed in oxides is \(\text{SiO}_2\) 46.54 per cent; \(\text{Al}_2\text{O}_3\) 39.50 per cent; \(\text{H}_2\text{O}\) 13.96 per cent. The analyses of many samples of kaolinite minerals have shown that there is very little substitution within the lattice. In a few instances, the evidence suggests a very small amount of substitution of iron and/or titanium for aluminum in the relatively poorly crystalline variety (see page 49).

The minerals of the kaolinite group consist of sheet units of the type just described continuous in the \(a\) and \(b\) directions and stacked one above the other in the \(c\) direction. The variation between members of this group consists in the way in which the unit layers are stacked above each other and possibly in the position of the aluminum atoms in the possible positions open to them in the octahedral layer.

In the case of kaolinite itself Brindley has investigated the stacking of the unit layers, and the following statements are taken largely from his work. The mineral is triclinic; \(a = 5.16\ \text{Å}; b = 8.94\ \text{Å}; c = 7.38\ \text{Å}; \alpha = 91.8^\circ; \beta = 104.5^\circ; \gamma = 90^\circ; \) and the space group is \(C_1^{-}C_2\). Successive unit layers are so arranged that oxygen atoms and OH groups of adjacent layers approach one another in pairs. This disposition can be obtained in a variety of ways, by placing one layer directly above another.
so that the \( c \) axis is perpendicular to the \( ab \) plane or by the displacement of one layer relative to its neighbor along either \( a \) or \( b \) so that the displacement is \( na_o/6 \) or \( mb_o/6 \), where \( n \) and \( m \) are integral and \( a_o \) and \( b_o \) are unit-cell dimensions. The displacement for kaolinite in accordance with \( \alpha \) and \( \beta \) angles is \( m = 0 \) and \( n = 2 \). The relative position of basal O atoms and uppermost OH groups of two adjacent kaolinite layers is shown in Fig. 5. The stacking of the units along the \( a \) and \( b \) axes is shown in Fig. 6.

Because of the superposition of O and OH planes in adjacent units, the units are held together fairly tightly by hydrogen bonding between the layers. The plane between the unit layer is a cleavage plane. However, in kaolinite the cleavage is not so pronounced as it is in other clay minerals where O planes are adjacent at unit boundaries so that there is no hydrogen bonding.

Numerous investigators\(^8\)–\(^{10}\) of clays have reported the finding of a kaolinite mineral of lower crystallinity than that of the well-crystallized material just noted. Brindley and his colleagues\(^6\),\(^8\) have investigated in detail some examples of rather poorly crystallized kaolinite and have shown that their examples from English fire clays contain fewer reflections than normal kaolinite. According to them the reflections can be indexed as monoclinic or pseudo-monoclinic, with a unit cell of the same dimensions as kaolinite but with \( \alpha = 90^\circ \). Also, they state that the structure is highly disordered along the \( b \) axis with the unit layers randomly displaced by multiples of \( b_o/3 \). The arrangement along the \( a \) axis is like that of kaolinite. They suggest that there is some randomness in the

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distribution of aluminum atoms among octahedral positions. The first-order spacings are slightly higher (7.15 to 7.20 Å) for the poorly crystalline than for the well-crystallized mineral, suggesting some occasional interlayer water between the kaolin units. Dehydration data tend to confirm the presence of such water (see page 212). X-ray-diffraction characteristics of the poorly crystallized kaolinite as contrasted to well-crystallized kaolinite are given in Fig. 7. Brindley\textsuperscript{11} suggested mellorite as a name for such poorly crystallized kaolinite, and Roberts\textsuperscript{12} has suggested levisite for similar material. As there are probably all gradations from well-crystallized kaolinite to that of complete randomness in the $b$ direction and in the population of aluminum positions, it appears doubtful that a specific name should be applied.

Available data suggest that there may be some slight substitution of titanium or iron for aluminum in the poorly crystallized kaolinite. Such substitutions appear to be restricted to the poorly crystallized kaolinite. It is not necessarily established that any of the titanium is in the structure, as anatase is an almost universal minor component of kaolins.


Dickite\textsuperscript{13} and nacrite\textsuperscript{14} have structures somewhat similar to that of kaolinite and are usually listed as clay minerals, although they are rarely found in clay materials. They are made up of unit layers of an alumina octahedral sheet and a silica tetrahedral sheet like that in kaolinite and differ only in the stacking of the layers. In dickite,\textsuperscript{13,14,16} the unit cell is made up of two unit layers. The exact stacking of successive layers is not well established. The parameters of the mineral are best accounted for by shifts along the \(a\) axis of \(n = 1\) in \(na_0/6\) and along the \(b\) axis of \(m = 3\) in \(mb_0/6\), with the shift being positive and negative in successive layers. A shift of \(m = 1\) is also a possibility but seems less likely. However, shifts of \(m = 1\) or 3 are not completely in accord with the diffraction data. According to Gruner,\textsuperscript{13} the mineral is monoclinic \(a = 5.15\) Å, \(b = 8.96\) Å, \(c = 14.45\) Å, \(\beta = 96°50'\), and the space group is \(C_4v\)-Cc.

In nacrite, the unit cell is made up of six unit layers, each having the


Structure of the Clay Minerals

arrangement described for kaolinite. According to Hendricks\textsuperscript{17} the unit dimensions are $a = 5.15$ Å, $b = 8.96$ Å, $c = 43$ Å, and $\beta = 90^\circ 20'$, so that the structure approaches rhombohedral symmetry. In nacrite, successive layers are stacked one above the other so that the $c$ axis is about perpendicular to the $ab$ plane; i.e., $n$ and $m$ are equal to zero. The space group is $C_1^{-1}$-$Cc$, according to Hendricks.\textsuperscript{17}

Occasionally kaolinite types of clay minerals are found which appear to be monomineral species on the basis of X-ray diffraction but have a considerably higher silica-to-alumina molecular ratio, which often approaches $1.5$. Such silica-rich kaolinites are called anauxite. The structure of anauxite has been the subject of considerable controversy, but the recent suggestion of Hendricks\textsuperscript{18} seems most plausible. According to Hendricks, anauxite consists of kaolinite unit layers between which units composed of double silica tetrahedral sheets are interlayered randomly. In the double silica units, the tetrahedrons of each sheet point toward the center, and a common O forms the tip of the tetrahedrons in both sheets (Fig. 8). The charge distribution is as follows:

\begin{align*}
60^- & \quad 12- \\
4Si^{4+} & \quad 16+ \\
4O^- & \quad 8- \quad \text{(Sheet common to both tetrahedral sheets)} \\
4Si^{4+} & \quad 16+ \\
60^- & \quad 12- \\
\end{align*}

\textsuperscript{17} Hendricks, S. B., Crystal Structure of Nacrite and the Polymorphism of the Kaolin Minerals, Z. Krist., 100, 509-518 (1938).

\textsuperscript{18} Hendricks, S. B., Lattice Structure of Clay Minerals and Some Properties of Clays, J. Geol., 60, 276-290 (1942).
The dimensions and characteristics of the double silica sheet are about those of kaolinite, and hence an interlamination with kaolinite sheets is possible without changing materially the diffraction characteristics. Also the optical properties of the two units would not be very different. The silica-to-alumina molecular ratio of anauxites is known to vary, and this may be accounted for by variations in the relative abundance of the interlayering of the double silica sheets.

HALLOYSITE MINERALS

As indicated earlier, there are two forms of halloysite (see page 31), one with the composition \((\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{10}\) and the other with the composition \((\text{OH})_4\text{Si}_4\text{Al}_4\text{O}_{10}\cdot4\text{H}_2\text{O}\). The latter form dehydrates to the former irreversibly at relatively low temperatures. Various structures for the halloysite minerals have been suggested by Mehmel,\textsuperscript{19} Edelman and Favejee,\textsuperscript{20} Stout,\textsuperscript{21} and Hendricks.\textsuperscript{16}

Hendricks has shown that the earlier suggested structures are not in accord with the observed intensities of the basal reflections or with the very easy dehydration of the mineral. The basal spacing of the dehydrated form is about 7.2 Å or about the thickness of the kaolinite layer, and the basal spacing of the hydrated form is about 10.1 Å. The difference, 2.9 Å, is about the thickness of a single molecular sheet of water molecules. Hendricks suggested therefore that the highly hydrated form consists of kaolinite layers separated from each other by single molecular layers of water. Later Hendricks and Jefferson\textsuperscript{22} suggested that the water molecule in this layer had a definite configuration (Fig. 9). Diffraction data for halloysite are not suited for detailed structural study, but the intensities of the basal reflections are in accord with Hendricks's suggested structure. The transition to the dehydrated form is due to the loss of the interlayer of water molecules.

In the halloysite minerals, the successive kaolinite layers are displaced randomly in both the \(a\) and \(b\) directions. According to Brindley\textsuperscript{9} the probable displacements are simple fractions of the cell dimensions, such as \(ma/6\) and \(nb/6\). He states that “the experimental results require

\textsuperscript{19} Mehmel, M., Ueber die Struktur von Halloysit und Metahalloysit, Z. Krist., 90, 35–43 (1935).
only that the displacements along the $a$ and $b$ axes shall be random with respect to each other."

Brindley and his colleagues\textsuperscript{23-25} have studied the transition of the hydrated to the dehydrated form of the mineral in great detail. According to them only partial dehydration takes place at low temperatures (60° to 75°C), and temperatures of the order of 400°C are necessary for complete removal of the interlayer water and the development of the 7.2-A spacing. At temperatures of 60° to 75°C or at a lower temperature for longer time, a partially dehydrated form develops which tends to

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persist and has, therefore, considerable stability. The partially hydrated form has a basal spacing of 7.36 to 7.9 Å, corresponding to a hydration of about 0.5 to 1.5H₂O. The partially hydrated form consists of a statistical distribution of hydrated layers and nonhydrated layers; the maximum value would correspond to a little more than 1 water layer for every 4 kaolinite layers. Brindley states that examples with hydrations ranging between 1.5H₂O and about 3H₂O have not been observed.

Bates et al. have shown the tubular nature (see Chap. 6) of the halloysite minerals from electron micrographs and have suggested that the 4H₂O form consists of tubes made up of overlapping, curved sheets of the kaolinite type with the c axis for any point on the tube nearly perpendicular to a plane tangent to the tube at that point. The axis of the tube may be parallel to either the a or b axis, or possibly to any intermediate crystallographic direction in the plane of the sheets. In the dehydration to the 2H₂O form the tubes frequently collapse, split, or unroll.

The difference in effective size of the O associated with the silicon and of the OH associated with the aluminum has been stated previously (pages 43, 44). Bates has shown that the a dimension in the O plane is 5.14 Å and in the OH plane is 5.06 Å, and that the b dimension in the O plane is 8.93 Å and in the OH plane is 8.62 Å. According to him this difference in the dimensions of the upper and lower plane of the silica-alumina layer will cause a curvature of the layers with a radius in accordance with the dimensions of the observed tubes (see Fig. 10). The curvature can develop in hydrated halloysite because of the irregular stacking of the layers and the interlayer water molecules, which cause a weak bond between successive layers. It does not develop in kaolinite because the regular stacking and close spacing of layers causes a relatively strong bond between successive layers. The electron micrographs of halloysite satisfactorily document Bates's morphology, but no detailed reconciliation of diffraction data with the curved structure has yet been accomplished.

**MONTMORILLONITE MINERALS**

The montmorillonite minerals occur only in extremely small particles so that single-crystal X-ray-diffraction data cannot be obtained. Structural concepts, therefore, must be deduced from powder data and inferences from better known structures, with the result that there is considerable uncertainty regarding details of their structure. Currently the generally accepted structure for the montmorillonite minerals follows the original suggestion made in 1933 by Hofmann, Endell, and Wilm modified by later suggestions of Maegdefrau and Hofmann, Marshall, and Hendricks. According to this concept, montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedrons point in the same direction and toward the center of the unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layer become O instead of OH. The layers are continuous in the a and b directions and are stacked one above the other in the c direction.

In the stacking of the silica-alumina-silica units, O layers of each unit are adjacent to O layers of the neighboring units with the consequence...
that there is a very weak bond and an excellent cleavage between them. The outstanding feature of the montmorillonite structure is that water and other polar molecules, such as certain organic molecules (see Chaps. 8 and 10), can enter between the unit layers, causing the lattice to expand in the c direction. The c-axis dimension of montmorillonite is, therefore, not fixed but varies from about 9.6 Å, when no polar molecules are between the unit layers, to substantially complete separation of the
individual layers in some cases. Figure 11 shows a diagrammatic sketch of this structure of montmorillonite.

Exchangeable cations occur between the silicate layers, and the c-axis spacing of completely dehydrated montmorillonite depends somewhat on the size of the interlayer cation, being larger the larger the cation. In the case of adsorption of polar organic molecules between the silicate layers, the c-axis dimension also varies with the size and geometry of the organic molecule. The thickness of the water layers between the silicate units depends on the nature of the exchangeable cation at a given water-vapor pressure (see Chap. 7). Under ordinary conditions a montmorillonite with Na⁺ as the exchange ion frequently has one molecular water layer and a c-axis spacing of about 12.5 Å; with Ca²⁺ there are frequently two molecular water layers and a c-axis spacing of about 15.5 Å. The expansion properties are reversible. However, when the structure is completely collapsed by removal of all of the interlayer polar molecules, reexpansion may proceed with difficulty.

Experiments by Mering and others with montmorillonite in the presence of large quantities of water suggest that with certain adsorbed cations, e.g., Na⁺, the unit layers completely separate but that with other cations, e.g., Ca²⁺ and H⁺, the separation is not complete.

It appears from the work of Bradley, Grim, and Clark that the thickness of the water layers between successive silicate layers is an integral number of molecules. That is, the water layer is one, two, three, or four molecular water layers thick. A natural montmorillonite may have a regular ordering of a single thickness of water layers, or it may be a random mixture of different "hydrates." Roth has shown that important physical characteristics of clays composed of montmorillonite are related to the regularity or randomness of the interlayer water layers.

Mering has demonstrated that the diffraction effects of Ca montmorillonite prepared at low relative humidities (50% ±) can be explained by a mixing of hydrates with thicknesses of 14 and 15 Å. Similar clays prepared at 90 per cent relative humidity show only a 15 Å reflection, 15 Å being the thickness of the double-layer hydrate of Bradley et al.

Hofmann, Endell, and Wilm described the montmorillonite structure as generally similar to that of pyrophyllite except for the expanding-

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lattice characteristic. They postulated a stacking of layers to give an orthorhombic unit.

Later Maegdefrau and Hofmann \(^{28}\) showed that as a general thing the unit layers are stacked without any fixed periodical arrangement in the \(a\) and \(b\) directions. Occasional montmorillonites do seem to have some regular periodicity in the horizontal crystallographic directions.

The theoretical charge distribution, without considering lattice substitutions within the layer, is as follows:

\[
\begin{align*}
&6\text{O}^{--} & 12- \\
&4\text{Si}^{++} & 16+ \\
&4\text{O}^{--}2(\text{OH})^- & 10- (\text{Layer common to tetrahedral and octahedral sheets}) \\
&4\text{Al}^{3+} & 12+ \\
&4\text{O}^{--}2(\text{OH})^- & 10- (\text{Layer common to tetrahedral and octahedral sheets}) \\
&4\text{Si}^{++} & 16+ \\
&6\text{O}^{--} & 12- \\
\end{align*}
\]

Interlayer layer of \(\text{H}_2\text{O}\) or other polar molecules

The theoretical formula without considering lattice substitutions is \((\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}\cdot n\text{H}_2\text{O}\) (interlayer), and the theoretical composition without the interlayer material is \(\text{SiO}_2 66.7\) per cent, \(\text{Al}_2\text{O}_3 28.3\) per cent, \(\text{H}_2\text{O} 5\) per cent.

As first emphasized by Marshall \(^{29}\) and Hendricks, \(^{19}\) montmorillonite always differs from the above theoretical formula because of substitution within the lattice of aluminum and possibly phosphorus for silicon in tetrahedral coordination and/or magnesium, iron, zinc, nickel, lithium, etc., for aluminum in the octahedral sheet. In the tetrahedral sheet the substitution of \(\text{Al}^{3+}\) for \(\text{Si}^{4+}\) appears to be limited to less than about 15 per cent. In the formula noted above, only two-thirds of the possible positions in the octahedral sheet are filled. The substitution of \(\text{Mg}^{2+}\) for \(\text{Al}^{3+}\) can be one for one, or three \(\text{Mg}^{2+}\) for two \(\text{Al}^{3+}\), with all possible octahedral positions being filled in the latter case. Substitutions within the octahedral sheet may vary from few to complete. Total replacement of 2\(\text{Al}^{3+}\) by 3\(\text{Mg}^{2+}\) yields the mineral saponite; replacement of aluminum by iron yields nontronite; by chromium, volkonskoite; by zinc, sauconite.

The \(\text{Mg}^{2+}\) ion of diameter 0.65 \(\text{Å}\) and the \(\text{Fe}^{3+}\) ion of diameter 0.67 \(\text{Å}\) are somewhat large to fit into the lattice, and as a consequence montmorillonite minerals with large substitutions of these ions are subject to a directional strain which results in elongate lath- or needle-shaped units (see Chap. 6).

Layer minerals of this general type in which all the possible octahedral positions are filled are called octahyllites, or trioctahedral, and those in
which only two-thirds of the possible positions are filled are called heptaphyllites, or dioctahedral. Numerous analyses of montmorillonite have shown that the substitutions within the octahedral sheet are such that the mineral is either almost exactly trioctahedral or dioctahedral and not intermediate. Ross and Hendricks34 have computed the structural fit for a large number of chemical analyses of montmorillonite. Unfortunately there are no accompanying X-ray data, and some of the samples may be mixtures of clay minerals. However, the number of analyses is so great that their conclusion seems well established, namely, that the number of ions in six coordination, \( i.e., \) in the octahedral positions, lie in two distinct ranges, 4.00 to 4.44 and 5.76 to 6.00. Further, it appears that, if the mineral is dioctahedral, there may be considerable variation in the exact position of the aluminums or other atoms in the possible octahedral positions.

A further way in which montmorillonite always differs from the theoretical formula is that the lattice is always unbalanced by the substitutions noted above, \( i.e., \) Mg\(^{++}\) for Al\(^{++}\), Al\(^{++}\) for Si\(^{++}\), etc. The unbalancing may result from substitution of ions of different valence in the tetrahedral or octahedral sheet or both. Unbalancing in one sheet may be compensated for in part, but only in part, by substitution in the other sheets of the unit layer. Thus, the substitutions of Al\(^{++}\) for Si\(^{++}\) may in part be compensated by filling slightly more than two-thirds of the octahedral positions. Compensation also may be by substitution of OH for \( \text{O} \) in the octahedral layer. It is significant that the substitutions in the montmorillonite lattice, with the internal compensating substitutions, always result in about the same net charge on the lattice. Many analyses have shown this to be about 0.66— per unit cell. This net-charge deficiency is balanced by exchangeable cations adsorbed between the unit layers and around their edges (see Chap. 7, Ion Exchange). This charge deficiency corresponds to about two-thirds unit per unit cell. It would require the substitution of one Mg\(^{++}\) for every sixth Al\(^{++}\), for example, or about one out of every six Si\(^{++}\) by Al\(^{++}\).

Montmorillonite has been synthesized from pure hydrous mixtures of magnesia and silica, in which case the charge deficiency cannot be due to lattice substitutions. It must be the result of vacancies in the lattice, and such vacancies probably also occur in natural minerals.

Ross and Hendricks34 have computed the structural formula from the chemical composition of many montmorillonites, and these have shown something of the range of substitutions within the lattice and the partial compensating substitutions within the structure. The nomenclature of the members of the montmorillonite group depends on the substitution

within the lattice, and Ross and Hendricks\textsuperscript{34} have assigned the names in Table 2 to montmorillonites with the compositions indicated. The names conform closely to general usage with the exception of beidellite, which many investigators consider to be discredited. Arrows are placed under the group having the charge deficiency, which requires the addition of a cation external to the silicate layer to balance the structure. In each case the balancing external cation has been indicated as Na\textsuperscript{+} for convenience. The water or other polar molecules between the silicate layers are omitted from the formulas.

MacEwan\textsuperscript{35} has considered the relation of the $a$ and $b$ dimensions of the montmorillonite unit to variations in its chemical composition. He has pointed out the conclusion that these axial lengths would increase in the order montmorillonite $\rightarrow$ nontronite $\rightarrow$ saponite. He has offered the following formula for computing $b_0$, from which $a_0$, of course, can also be computed:

$$b_0 = 8.91 + 0.06r + 0.034s + 0.048t$$

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where \( r \) = number of Al ions in tetrahedral coordination
\( s \) = number of Mg ions in octahedral coordination
\( t \) = number of Fe ions in octahedral coordination (per unit cell, in each case)

The formula is based on observed values for muscovite, talc, and nontronite with the assumption that the effects of the above substitutions are proportional and additive. MacEwan states that the formula gives reasonably good agreement with the observed values. It appears from MacEwan's data that changes in \( b \) are much greater for variations in the population of octahedral positions than for tetrahedral positions.

The ratio of silicon to aluminum in the montmorillonite lattice apparently can vary from about 1:1 to 1:3. In the former case there is a maximum filling of octahedral positions by \( \text{Al}^{3+} \) (about 4.44 per unit) with added replacement of \( \text{Si}^{4+} \) by \( \text{Al}^{3+} \). The replacement of \( \text{Si}^{4+} \) by \( \text{Al}^{3+} \) causes the unbalanced charge and also compensates for the excess charge in the octahedral layer. For the highest ratio all tetrahedral positions are populated by \( \text{Si}^{4+} \), and the mineral is dioctahedral with the maximum replacement of \( \text{Al}^{3+} \) by a divalent ion to cause the charge deficiency.

Iron can apparently proxy for aluminum in all positions in the octahedral layer and not at all in the tetrahedral layer. Iron-rich varieties, i.e., nontronite, on the basis of currently available analyses, show little replacement of \( \text{Fe}^{3+} \) by \( \text{Mg}^{2+} \), and the charge deficiency seems to result mainly from substitutions of \( \text{Al}^{3+} \) for \( \text{Si}^{4+} \). In the trioctahedral montmorillonites the charge deficiency results mainly from substitutions of \( \text{Al}^{3+} \) for \( \text{Si}^{4+} \). It would seem from data of Ross and Hendricks that up to about one atom of aluminum or iron per unit cell may be present in the octahedral layer of trioctahedral montmorillonites. The excess charge in the octahedral layer is balanced by deficiencies in the tetrahedral layer due to larger replacements of \( \text{Al}^{3+} \) for \( \text{Si}^{4+} \).

The opinion has frequently been expressed that the structure of Hofmann et al., Marshall, and Hendricks does not adequately account for all the properties of montmorillonite, notably its ion-exchange capacity. Edelman and Favejee have suggested an alternative structure that, it is claimed, explains these properties more adequately. This structure differs from that of Hofmann et al. in that every other silica tetrahedron in both silica sheets is inverted, so that half of them point in the opposite direction. Those that point away from the silicate sheet would have the tip O replaced by OH. In this structure the silicon atoms are not all in a single plane in the silica tetrahedral sheets, and there must be some substitutions of OH for O in the octahedral layers to balance the structure (Figs. 12 and 13). The charge distribution is as follows:
Clay Mineralogy

\[
\begin{align*}
2(OH)^- & \quad 2- \\
2Si^{4+} & \quad 8+ \\
6O^{--} & \quad 12- \\
2Si^{4+} & \quad 8+ \\
2O^{--}4(OH)^- & \quad 8- \\
4Al^{3+} & \quad 12+ \\
2O^{--}4(OH)^- & \quad 8- \\
2Si^{4+} & \quad 8+ \\
6O^{--} & \quad 12- \\
2Si^{4+} & \quad 8+ \\
2(OH)^- & \quad 2-
\end{align*}
\]

Interlayer H₂O or other polar groups.

The structural formula is \((OH)₂Si₄Al₄O₁₆·H₂O\) (interlayer). In this structure, no substitution is necessary within the lattice to account for the exchange capacity. The lattice may be completely balanced. The exchange reaction is believed due primarily to replacement of the H of the OH of the projecting tetrahedrons. As originally postulated, there are far more available OH groups than required by the exchange capacity. Edelman and Favejee\(^3\) postulated that only some of them were available for exchange. Evidence from X-ray-diffraction data based on Fourier syntheses,\(^3\) chemical data indicating lattice substitution, and careful dehydration studies, all are strongly against the original Edelman and Favejee\(^3\) structure. Edelman\(^7\) has recently suggested a modified structure in which only about 20 per cent of the tetrahedrons are inverted, which would satisfy the discrepancy with the exchange capacity. It is questionable whether or not X-ray data would be adequate to provide evidence for or against the modified structure. However, the modified structure still does not seem to fit with chemical data indicating lattice replacements and with the geometry of the adsorption of organic molecules. Studies of the methylation of certain organics during their adsorption by montmorillonite have led some workers (Berger,\(^3\) Duell\(^2\)) to favor this structure, since more OH groups seem to be called for on the surface of the montmorillonite silicate unit than are provided for by the structure of Hofmann \textit{et al.}\(^2\). Further studies are necessary before the possible structural implications of such organic-montmorillonite reactions become clear.


McConnell\textsuperscript{40} has recently suggested a revision in the structure of Hofmann \textit{et al.}\textsuperscript{37} whereby some of the silica tetrahedrons are replaced by (OH)\textsubscript{4} tetrahedrons. This is essentially a hole in the silicon positions.

\textsuperscript{40} McConnell, D., The Crystal Chemistry of Montmorillonite, \textit{Am. Mineral.}, 35 166-172 (1950).
Clay Mineralogy

Fig. 13. Diagrammatic sketch of the structure of montmorillonite suggested by Edelman and Favejee.\textsuperscript{20}

with adjacent balancing by OH for O. This would provide the needed quantity of surface OH required by certain organic-adsorption characteristics and, according to McConnell, is in accord with the dehydration of the mineral. Further investigations are necessary before the feasibility of McConnell’s suggestion can be evaluated.
ILLITE MINERALS

The structure of the micas, the variations in their composition, and their polymorphic variations have been worked out in considerable detail by Pauling,1 Mauguin,41,42 Jackson and West,43,44 Winchell,45 and Hendricks and Jefferson.46 The basic structural unit is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedrons in each silica sheet point toward the center of the unit and are combined with the octahedral sheet in a single layer with suitable replacement of OH by O. The unit is the same as that for montmorillonite except that some of the silicons are always replaced by aluminums and the resultant charge deficiency is balanced by potassium ions. In many of the well-crystallized micas one-fourth of the silicons are replaced by aluminums. The unit layers extend indefinitely in the a and b directions and are stacked in the c direction. The potassium ions occur between unit layers where they just fit into perforations in the surface O layers. Adjacent layers are stacked in such a way that the potassium ion is equidistant from 12 oxygens, 6 of each layer (Fig. 14).

Muscovite is dioctahedral; i.e., only two-thirds of the possible octahedral positions are filled, and the octahedral sheet is populated only by aluminums. The structural formula is (OH)4K2(Si6'Al2)Al4O20, and the theoretical composition is K2O 11.8 per cent, SiO2 45.2 per cent, Al2O3 38.5 per cent, H2O 4.5 per cent. The mineral is monoclinic, and the unit cell is composed of two silica-alumina-silica layers; the dimensions are a = 5.2 A, b = 9.0 A, c = 20.0 A, β = 95°30' with space group C2/v-C2/c.

The biotite micas are trioctahedral with the octahedral positions populated mostly by Mg++, Fe++, and/or FeH++. Examples are biotite, (OH)4K2(Si6Al2)(Mg·Fe)6O20, with the relative abundance of the iron and magnesium varying widely, and phlogopite, (OH)4K2(Si6Al2)Mg4O20. Hendricks46 has shown the existence of at least six polymorphic variations of biotite due to variations in the number of silica-alumina-silica units per unit cell and in the manner of stacking of the unit cells. Unit cells

composed of 1, 2, 3, 6, and 24 silica-alumina-silica units are known, with stackings yielding monoclinic, rhombohedral, or triclinic forms.

It is important that, in the large well-crystallized micas with no imperfections in the regularity of stacking, there seem to be no isomorphous gradations from dioctahedral to trioctahedral types.

The charge distribution within the layers of the well-crystallized micas is as follows:

\[
\begin{align*}
K^+ & \quad 1^+ \\
6O^- & \quad 12^- \\
3Si^{++}1Al^{+++} & \quad 15^+ \\
4O^-2(OH)^- & \quad 10^- 
\end{align*}
\]
Structure of the Clay Minerals

4Al³⁺ (Dioctahedral) or
6R (Trioctahedral, R = Mg++, Fe⁺⁺, Fe³⁺, Li⁺, Ti⁺⁺)  12⁺
4O²⁻2(OH)⁻  10⁻
3Si⁴⁺1Al³⁺  15⁺
6O⁻⁻  12⁻
K⁺  1⁺

The illite clay minerals differ from the well-crystallized micas in several possible ways, all of which may be exhibited by a given sample; these are as follows: There is less substitution of Al³⁺ for Si⁴⁺; in the well-crystallized micas one-fourth of the Si⁴⁺ are replaced, whereas in the illites frequently only about one-sixth are replaced. As a consequence of this smaller substitution, the silica-to-alumina molecular ratio of the illites is higher than that of the well-crystallized micas, and the net-unbalanced-charge deficiency is reduced from 2 per unit cell to about 1.3 per unit cell. The potassium ions between the unit layers may be partially replaced by other cations, possibly Ca⁺⁺, Mg⁺⁺, H⁺. There is some randomness in the stacking of the layers in the c direction, and the size of the illite particles occurring naturally is very small, of the order of 1 to 2 microns or less.

Because of the foregoing variations, illite clay minerals show differences in their characteristics from those of the well-crystallized micas. The 10-A diffraction line of the micas is shown by illite usually as a characteristic diffraction effect, but it is often modified into a band which tends to tail off slightly toward the low-angle region as a consequence of the small particle size, variation in the interlayer cation, and occasional slight interlayer hydration. The occasional layers may simply be the nontypical features associated with any particle surface. Also because of these defects, hkl reflections are weak, or absent in the case of those normally weak in the well-crystallized micas. Most of the illite clay minerals so far described are dioctahedral, but some are known that are trioctahedral with unit cells composed of one, two, or three silica-alumina-silica layers. Careful X-ray-diffraction data (see page 93) will permit the identification of the polymorphic form of illite if the sample is reasonably pure and if the crystallinity is not too poor. In some cases it is not possible with currently available analytical techniques to identify the polymorphic forms of the illites.

Dioctahedral illites are known in which the aluminum is replaced by some iron and magnesium. Whether or not there is any isomorphous relationship between the dioctahedral and trioctahedral illites is not definitely known, but none has been established thus far.

Glauconite is a dioctahedral illite with considerable replacement of $\text{Al}^{3+}$ by $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, and $\text{Mg}^{2+}$, frequently with even less than two-thirds of the possible positions filled. There is consequently a charge deficiency in the octahedral sheet as well as in the tetrahedral sheets, and the interlayer cations seem to balance both these charges. Often $\text{Ca}^{2+}$ and $\text{Na}^+$ as well as $\text{K}^+$ are the interlayer cations. Hendricks and Ross give the following formula as characteristic of many glauconites: $(\text{OH})_{4-}(\text{K},\text{Ca},\text{Na})_{1.68} (\text{Si}_{7.30} \text{Al}_{0.70}) (\text{Al}_{2.34} \text{Fe}_{3.44}^{3+} \text{Fe}_{0.18}^{2+} \text{Mg}_{0.80}) \text{O}_{20}$. A further characteristic of glauconite is that the unit cell is composed of a single silicate layer rather than the double layer of most other dioctahedral micas.

Grim, Bradley, and Brown have presented the following formula relating the $b_0$ dimension to the chemical composition of the micas. The formula is based on the measured $b_0$ dimensions of pyrophyllite, muscovite, and talc with the assumptions that the effect of lattice substitutions is additive and linear and that the increase per ion is proportional to the ionic diameter. Brown states that better correlations between observed and calculated results are obtained if all the iron is assumed to have the radius of the ferrous ion and if the lithium ion is treated as if it had the same effect as the aluminum ion. The Brown formula is

$$b_0 = 8.91 + 0.12\text{Al} + 0.067\text{Mg} + 0.084\text{Fe} + 0.022\text{Ti}$$

where $\text{Al} = \text{number of } \text{Al}^{3+} \text{ in tetrahedral coordination per half cell}$

$\text{Mg} = \text{number of } \text{Mg}^{2+} \text{ in octahedral coordination per half cell}$

$\text{Fe} = \text{number of iron ions in octahedral coordination per half cell}$

$\text{Ti} = \text{number of } \text{Ti}^{4+} \text{ ions in octahedral coordination per half cell}$

The structure of illite differs from that of montmorillonite in several important ways as follows: The charge deficiency due to substitutions per unit cell layer is about 1.30 to 1.50 for illite and 0.65 for montmorillonite. The seat of this charge deficiency in illite is largely in the silica sheet and therefore close to the surface of the unit layer, whereas in montmorillonite it is frequently, perhaps chiefly, in the octahedral sheet at the center of the unit layer. Also in the case of illite the balancing cation between the unit layers is chiefly or entirely potassium. Because of these differences the illite structural unit layers are relatively fixed in position, so that polar ions cannot enter between them and cause expansion. Also the interlayer balancing cations are not exchangeable (see Chap. 7).

It is conceivable that all gradations can exist between illite and well-
crystallized muscovites and biotites on the one hand and montmorillonite on the other hand. Data are not yet available to settle this point positively, but it is noteworthy that the illites so far studied in detail have shown similar and distinctive attributes rather than complete gradational variations with muscovite or biotite. With regard to gradations with montmorillonite the data are less clear. Many clays are known which seem to be gradational between illite and montmorillonite but which are actually composed of interlayered mixtures of true illite and montmorillonite (see mixed-layered minerals, pages 79, 80). It is possible, even likely, that clay minerals are to be found with a stacking of layers differing slightly from illite in having less unbalanced charge and with substantial replacement of K⁺ by another cation like Na⁺. It would be expected that in such specimens some water could penetrate between the unit layers with some accompanying expansion. In such specimens there might well be some variation in the unbalancing between different layers, and the nature of the balancing cations might vary from layer to layer as well as between the same layer. In such material, expansion between all layers would not be the same and might even vary within a single interface between adjacent units. The classification of such material would be difficult, and the separation of illite and montmorillonite must frequently be purely arbitrary with, in general, definitely expanding material being called montmorillonite and nonexpanding being called illite.

**CHLORITE MINERALS**

The structure of chlorite was first suggested by Pauling. Later McMurchy examined the mineral in great detail, verifying Pauling’s suggested structure and providing additional information on its symmetry and dimensions. Recently Brindley and Robinson have further studied the mineral and considerably amplified knowledge of the general chlorite structure and the variations of different members.

All the true chlorites have the same general structural framework. The structure consists of alternate mica-like and brucite-like layers. The layers are continuous in the a and b dimensions and are stacked in the c direction with basal cleavage between the layers. The mica-like layers are trioctahedral with the general composition \((\text{OH})_4(\text{SiAl})_6(\text{Mg}+\text{Fe})_2\text{O}_{20}\). The brucite-like layer has the general composition \((\text{Mg}+\text{Al})_6(\text{OH})_{12}\). The

---

mica layer is unbalanced by substitution of $\text{Al}^{3+}$ for $\text{Si}^{4+}$, and this deficiency of charge is balanced by an excess charge in the brucite sheet as a consequence of substitution of $\text{Al}^{3+}$ for $\text{Mg}^{2+}$. The general chlorite structure is illustrated in Figs. 15 and 16. The charge distribution in the layers is as follows, where $X = 1$ or 2:

$$
\begin{align*}
6(\text{OH})^- & \quad 6- \\
(6 - 2X)\text{Mg}^{2+} \cdot 2X\text{Al}^{3+} & \quad [2(6 - 2X) + 3(2X)] + \\
6(\text{OH})^- & \quad 6-
\end{align*}
$$

Fig. 15. Diagrammatic sketch of the structure of chlorite, after McMurchy.
Two brucite-like and two mica-like layers form the unit cell. McMurchy gives the following specifications for the chlorite he studied: monoclinic, \(a = 5.3 \text{ Å}, b = 9.3 \text{ Å}, c = 28.52 \text{ Å}, \beta = 97°8',\) and space group \(C_{2h}^k - C2/c.\) Subsequently Robinson and Brindley have stated "the displacements are exactly \(a_0/3\) and since \(b_0/a_0 = \sqrt{3},\) the unit cell may be regarded as rhombohedral with the trigonal axis perpendicular to the cleavage plane, or alternatively as an orthohexagonal cell with a volume three times that of the monoclinic prism and with dimensions in \(kX\) units \(a_0 = 5.32, b_0 = 9.21, c_0 = 3 \times 14.2.\)"
Various members of the chlorite group differ from each other in the kind and amount of substitutions within the brucite layer and the tetrahedral and octahedral positions of the mica layer. They also differ in the detailed orientation of successive octahedral and tetrahedral layers, in the relation of the mica to brucite layers, and in the stacking of successive chlorite units.

Substitutions within the tetrahedral sheets vary from about Si$_3$Al to Si$_2$Al$_2$ and substitutions within the octahedral layers from Mg$_3$Al to Mg$_4$Al$_5$, with Fe$^{++}$ and Mn$^{++}$ partially replacing Mg$^{++}$ and Fe$^{+++}$ or Cr$^{++}$ partially replacing Al$^{+++}$. The substitutions of Al$^{+++}$ for Si$^{++}$ in the tetrahedral sheets expands them sufficiently to accommodate the somewhat larger octahedral layers between them.

By detailed study of single crystals, Brindley and his colleagues have shown that chlorites exhibit polymorphic forms similar to the biotite micas. They have found structures consisting of several different stacking arrangements of the chlorite layers. Units with three, six, and nine chlorite layers in the orthohexagonal cell have been described. For details of these polymorphic forms and other details of the chlorite structure the original work of Brindley et al. should be consulted.

Fine-grained chlorites are known in some clay materials. The range of polymorphic forms of the chlorite minerals and the variations in structure between clay-mineral chlorite and well-crystallized chlorite occurring in large units have not been established. It is not definitely known, for example, whether somewhat more hydrous forms of chlorite, like illite in relation to muscovite and biotite, are to be found in clays and soils. Available data seem to suggest that clay-mineral chlorites differ from well-crystallized material in a somewhat random stacking of layers and perhaps in some hydration.

Some evidence is available that some chlorites in sediments may be dioctahedral.

VERMICULITE

The structure of vermiculite was first worked out by Gruner. Later Hendricks and Jefferson confirmed Gruner's general conclusions.
but changed certain structural details. Recently Barshad\textsuperscript{54-60} and Walker\textsuperscript{61,62} independently have added much to our knowledge of the structure of the mineral. Gruner\textsuperscript{54} also showed that many materials classed as vermiculite are mixed-layer mica-vermiculite structures.

Gruner\textsuperscript{54} showed that the structure consists of sheets of trioctahedral mica or talc separated by layers of water molecules occupying a definite space (4.98 Å) which is about the thickness of two water molecules. In its natural state, therefore, the mineral consists of an alternation of mica and double water layers. Gruner\textsuperscript{54} assigned vermiculite to the space group $C_{6h}-C2/c$.

Based on single-crystal data, Hendricks and Jefferson\textsuperscript{56} assigned the following crystallographic constants to the mineral: $c = 28.91$ Å, $b = 9.20$ Å, $a = 5.34$ Å, $\beta = 93^\circ 15'$. They showed that vermiculites have the same types of shifts along the $a$ axis as muscovite, talc, and pyrophyllite and have a partially random displacement of structural layers parallel to the $b$ axis. They give the space group as $C_c-C\bar{1}$ and point out the pseudo nature of the space group because of the random displacement parallel to the $b$ axis.

The structure is unbalanced chiefly by substitutions of $\text{Al}^{3+}$ for $\text{Si}^{4+}$. These substitutions may be partially balanced by other substitutions within the mica lattice, but there is always a residual net-charge deficiency of 1 to 1.4 per unit cell. The charge deficiency is satisfied by cations which occur chiefly between the mica layers and are largely exchangeable. In the natural mineral, which has the same cation-exchange capacity as montmorillonite, or somewhat higher, the balancing cation is $\text{Mg}^{2+}$, sometimes with a small amount of $\text{Ca}^{2+}$ also present.

A general formula for natural vermiculite is $(\text{OH})_x(Mg-Ca)_x(Si_{8-x}Al_x)(Mg-Fe)_{y-2x}yH_2O$ with $X = 1$ to 1.4 and $y \approx 8$. The $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ are the balancing and largely exchangeable cations. The charge distribution in the layers is as follows:

\begin{align*}
&yH_2O \text{ double water layers} \\
&X(\text{Mg}^{2+}-\text{Ca}^{2+}) \quad X^+ \\
&6O^- \quad 12- \\
&(4 - X)\text{Si}^{4+}-\text{XAl}^{3+} \quad (16 - X)^+ 
\end{align*}


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\[
\begin{align*}
4O^- - 2(OH)^- &
\quad 10^- \\
6(Mg,Fe)^{++} &
\quad 12+ \\
4O^- - 2(OH)^- &
\quad 10^- \\
(4 - X)Si^{++}Al^{++} &
\quad (16 - X)^+ \\
6O^- &
\quad 12- \\
X(Mg^{++}Ca^{++}) &
\quad X+ \\
\quad yH_2O \text{ double water layers}
\end{align*}
\]

On heating vermiculite to temperatures as high as 500°C, the water is driven out from between the mica layers, but the mineral quickly rehydrates on exposure to moisture at room temperature. The mineral, therefore, has an expanding lattice, but the expansion is restricted to about 4.98 Å, or two water layers. If the mineral is heated to 700°C, there is no expansion again. In such material the 14-A line and higher orders of it disappear, and a new line at 9.3 Å with other new mica lines appear on the diffraction pattern.

There has been considerable discussion regarding the exact structure of the water layers in vermiculite, and as yet there is no general agreement among investigators. Gruner suggested that the water might occur as charged hydronium \((H_3O)^+\) groups. Hendricks and Jefferson postulated an extended hexagonal network of water molecules (Fig. 17) (see Chap. 8 for a further discussion). It has recently been pointed out by Barshad and Walker independently that the nature of the exchangeable cations must influence the state of the interlayer water since they occur between the mica layers. These investigators have shown this to be the case (Table 3).

Walker views the state of the water in natural vermiculite as follows:

### Table 3. Thickness of Water Layers in Vermiculite Saturated with Various Cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>(d(002), \text{ Å})</th>
<th>Thickness of water layer, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg^{++}</td>
<td>14.39</td>
<td>5.11</td>
</tr>
<tr>
<td>Ca^{++}</td>
<td>15.0</td>
<td>5.75</td>
</tr>
<tr>
<td>Sr^{++}</td>
<td>15.0</td>
<td>5.75</td>
</tr>
<tr>
<td>Ba^{++}</td>
<td>12.3</td>
<td>3.04</td>
</tr>
<tr>
<td>Li^{+}</td>
<td>12.2</td>
<td>2.04</td>
</tr>
<tr>
<td>Na^{+}</td>
<td>14.8</td>
<td>5.55</td>
</tr>
<tr>
<td>K^{+}</td>
<td>10.6 diffuse</td>
<td>About 1.54</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>10.8 diffuse</td>
<td>About 1.54</td>
</tr>
</tbody>
</table>

The water exists in two forms, “bound” and “unbound.” The bound water occurs around the Mg^{++} as a hydration envelope of six water molecules per Mg^{++}, probably taking the form of an octahedral grouping.
The available space, 4.98 Å, is consistent with this grouping if the octahedral groups lie on their sides so that they present their minimum width to adjacent sheets. The unbound water fills in the space between the octahedral water units. Walker computes the ratio of unbound water to total interlayer water to be about 8:14. Walker shows that, if vermiculite is heated to about 110°C in a closed tube, so that rehydration is not possible, partial but regular collapse of the structures takes place to 11.8 Å, representing a water-layer thickness of 2.54 Å, which is equivalent to one molecular water layer. Walker reasons that in such partial collapse the unbound water is driven off and also the octahedral net around the Mg²⁺ is broken, with these water molecules pressed flat between the mica layers. Such partially collapsed vermiculite has a strong tendency
to rehydrate, which may be due to the strong tendency of Mg$^{++}$ to rebuild its octahedral envelope.

In the case of vermiculite prepared with exchangeable Ba$^{++}$ and Li$^+$, there seems to be a single water layer between the mica layers. For vermiculites with K$^+$ and NH$_4^+$, the space is smaller than that required for a single molecular water layer, and Barshad$^{39}$ considers the mineral to be dehydrated. Walker,$^6$ however, considers that some water is present with the K$^+$ and NH$_4^+$ and that the reduced space is due to a partial embedding in the silicon-oxygen sheets. He points out that,

![Diagram](image)

**FIG. 18.** Configuration of the interlayer water in vermiculite (diagrammatic), from Walker.$^6$ (a) Fully hydrated. (b) About half hydrated after removal of the unbound water. Of the six water molecules in the original hydration shell of magnesium (see a), only four are now in actual contact with the ion. (c) Fully dehydrated with magnesiums in holes in the silicate layers.

when K$^+$-saturated vermiculite is heated, the basal spacing is further reduced to 10.1 Å. Walker’s concept is illustrated in Fig. 18. (For a further discussion of the hydration of vermiculite, see Chap. 8.)

Since vermiculite has an expanding structure and an unbalanced lattice with high cation-exchange capacity, it is important to consider its relation to montmorillonite, which also has these characteristics. Vermiculite differs from montmorillonite in that the expansion with water is limited to about 4.98 Å. Vermiculites adsorb certain organic molecules (see Chap. 10) between the mica layers but differ from montmorillonite in that the adsorbed layer is thinner and less variable. These characteristics may be the result of the relatively larger particle size of the vermiculite layers, and possibly also of the fact that there is considerably less randomness in the stacking of the vermiculite layers. In fact, in vermiculite the randomness may be in only one horizontal direction. All
rows of tetrahedral apexes at alternate intervals in the top and bottom of the sheets. The ribbed sheets are arranged so that the apexes of successive sheets point together, and the sheets are held together by aluminum and/or magnesium in octahedral coordination between the apex oxygens of successive sheets (Fig. 19). The octahedral layer is similar to that in the layer clay minerals, but it is continuous in only one direction. The octahedral layer is completed by central OH groups and by hydroxyls at the open sides. The mineral has good cleavage parallel to (110) caused by the weak link through O of the silica chains in the ribbed layer. Chains of water molecules running parallel to \( c \) fill the interstices between the amphibole chains. The cavities will accommodate four molecules of water per unit cell, and this water would account for the dehydration loss at low temperatures. The dimensions of the cell suggested by Bradley are \( a_0 \sin \alpha = 12.9 \) Å, \( b_0 = 18 \) Å, and \( c_0 = 5.2 \) Å. There are two molecules in the unit cell, and the space group is probably \( C_{2v}-C2/m \). The structure is balanced, and the composition of the ideal cell is \((OH_2)_4-(OH)_2Mg_5Si_8O_{20.4}H_2O\), in which trivalent cations are considered equivalent to \( 1.5Mg^{++} \). Some substitution of \( Al^{3+} \) for Si\(^{4+}\) is considered probable. Bradley points out that substitution of \( Al^{3+} \) for either \( Mg^{++} \) or Si\(^{4+}\) or both should weaken the structure, so that it appears doubtful that extensive replacement takes place, and an aluminum end member would not be expected.

There are general similarities but also distinct differences in the diffraction data for attapulgite and some sepiolites (see the tables of Chap. 5). It appears likely, therefore, that the general structural framework of all these clay minerals is the same but that there are distinct differences in details. Considerably more work is necessary before these details become known. Structural studies of the sepiolites are particularly needed so that structural variations between them and attapulgite can become known.

**MIXED-LAYER MINERALS**

Many clay materials are composed of more than one clay mineral, and the clay minerals may be mixed in several ways. The mixture may be of discrete clay-mineral particles in which there is no preferred geometric orientation of one particle with respect to its neighboring clay-mineral particles.

Another type of mixing is the interstratification of the layer clay minerals in which the individual layers are of the order of a single or a few aluminosilicate sheets. These so-called mixed-layer structures are a consequence of the fact that the layers of the different layer clay minerals are very similar, all being composed of silica tetrahedral-hexagonal layers and closely packed octahedral layers of oxygens and hydroxyl groups.
Mixed-layer structures as stable as those composed of a single kind of layer are therefore possible.

Mixed-layer structures are of two different types. The interstratification may be regular; i.e., the stacking along the c axis is a regular repetition of the different layers. In such cases, the resulting structure has distinctive characteristics; the unit cell is equivalent to the sum of the component layers, and regular (001) reflections are obtained. An example of a regular mixed-layer mineral is chlorite composed of a regular alternation of mica and brucite layers (see pages 69–72).

Another kind of mixed-layer structure is due to a random irregular interstratification of layers in which there is no uniform repetition of layers. The importance of such random mixing was pointed out by Gruner and later elaborated by Hendricks and Teller and Bradley. Mixed-layer structures appear to be very common in clay materials. Their study is particularly difficult, and in many cases investigators have failed to recognize their presence. Mixed layers of illite and montmorillonite and of chlorite and vermiculite are particularly common. Clay-mineral occurrences which are probably mixtures of illite and kaolinite have also been described.

As pointed out previously (pages 38–42), the literature contains the names of many discredited or questionable clay-mineral species. Probably a great many of these “species” are mixed-layer combinations. Careful X-ray-diffraction techniques (page 102) are required to detect the occurrence of mixed-layer minerals. Sometimes differential thermal procedure will aid in their detection. Very frequently mixed layering cannot be detected solely on the basis of optical measurements, and the widespread occurrence of mixed-layer minerals is an important reason why clay-mineral identifications based solely on optical measurements must be made with great caution.

Since random mixed-layer minerals have an inherent variability, they cannot be given specific names. They can only be designated as mixtures of the layers involved.

**ADDITIONAL REFERENCES**

**Kaolinite Minerals**

Alvfeldt, O., X-ray Study on Kaolinite as an Alteration Product of Spodumene from Varuträsk, Geol. Fören. i. Stockholm Föhr., 63, 49–51 (1941).


Structure of the Clay Minerals


**Halloysite Minerals**


**Montmorillonite**


Clay Mineralogy


Illite


Chlorite


Vermiculite


Structure of the Clay Minerals


**Sepiolite-Attapulgite-Palygorskite**

Deribere, M., Le Minéral papyrace de la table (Savoie), Bull. soc. franç. minéral., 66, 222-237 (1943).
CHAPTER 5
X-ray-diffraction Data

GENERAL STATEMENT

In this chapter X-ray-diffraction data are given for the clay minerals, together with a discussion of the application of these data in their identification. The diffraction characteristics of many of the clay minerals have considerable similarity so that identifications based on diffraction data are frequently complicated.

X-ray-diffraction data are given in this chapter and the tables to follow in kX units, i.e., they are based on comparisons with the values for calcite. Recent determinations of Avogadro's number, on which the calculated value of the absolute calcite spacing depends, show that values expressed in kX units are converted to angstroms by multiplying by 1.00202. The difference between kX and angstrom units is significant only when measurements are accurate to 0.5 per cent.

The diffraction data are given in kX units since the most complete data available are in this unit in the recent volume "X-ray Identification and Structure of the Clay Minerals" edited by G. W. Brindley and published as a monograph by the Mineralogical Society of Great Britain. The diffraction data here are taken from this volume, for which permission was kindly granted.

Clay minerals exist for the most part only in very fine particles, and some form of the powder method usually must be used to obtain the diffraction data. Because of certain inherent characteristics of the clay minerals, special cameras and special techniques are frequently required for clay-mineral work. Cameras and techniques entirely adequate for other materials have been found to be unsatisfactory for clay-mineral investigations. Brindley has recently considered X-ray methods as applied to clay-mineral researches, and the following discussion is largely

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X-ray-diffraction Data

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taken from his work. For a consideration of X-ray methods in general, the standard works of Bragg,5,6 Buerger,7 James,8 Wilson,9 et al.10 should be consulted.

In the clay minerals there are few, if any, reflections obtained from spacings less than about 1 kX, and therefore with copper Kα radiation, it is unnecessary to extend either the film or the camera to values of 2θ greater than about 90° or 100°. The specimen, therefore, can be brought nearer the focus of the X-ray tube and the exposure time shortened by omitting that part of the usual cylindrical camera corresponding to 90° < 2θ < 180°.

The first-order basal reflections of the clay minerals are frequently their most important reflections. Such reflections may correspond to spacings as large as 20 to 30 Å, and it is to obtain clear recordings of such low-angle reflections that special cameras and special techniques have been devised. Further, it may be necessary to study the exact shape or profile of such a reflection, and for this purpose cameras capable of recording spacings of the order of 50 Å are required.11,12 Cameras with diameters of 9 to 20 cm are commonly employed in clay-mineral work.

Most of the clay minerals occur in flake-shaped units, and consequently when a powder is packed, an aggregate orientation of the flakes develops readily. Thus, care must be taken in the preparation and mounting of clay samples in the camera, or enhanced basal reflections will be obtained from an aggregate arrangement. For some types of work where basal reflections are particularly desirable, as in the study of mixed-layered structures, advantage may be taken of this tendency to develop oriented aggregates. Bradley, Grim, and Clark13 have described a method of forming well-oriented aggregates and using them in X-ray-diffraction studies.

In the montmorillonite and vermiculite clay minerals the basal spacings vary with the humidity of the atmosphere to which they are subjected.

It may, therefore, be necessary to control the humidity of the atmosphere within the camera. Recently techniques using clay-mineral–organic complexes\textsuperscript{14,15} have been devised for these minerals (see pages 93 and 99) which are superior for identification purposes.

Imperfections of crystals affect their diffraction characteristics, and they are particularly important for the clay minerals. The imperfections may be of several kinds, as follows:

Because of the highly symmetrical arrangement of the atoms in the various layers and the relatively weak binding force between them, the layers can be displaced with respect to one another. The geometrical relation between adjacent sheets of atoms in contact may remain the same, although the relation between more distant atoms is changed. The result of such imperfections is the absence of certain types of reflections. Two-dimensional diffraction effects become the major feature when the layers are displaced randomly in two directions. If, for example, displacements occur along both the \(a\) and \(b\) axes, the only \(hkl\) reflections which are possible are the basal (00\(l\)) reflections. Two-dimensional diffraction effects then arise from the regularity within the layers and require only two indices, namely, \(hk\). They give broad diffraction bands rather than sharp lines and are generally easily recognized.

Another type of imperfection is found in the mixed-layered structures when layers of different types are interstratified. Because of the fact that many clay-mineral layers are very similar, being composed of silica tetrahedral sheets and closely packed layers of oxygen and hydroxyls, they can interstratify to build structures as stable or almost as stable as structures composed of a single layer. When the alternation of different layers is regular, the result is equivalent to a single unit of larger unit-cell dimensions, \(e.g.,\) chlorite. When the alternation of different layers is irregular, new diffraction effects arise, in particular a nonintegral series of reflections from the basal planes (see pages 102–104).

The shape and size of the crystal particles exposed to X-ray influence the diffraction effects. Thus, if the crystal particles have a distinct shape, \(e.g.,\) plate-like or rod-like, certain reflections may be broader than others. Theoretically a study of the diffuseness of the reflections and their profile should provide information on the shape and size of the crystals. However, because the lattice imperfections of the clay minerals cause somewhat similar diffraction effects, only qualitative results could be hoped for at best, and much more useful results on size and shape are likely to be revealed by the electron microscope.


KAOLINITE AND HALLOYSITE MINERALS

Diffraction data for kaolinite and halloysite (low-hydration type) are given in Table 4 from Brindley and Robinson\textsuperscript{16–18} taken from Brindley’s text.\textsuperscript{19} Diffraction data for nacrite and dickite are given in Table 5 from Gruner\textsuperscript{20,21} and Brindley,\textsuperscript{19} also taken from Brindley’s text.\textsuperscript{19} In general the determination of the kaolinite group by X-ray diffraction is simple, but the identification of the particular members of the group may be more difficult. The prominent basal reflections at about 7.14 kX (001) and 3.57 kX (002) are usually adequate for identification.

The chloritic clay minerals may be confused with the kaolinite minerals, especially if the experimental technique is not adequate to reveal the 14-kX chlorite reflection. However, usually the third order at 4.7 kX is seen to indicate the presence of chlorite. Chlorites rich in iron frequently give weak first- and third-order reflections, and differentiation from kaolinite is particularly difficult. In such cases only a little chlorite may be suggested by the diffraction data, and further tests are necessary to estimate the abundance of the mineral accurately. Such a further test may be treatment with warm HCl to take advantage of the greater solubility of chlorite in this acid. Also kaolinite on heating to 600°C tends to lose its crystalline character, whereas chlorite at this temperature is only partially dehydrated, causing increased intensity of the 14-kX reflection. Frequently other analytical methods, such as differential thermal analyses, are necessary to supplement the X-ray data to establish the presence of chlorite.

Nacrite, dickite, and kaolinite can be differentiated from each other on the basis of X-ray-diffraction data if the technique used provides adequate resolution (Table 5).

Diffraction characteristics of well-crystallized versus poorly crystallized kaolinite are given in Fig. 7 of Chap. 4. The transition from well-crystallized to poorly crystallized kaolinite is shown by a broadening and

Clay Mineralogy

Table 4. Lattice Spacings, Indices, and Intensities in Powder Diagrams of Well-crystallized Kaolinite, Poorly Crystallized Kaolinite, and the Low-hydration Variety of Halloysite

(From Brindley and Robinson 18-19 taken from Brindley's text 19)

<table>
<thead>
<tr>
<th>Well-crystallized kaolinite</th>
<th>Poorly crystallized kaolinite</th>
<th>Halloysite, low-hydration variety</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>d</td>
<td>hkl</td>
</tr>
<tr>
<td>----</td>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>10+</td>
<td>7.15</td>
<td>001</td>
</tr>
<tr>
<td>4</td>
<td>4.45</td>
<td>020</td>
</tr>
<tr>
<td>6</td>
<td>4.35</td>
<td>110</td>
</tr>
<tr>
<td>6</td>
<td>4.17</td>
<td>111</td>
</tr>
<tr>
<td>3</td>
<td>4.12</td>
<td>111*</td>
</tr>
<tr>
<td>4</td>
<td>3.937</td>
<td>021</td>
</tr>
<tr>
<td>3</td>
<td>3.734</td>
<td>021</td>
</tr>
<tr>
<td>2</td>
<td>3.566</td>
<td>002</td>
</tr>
<tr>
<td>4</td>
<td>3.365</td>
<td>111</td>
</tr>
<tr>
<td>2</td>
<td>3.138</td>
<td>112</td>
</tr>
<tr>
<td>2</td>
<td>3.091</td>
<td>112</td>
</tr>
<tr>
<td>2</td>
<td>2.748</td>
<td>022</td>
</tr>
<tr>
<td>8</td>
<td>2.553</td>
<td>201</td>
</tr>
<tr>
<td>4</td>
<td>2.521</td>
<td>130</td>
</tr>
<tr>
<td>9</td>
<td>2.486</td>
<td>112</td>
</tr>
<tr>
<td>7</td>
<td>2.374</td>
<td>003</td>
</tr>
<tr>
<td>10</td>
<td>2.331</td>
<td>131</td>
</tr>
<tr>
<td>9</td>
<td>2.284</td>
<td>113</td>
</tr>
<tr>
<td>1</td>
<td>2.243</td>
<td>132, 040</td>
</tr>
<tr>
<td>3</td>
<td>2.182</td>
<td>132, 250</td>
</tr>
<tr>
<td>1</td>
<td>2.057</td>
<td>222</td>
</tr>
<tr>
<td>4</td>
<td>1.935</td>
<td>132</td>
</tr>
<tr>
<td>1</td>
<td>1.865</td>
<td>042</td>
</tr>
<tr>
<td>1</td>
<td>1.805</td>
<td>114, 223</td>
</tr>
</tbody>
</table>
TABLE 4. LATTICE SPACINGS, INDICES, AND INTENSITIES IN POWDER DIAGRAMS OF WELL-CRYSTALLIZED KAOLINITE, POORLY CRYSTALLIZED KAOLINITE, AND THE LOW-HYDRATION VARIETY OF HALLOYSITE. (Continued)

<table>
<thead>
<tr>
<th>Well-crystallized kaolinite</th>
<th>Poorly-crystallized kaolinite</th>
<th>Halloysite, low-hydration variety</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>d</td>
<td>hkl</td>
</tr>
<tr>
<td>1</td>
<td>1.704</td>
<td>222</td>
</tr>
<tr>
<td>2</td>
<td>1.682</td>
<td>150, 241, 311, 311, 222</td>
</tr>
<tr>
<td>8</td>
<td>1.659</td>
<td>201 → 201</td>
</tr>
<tr>
<td>6</td>
<td>1.616</td>
<td>242, 310</td>
</tr>
<tr>
<td>4</td>
<td>1.581</td>
<td>152, 211</td>
</tr>
<tr>
<td>5</td>
<td>1.539</td>
<td>203</td>
</tr>
<tr>
<td>9</td>
<td>1.486</td>
<td>331 → 331</td>
</tr>
<tr>
<td>2</td>
<td>1.464</td>
<td>223, 115</td>
</tr>
<tr>
<td>2</td>
<td>1.464</td>
<td>332</td>
</tr>
<tr>
<td>4</td>
<td>1.449</td>
<td>061</td>
</tr>
<tr>
<td>4</td>
<td>1.426</td>
<td>005</td>
</tr>
</tbody>
</table>

Values obtained with filtered Cu Kα radiations; camera radius 100 mm.
* Weak lines not always observed; may be due to an impurity.
\( b \) = broad lines.

weakening of the reflections with the complete elimination of the weaker ones. There is a tendency for adjacent reflections to fuse into one. The basal reflection also increases from 7.14 to as much as 7.20 kX. The group of lines from (020) \( (d = 4.46) \) to (002) \( (d = 3.57) \) particularly reflect the change to lower crystallinity. In this region the clearly resolved doublet (111) and (111) of well-crystallized material gives way to a single band, affording good evidence for the decrease in crystallinity. It is frequently difficult to determine precisely the crystallinity of very
Table 5. Lattice Spacings and Estimated Intensities in Powder Diagrams of Nacrite and Dickite
(From Gruner\textsuperscript{20,21} and Brindley and Robinson\textsuperscript{16} taken from Brindley's text\textsuperscript{19})

<table>
<thead>
<tr>
<th>Nacrite*</th>
<th>Dickite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gruner\textsuperscript{21}</td>
<td>Gruner\textsuperscript{20}†</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>$I$</td>
</tr>
<tr>
<td>7.08</td>
<td>10</td>
</tr>
<tr>
<td>4.40</td>
<td>8</td>
</tr>
<tr>
<td>4.13</td>
<td>3</td>
</tr>
<tr>
<td>3.98</td>
<td>2b</td>
</tr>
<tr>
<td>3.58</td>
<td>9</td>
</tr>
<tr>
<td>3.44</td>
<td>1b</td>
</tr>
<tr>
<td>3.04</td>
<td>1b</td>
</tr>
<tr>
<td>2.537</td>
<td>1b</td>
</tr>
<tr>
<td>2.418</td>
<td>10</td>
</tr>
<tr>
<td>2.393</td>
<td>1-2</td>
</tr>
<tr>
<td>2.319</td>
<td>17</td>
</tr>
<tr>
<td>2.263</td>
<td>1b</td>
</tr>
<tr>
<td>2.069</td>
<td>1b</td>
</tr>
<tr>
<td>1.902</td>
<td>2-3ab</td>
</tr>
<tr>
<td>1.795</td>
<td>1</td>
</tr>
<tr>
<td>1.744</td>
<td>1b</td>
</tr>
<tr>
<td>1.675</td>
<td>2b</td>
</tr>
<tr>
<td>1.616</td>
<td>2b</td>
</tr>
<tr>
<td>1.583</td>
<td>1</td>
</tr>
<tr>
<td>1.486</td>
<td>8</td>
</tr>
<tr>
<td>1.455</td>
<td>1b</td>
</tr>
<tr>
<td>1.434</td>
<td>1/2</td>
</tr>
<tr>
<td>1.358</td>
<td>1-2ab</td>
</tr>
<tr>
<td>1.314</td>
<td>1/2</td>
</tr>
<tr>
<td>1.284</td>
<td>1</td>
</tr>
<tr>
<td>1.263</td>
<td>3</td>
</tr>
<tr>
<td>1.230</td>
<td>2b</td>
</tr>
<tr>
<td>1.208</td>
<td>1/2</td>
</tr>
<tr>
<td>1.195</td>
<td>1</td>
</tr>
<tr>
<td>1.172</td>
<td>1b</td>
</tr>
<tr>
<td>1.317</td>
<td>1b</td>
</tr>
<tr>
<td>1.381</td>
<td>1</td>
</tr>
<tr>
<td>1.374</td>
<td>1</td>
</tr>
<tr>
<td>1.317</td>
<td>4</td>
</tr>
</tbody>
</table>

* Nacrite; unfiltered Cu $K\alpha$ radiations, camera radius 57.3 mm.
† Dickite; unfiltered Fe $K\alpha$ radiations, camera radius 57.3 mm.
‡ Dickite; filtered Cu $K\alpha$ radiations, camera radius 100 mm.
$b$ = broad lines; $vb$ = very broad lines.
X-ray-diffraction Data

fine kaolinite, since the small size would also cause a broadening and weakening of reflections.

In the case of halloysite (2H₂O) the broadening of reflections, the development of bands replacing adjacent lines, and the elimination of weak reflections is carried to the stage (see Fig. 7, Chap. 4) where differentiation is usually not difficult.

Halloysite (4H₂O) gives a basal reflection at about 10.1 kX, a second-order reflection at about 5 kX, which is usually unobservable, and a third-order reflection almost coinciding with the second order for halloysite (2H₂O). Except for these few basal reflections, the patterns of the two forms of halloysite consist of identical bands. Brindley¹⁹ and Brown and MacEwan²² have shown in detail the diffraction effect resulting from mixed layering of 4H₂O and 2H₂O forms when the interlayer water is gradually eliminated. The 10.1-kX spacing of halloysite (4H₂O) occurs at about the same place as the (001) basal spacing of the illites, but other reflections usually serve to differentiate these minerals easily. Also the reflection can be shifted in the halloysite mineral by drying at low temperature, and the halloysite will adsorb certain organic molecules (see Chap. 10), so that auxiliary procedures are available to identify the mineral.

MONTMORILLONITE MINERALS

The diffractions shown by powder diagrams of the montmorillonite minerals can be placed in two categories. One class consists of basal reflections, which vary with the state of hydration of the mineral, i.e., with the thickness and regularity of the water layers between the silicate sheets. The c-axis spacing, the diffuseness of the reflections, and the number of orders shown vary from sample to sample depending on the thickness of the water layers and their regularity, which factors in turn are dependent on the exchangeable cation present and the conditions, e.g., water-vapor pressure, under which the sample has been prepared. Because of the variability of the basal spacings no table can be given for them.

The second class of diffractions consists of general diffractions which are characteristic of the structure of the montmorillonite layers themselves and are not dependent on the interlayer hydration. These are hk bands, which in general are the same for all montmorillonites. The differences shown by various montmorillonites are in details of spacings

Clay Mineralogy

and relative intensities. Table 6, after MacEwan,\(^2\)\(^3\) gives data for the general diffractions of some montmorillonite minerals.

**Table 6. Data for General Diffractions of the Montmorillonite Minerals**

(After MacEwan\(^2\)\(^3\))

<table>
<thead>
<tr>
<th>Indices</th>
<th>(d) (calc)</th>
<th>Montmorillonite (Wyoming bentonite)</th>
<th>Hectorite</th>
<th>Triocahedral soil montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(d)</td>
<td>I</td>
<td>S</td>
</tr>
<tr>
<td>11, 02</td>
<td>4.49</td>
<td>4.60</td>
<td>(v)</td>
<td>(vbr)</td>
</tr>
<tr>
<td>13, 20</td>
<td>2.59</td>
<td>2.55</td>
<td>(s)</td>
<td>(vbr)</td>
</tr>
<tr>
<td>22, 04</td>
<td>2.25</td>
<td>2.217</td>
<td>(vw)</td>
<td>(br)</td>
</tr>
<tr>
<td>31, 15, 24</td>
<td>1.703</td>
<td>1.689</td>
<td>(m)</td>
<td>(br)</td>
</tr>
<tr>
<td>33, 06</td>
<td>1.500</td>
<td>1.489</td>
<td>(s)</td>
<td>(vsh)</td>
</tr>
<tr>
<td>26, 40</td>
<td>1.298</td>
<td>1.286</td>
<td>(m)</td>
<td>(br)</td>
</tr>
<tr>
<td>35, 17, 42</td>
<td>1.249</td>
<td>1.241</td>
<td>(m)</td>
<td>(sh)</td>
</tr>
<tr>
<td>08, 44</td>
<td>1.125</td>
<td>1.118</td>
<td>(vw)</td>
<td>(sh)</td>
</tr>
<tr>
<td>37, 28, 51</td>
<td>1.034</td>
<td>1.027</td>
<td>(vw)</td>
<td>(br)</td>
</tr>
<tr>
<td>19, 53, 46</td>
<td>0.882</td>
<td>0.9745</td>
<td>(w)</td>
<td>(br)</td>
</tr>
<tr>
<td>55</td>
<td>0.900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30, 60</td>
<td>0.8665</td>
<td>0.8625</td>
<td>(w)</td>
<td>(sh)</td>
</tr>
</tbody>
</table>

\(S\) = shape of band; \(v\) = very strong; \(s\) = strong; \(m\) = medium; \(w\) = weak; \(vw\) = very weak; \(vw\) = very, very weak; \(v\) = just visible; \(vbr\) = very broad; \(br\) = broad; \(sh\) = sharp; \(vsh\) = very sharp.

The \(a_0\) and \(b_0\) parameters are deduced from measurements and adjusted to make \(b_0 = a_0 \sqrt{3}\).

The second column gives the calculated edges of the bands with the \(a_0\) and \(b_0\) axes given at the bottom of the column.

Where two or more spacings are given against a particular index, or group of indices, it is to be understood that they probably represent subsidiary maxima or apparent edges of bands (usually rather uncertain, except for the innermost one). Spacings enclosed in parentheses are uncertain and may be due to impurities in some cases.

By using oriented aggregates, as MacEwan\(^2\)\(^3\) has emphasized, patterns which contain either the (00l) or the \(hk\) lines can be obtained by suitably mounting the specimen in front of the X-ray beam.

X-ray-diffraction Data

As will be shown elsewhere (see Chap. 10), montmorillonite possesses the property of adsorbing certain organic molecules between the individual silicate layers with a consequent shift in the c dimension depending on the size and configuration of the organic molecule. Such resulting montmorillonite-organic complexes, as Bradley showed, have a high degree of regularity, yielding sharp (00l) lines of many orders. For example, treatment of a sample of montmorillonite with ethylene glycol provides a sharp (001) reflection at 17 kX. Treatment with organic compounds permits the detection of small amounts of the mineral which would otherwise be missed in complex mixtures.

ILLITE MINERALS

Diffraction data for muscovite and biotite and three illites are given in Table 7, from Grim, Bradley, and Brown. The illite minerals can usually be identified on the basis of X-ray diffraction by their (00l) spacings with the first order at about 10 kX. Some difficulty may be encountered with completely collapsed montmorillonite, but the slightly lower (001) reflection for it and the characteristics of the remainder of the pattern are generally adequate to distinguish it from illite.

Differentiation of the polymorphic forms of mica by X-ray diffraction is not always an easy matter. Grim, Bradley, and Brown have shown that the reflections in the region between 4.4 and 2.6 kX can usually be used to distinguish micas of one-, two-, and three-layer unit cells (see Table 8). This region includes only (02l) and (11l) reflections except for one strong basal order at 3.33 kX.

Grim, Bradley, and Brown, Walker, and others have pointed out that the position of the (060) reflection and the intensity of the second-order basal reflection can usually be used to distinguish between dioctahedral and trioctahedral micas. For the dioctahedral forms, (060) is close to 1.50 kX and (002) is strong. For the trioctahedral forms, (060)
### Clay Mineralogy

#### Table 7. Lattice Spacings and Estimated Intensities in Powder Diagrams of Muscovite, Biotite, and Various Illites

(From Nagelschmidt,\textsuperscript{4} Grim et al.,\textsuperscript{5} Mackenzie et al.,\textsuperscript{6} and Walker,\textsuperscript{7} taken from Grim et al.\textsuperscript{8})

<table>
<thead>
<tr>
<th></th>
<th>Muscovite*</th>
<th>Biotite*</th>
<th>Illite†</th>
<th>Illite‡</th>
<th>Illite§</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d</td>
<td>I</td>
<td>d</td>
<td>I</td>
<td>d</td>
</tr>
<tr>
<td>9.98</td>
<td>s</td>
<td>10.1</td>
<td>vs</td>
<td>9.9</td>
<td>s</td>
</tr>
<tr>
<td>5.0</td>
<td>s</td>
<td>4.97</td>
<td>w</td>
<td>4.9</td>
<td>m</td>
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<tr>
<td>4.49</td>
<td>s</td>
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<td>w</td>
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<tr>
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<td>w</td>
<td>4.11</td>
<td>w</td>
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<td>w</td>
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<tr>
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<td>w</td>
<td>3.7</td>
<td>ve</td>
<td>3.64</td>
<td>mw</td>
</tr>
<tr>
<td>3.5</td>
<td>m</td>
<td>3.4</td>
<td>vwe</td>
<td>3.35</td>
<td>ve</td>
</tr>
<tr>
<td>3.33</td>
<td>vs</td>
<td>3.36</td>
<td>vs</td>
<td>3.31</td>
<td>m</td>
</tr>
<tr>
<td>3.2</td>
<td>m</td>
<td>3.15</td>
<td>vwe</td>
<td>3.2</td>
<td>vwe</td>
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<tr>
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<td>m</td>
<td>2.91</td>
<td>vw</td>
<td>2.84</td>
<td>w</td>
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<tr>
<td>2.88</td>
<td>m</td>
<td>2.84</td>
<td>ve</td>
<td>2.85</td>
<td>m d</td>
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<tr>
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<td>m</td>
<td>2.65</td>
<td>s</td>
<td>2.56</td>
<td>s</td>
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<tr>
<td>2.57</td>
<td>vs</td>
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<td>w</td>
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<tr>
<td>2.475</td>
<td>w b</td>
<td>2.45</td>
<td>s</td>
<td>2.44</td>
<td>w</td>
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<td>m</td>
<td>2.39</td>
<td>m</td>
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<tr>
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<td>w</td>
<td>2.282</td>
<td>vw</td>
<td>2.24</td>
<td>m</td>
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<tr>
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<td>w</td>
<td>2.183</td>
<td>s</td>
<td>2.18</td>
<td>w</td>
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<tr>
<td>2.134</td>
<td>s</td>
<td>2.11</td>
<td>w</td>
<td>2.14</td>
<td>m</td>
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<tr>
<td>1.995</td>
<td>vs</td>
<td>2.002</td>
<td>s</td>
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<td>m</td>
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<td>vw</td>
<td>1.94</td>
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<td>s</td>
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<td>1.474</td>
<td>vwe</td>
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<td>s</td>
<td>1.361</td>
<td>m</td>
<td>1.361</td>
<td>m</td>
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<tr>
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<td>ve</td>
<td>1.34</td>
<td>vwe</td>
<td>1.34</td>
<td>ve</td>
</tr>
<tr>
<td>1.421</td>
<td>ve</td>
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<td>w</td>
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<td>m</td>
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<td>1.377</td>
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<td>w</td>
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<td>w</td>
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<tr>
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<td>m</td>
<td>1.24</td>
<td>w</td>
<td>1.24</td>
<td>mw</td>
</tr>
</tbody>
</table>

Values for biotite and Walker's illite with Fe Kα radiations; other samples with Cu Kα radiations.

* Muscovite and biotite from Nagelschmidt.\textsuperscript{4}
† Illite, Gilead, Illinois, from Grim, Bray, and Bradley.\textsuperscript{5}
‡ Illite, Ballater, Scotland, from Mackenzie, Walker, and Hart.\textsuperscript{6}
§ Illite, Carden Wood, Scotland (trihedral), from Walker.\textsuperscript{7}
X-ray-diffraction Data

Table 8. X-ray-diffraction Data for Distinguishing Polymorphic Forms of Mica

(From Grim, Bradley, and Brown)

<table>
<thead>
<tr>
<th>Muscovite</th>
<th>Two-layer phlogopite</th>
<th>Single-layer lepidolite</th>
<th>Three-layer hexagonal zwinnwaldite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indices</td>
<td>d I</td>
<td>Indices d I</td>
<td>Indices d I</td>
</tr>
<tr>
<td>111</td>
<td>4.29 w</td>
<td>021 4.14</td>
<td>013</td>
</tr>
<tr>
<td>022</td>
<td>4.11 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>3.95 vw</td>
<td></td>
<td></td>
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<tr>
<td>113</td>
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<td>023</td>
<td>3.72 m</td>
<td>3.79 w</td>
<td></td>
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<td>113</td>
<td>3.55 vw</td>
<td>3.63 vw</td>
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</tr>
<tr>
<td>114</td>
<td>3.475 m</td>
<td>3.53 w</td>
<td></td>
</tr>
<tr>
<td>024</td>
<td>3.32 *</td>
<td>3.39 *</td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>3.20 m-s</td>
<td>3.27 w</td>
<td></td>
</tr>
<tr>
<td>115</td>
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</tr>
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<td>025</td>
<td>2.98 s</td>
<td>3.03 w-m</td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>2.86 m</td>
<td>2.91 vw</td>
<td>113 2.93 m</td>
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<td>116</td>
<td>2.78 m</td>
<td>2.83 w</td>
<td></td>
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<tr>
<td>026</td>
<td>2.68</td>
<td>2.73 vw</td>
<td>023 2.71 vw</td>
</tr>
</tbody>
</table>

* Coincident with (006); † coincident with (003).

lies between 1.525 and 1.535 kX and (002) is weak or absent. There are some exceptions to this rule, e.g., glauconite, and it must be used with caution. The (060) line is useful in identifying other clay minerals; for kaolinite it is at 1.485 kX and for chlorites at 1.53 to 1.56 kX. This line cannot be used to separate illites and montmorillonites, and care must be taken to avoid confusion with quartz, which can give a reflection at 1.53 kX, if present in abundance of more than about 10 per cent.

Grim, Bradley, and Brown have attempted a correlation of the effect of major substitutions in the mica lattice and the intensities of the (00l) reflections. They have made no computations for substitutions of Li+ and Ti++. Substitutions of Al³⁺ for Si⁴⁺ in the tetrahedral sheet make little or no difference in basal intensities, whereas substitutions in the octahedral sheet cause large intensity variations. The results of Brown’s analyses are given in Figs. 20 and 21. He points out that a comparison of calculated and observed values should make possible a guess at the composition of the octahedral layer, and hence a guess at whether the mica is dioctahedral or trioctahedral (if Li+ and Ti++ are absent or very scant).

Suppose the mica is dioctahedral, then if the second order basal reflection is of the same order of strength as the first and third order, the mica is a highly aluminous member. If the second order basal reflection is weak, or missing, then the
FIG. 20. Graph showing the change in intensities of the (001) reflections with varying composition of the octahedral layer for a dioctahedral mica, after Grim, Bradley, and Brown.28

FIG. 21. Graph showing the change in intensities of the (001) reflections with varying composition of the octahedral layer for a trioctahedral mica, after Grim, Bradley and Brown.29
mica is mainly ferriferous in octahedral positions. If the mineral is known to be of the trioctahedral variety the third and fifth orders should be compared. If the third and fifth orders are of similar intensity, then the mica is of the magnesium end of the series, but if the third order is stronger than the fifth order, then the mica is highly ferriferous.

The intensities shown in Figs. 20 and 21 were calculated from the formula for a single crystal

$$I_{001} = F_{001}^2 \Xi$$

where $F_{001}$ = the structure factor for a particular plane (00l)

$$\Xi = \frac{1 + \cos^2 2\theta}{\sin 2\theta}$$

$\theta$ = Bragg reflection angle

The radiation is assumed to be Cu K\(\alpha\) with $\lambda = 1.54$ kX.

The intensities for the corresponding power diagrams can be calculated by multiplying each intensity value by the factor

$$\frac{\Xi_{\text{powder}}}{\Xi_{\text{single crystal}}} = \frac{1}{\sin \theta}$$

for each plane.

**CHLORITE MINERALS**

X-ray-diffraction data for several chlorite minerals are given in Table 9 after McMurchy\(^{30}\) and Brindley and Ali taken from Brindley and Robinson.\(^{31}\) The variation from one chlorite to another is to be found in slight modifications of intensities or lattice spacings due to small variations of unit-cell dimensions and population of various cation positions. The identification of the various forms of chlorite is very difficult and may be impossible unless chemical and optical data are available to supplement the X-ray analysis. The small size of the clay-mineral chlorite particles and their less regular crystallinity cause some diffuseness of reflections and the absence of some ordinarily weak reflections. As a consequence it is possible now to identify a clay mineral only as belonging to the chlorite group of clay minerals.

Care must be taken in the identification of the chlorite minerals by X-ray diffraction, particularly to avoid confusion with montmorillonite, vermiculite, and kaolinite. Most chlorites give a clear sequence of four or five basal reflections from the 14-kX basal spacing. Chlorites rich in iron, however, give weak first and third orders and strong second and

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Such chlorites may be readily confused with kaolinite unless supplementary techniques are used, as described on page 87.

**Table 9. Diffraction Data from Powder Diagrams of Some Chlorite Minerals**

(After McMurchy and Brindley and Ali taken from the text by Brindley and Robinson)

<table>
<thead>
<tr>
<th>hkl</th>
<th>Sheridanite*</th>
<th>Sheridanite†</th>
<th>Penninite†</th>
<th>Penninite† after 600°C</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>d</td>
<td>I</td>
<td>d</td>
<td>I</td>
</tr>
<tr>
<td>001</td>
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</tr>
<tr>
<td>004</td>
<td>3.509</td>
<td>10</td>
<td>3.518</td>
<td>10</td>
</tr>
<tr>
<td>005</td>
<td>2.828</td>
<td>7</td>
<td>2.816</td>
<td>6</td>
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<tr>
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<td>7</td>
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<td>132, 201</td>
<td>2.542</td>
<td>5</td>
<td>2.521</td>
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<td>2.430</td>
<td>6</td>
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<td>2.247</td>
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<td>2.240</td>
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<tr>
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<td>1.650</td>
<td>1/2</td>
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<tr>
<td>137, 208</td>
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<td>10</td>
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<td>060, 331, 331</td>
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<td>1.502</td>
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<tr>
<td>0010</td>
<td>1.417</td>
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<td>1.409</td>
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<tr>
<td>139, 208</td>
<td>1.390</td>
<td>10</td>
<td>1.386</td>
<td>5</td>
</tr>
<tr>
<td>400</td>
<td>1.319</td>
<td>4</td>
<td>1.312</td>
<td>1</td>
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</tbody>
</table>

* Sheridanite from McMurchy; unfiltered Cu K radiation; camera radius 57.3 mm.
† Sheridanite, penninite, from Brindley and Ali; filtered Cu Ka radiation; camera radius 100 mm.

The characteristic 14-kX spacing may be confused with that of montmorillonite or vermiculite even though it is generally sharper in the chlorites. For chlorites the 14-kX spacing is not changed on moderate heatings to about 200°C, as it is in vermiculite, nor is it changed by treatment with a polar organic molecule (like glycol), as it is in the montmorillonites.
VERMICULITE MINERALS

Diffraction data for two vermiculites are given in Table 10 after Gruner.\textsuperscript{32} Diffraction data for another sample not heated and heated to successively higher temperatures are given in Table 11 after Walker.\textsuperscript{33} The strong reflection at 14 kX is characteristic of the mineral, but care must be used to differentiate vermiculite from chlorite, which also has a reflection at 14 kX, and from montmorillonite, which may show a reflection at this position.

Vermiculite can usually be distinguished from chlorite on the basis of the intensity of the (00l) reflections: In vermiculite the 14-kX line is the strongest reflection, and the 7-kX line and subsequent basal orders are relatively weaker; whereas in chlorite several basal orders may occur of approximately equal intensity. Vermiculite can be further distinguished from chlorite by the fact that the basal spacings are more readily shifted by heating. Also, treatment with certain organic molecules causes a shift in the basal reflections for vermiculite and not for chlorite.

Possible confusion of kaolinite with minerals giving a 14-kX reflection have already been considered (see page 87). Care must be taken not to confuse mixtures of kaolinite and vermiculite with chlorite, and this usually requires that diffraction data be obtained for samples which have been heated as well as for the natural sample.

Vermiculites and montmorillonite may both show a 14-kX reflection. A distinction can usually be made because this reflection changes readily for slight variations of relative humidity in montmorillonite, whereas the vermiculites are stable over a wide range of moisture contents. Further, it appears that vermiculite forms only a single molecular layer of organic molecules between the mica sheets, whereas montmorillonites may form multimolecular layers with certain organic molecules.

SEPIOLITE-ATTAPULGITE-PALYGORSKITE MINERALS

Diffraction data for sepiolite, after Longchambon,\textsuperscript{34} and attapulgite, after Bradley,\textsuperscript{35} are given in Tables 12 and 13, respectively. The general


\textsuperscript{34} Longchambon, H., Sur certaines caractéristiques de la sepiolite d’Ampandandrava et la formule des sepiolites, \textit{Bull. soc. franç. minéral.}, 60, 232-276 (1937).

\textsuperscript{35} Bradley, W. F., The Structural Scheme of Attapulgite, \textit{Am. Mineral.}, 25, 405-413 (1940).
### Table 10. Diffraction Data for Vermiculite from Powder Diagrams

(After Gruner 32)

<table>
<thead>
<tr>
<th>Indices</th>
<th>Baltimore, Maryland</th>
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<tr>
<td>002</td>
<td>13.4</td>
<td>8</td>
</tr>
<tr>
<td>004</td>
<td>7.03</td>
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<tr>
<td>008$\beta$</td>
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<td>130, 202, 132, 200, 136$\delta$, 204$\delta$</td>
<td>2.6 $\beta$</td>
<td>1 $\beta$</td>
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<td>2 $\beta$</td>
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<td>1316$\delta$, 2018$\delta$</td>
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</tr>
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<td>0.5</td>
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</tbody>
</table>

Photographs taken with unfiltered Fe K radiations. Because of the method of mounting, the basal reflections are somewhat enhanced relatively in intensity. $i = \text{indistinct edge of line}; b = \text{broad line}; vb = \text{very broad line}; \beta = \text{a line produced by K$\beta$ radiation of iron.}$
### X-ray-diffraction Data

#### Table 11. Diffraction Data for Vermiculite from West Chester, Pennsylvania, Heated and Unheated

*(After Walker)*

<table>
<thead>
<tr>
<th>Unheated</th>
<th>Heated to 200°C for 2 hr</th>
<th>Heated to 500°C for 24 hr</th>
<th>Heated to 700°C for 24 hr</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$d$</td>
<td>$I$</td>
<td>$d$</td>
</tr>
<tr>
<td>14.2</td>
<td>10</td>
<td>14.0</td>
<td>10</td>
</tr>
<tr>
<td>7.1</td>
<td>2$^d$</td>
<td></td>
<td>4.56</td>
</tr>
<tr>
<td>4.75</td>
<td>0.5</td>
<td></td>
<td>3.50</td>
</tr>
<tr>
<td>3.75</td>
<td>3</td>
<td></td>
<td>3.51</td>
</tr>
<tr>
<td>3.42</td>
<td>5</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>2.81</td>
<td>4</td>
<td>2.86</td>
<td>2</td>
</tr>
<tr>
<td>2.74</td>
<td>1</td>
<td>2.75</td>
<td>2</td>
</tr>
<tr>
<td>2.63</td>
<td>5</td>
<td>2.61</td>
<td>4</td>
</tr>
<tr>
<td>2.53</td>
<td>3</td>
<td></td>
<td>2.49</td>
</tr>
<tr>
<td>2.373</td>
<td>4$^b$</td>
<td>2.38</td>
<td>2</td>
</tr>
<tr>
<td>2.291</td>
<td>0.5</td>
<td>2.29</td>
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</tr>
<tr>
<td>2.084</td>
<td>0.5</td>
<td>2.09</td>
<td>2</td>
</tr>
<tr>
<td>2.006</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.963</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.736</td>
<td>1</td>
<td>1.73</td>
<td>1</td>
</tr>
<tr>
<td>1.649</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.530</td>
<td>6</td>
<td>1.528</td>
<td>6</td>
</tr>
<tr>
<td>1.501</td>
<td>0.5</td>
<td></td>
<td>1.439</td>
</tr>
<tr>
<td>1.438</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.406</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.325</td>
<td>2</td>
<td>1.32</td>
<td>4</td>
</tr>
<tr>
<td>1.311</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.270</td>
<td>0.5</td>
<td>1.269</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Photographs taken with Fe $K_{\alpha}$ radiations.

After heating, samples cooled without sealing to prevent rehydration.

Relative intensity estimated visually; $d =$ diffuse; $b =$ broad.
Clay Mineralogy

difference in the diffraction patterns of these minerals as compared to those of other clay minerals makes them readily distinguishable.

Sepiolite shows a characteristic diffraction at 12.15 kX and attapulgite at 10.48 kX. These spacings do not change with variations in relative humidity or moderate heating up to about 300°C. Also they are not changed by treatment with organic polar molecules, and therefore they should not be confused with the expanding, layer clay minerals or with halloysite. They do exhibit a change in diffraction characteristics on heating to over 300°C (see Chap. 9), which can be used as a further means of identifying them.

### Table 12. Lattice Spacings and Estimated Intensities of Sepiolite

<table>
<thead>
<tr>
<th>d</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.15 ± 0.15</td>
<td>10</td>
</tr>
<tr>
<td>7.6 ± 0.10</td>
<td>3</td>
</tr>
<tr>
<td>6.05 ± 0.105</td>
<td>2</td>
</tr>
<tr>
<td>4.60 ± 0.10</td>
<td>10</td>
</tr>
<tr>
<td>3.82 ± 0.02</td>
<td>5</td>
</tr>
<tr>
<td>3.60 ± 0.02</td>
<td>1</td>
</tr>
<tr>
<td>3.40 ± 0.02</td>
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</tr>
<tr>
<td>3.22 ± 0.02</td>
<td>5</td>
</tr>
<tr>
<td>2.61 ± 0.02</td>
<td>8</td>
</tr>
<tr>
<td>2.45 ± 0.02</td>
<td>7</td>
</tr>
<tr>
<td>2.28</td>
<td>6</td>
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<tr>
<td>2.09</td>
<td>5</td>
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<td>1.97</td>
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<tr>
<td>1.36</td>
<td>2</td>
</tr>
<tr>
<td>1.31</td>
<td>3</td>
</tr>
</tbody>
</table>

MIXED-LAYER STRUCTURES

In the case of mixtures of discrete clay-mineral particles, a diffraction pattern will contain reflections typical of each component. The characteristics will be no different from that resulting from a mixture of clay minerals and nonclay minerals, for example, when quartz is present in the clay material.

In the case of a mixture which is a regular interstratification of layer clay minerals, the diffraction effect is equivalent to a larger unit cell which is a multiple of the individual layers. The regularity of the structures is maintained on a larger scale, and an integral series of (00l)
X-ray-diffraction Data

Reflections is obtained from the larger unit cell. The structure of chlorite is an example of this type of mixing.

If the mixture is a random interstratification of layer clay minerals, and only a very few layers of a second type are present, the reflections will differ very little from those of the dominant layer. If, however, the

TABLE 13. X-RAY-DIFFRACTION DATA FOR ATTAPULGITE
(After Bradley3.)

<table>
<thead>
<tr>
<th>Data calculated from proposed structure</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hkl</td>
</tr>
<tr>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
</tr>
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<td>130</td>
<td>130</td>
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<tr>
<td>220</td>
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<td>040</td>
<td>040</td>
</tr>
<tr>
<td>310</td>
<td>310</td>
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<tr>
<td>240</td>
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<tr>
<td>330</td>
<td>330</td>
</tr>
<tr>
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<td>400</td>
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<tr>
<td>510</td>
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<tr>
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<td>660</td>
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<td>800</td>
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</tr>
<tr>
<td>680</td>
<td>680</td>
</tr>
<tr>
<td>0120</td>
<td>0120</td>
</tr>
</tbody>
</table>

Data obtained with Cu Kα radiations.

second type of layer is present in considerable abundance (> 10%±), new diffraction effects will arise; in particular, a nonintegral series of reflections is obtained from the basal planes. Also the layers can contribute to the scattering only as individuals. Prism zone reflections and the scattering distribution from the bases are to be expected, but special sequences such as the (11l) and (02l) interference for muscovite, which depend on a specific mutual orientation of neighboring layers, cannot be given by a mixed structure. There is, therefore, likely to be no diffraction distinction between muscovite and biotite in mixed-layer structures.
In mixed-layer structures the basal reflections are composites of adjacent reflections of the same orders of the different layers and at an intermediate position between them, or a composite of overlapping reflections of different orders of the different layers. The position and intensity of the composite reflections will vary with the relative abundance of the different individual layers. For example, in a random mixed-layer structure of 10-\(k\alpha\) and 15-\(k\alpha\) layers, the first observed reflection will be a composite of (001) of both layers and will have a spacing intermediate between 10 and 15 \(k\alpha\), the exact position depending on the relative abundance of the individual layers. A strong reflection at 5 \(k\alpha\) will appear; this will be a composite of (002) of the 10-\(k\alpha\) layers and (003) of the 15-\(k\alpha\) layers. Only if the relative amount of the 15-\(k\alpha\) layer is large will a slight reflection be found at about 7.5 \(k\alpha\).

In the case of random mixture of a 17.7-\(k\alpha\) layer and a 10-\(k\alpha\) layer, where both are present in considerable abundance, the first reflection will be a composite of (001) of both layers, and the second reflection will be a composite of (001) of the 10-\(k\alpha\) layer and (002) of the 17.7-\(k\alpha\) layer. The position and relative intensity of the composite peaks, or, more properly, bands, will vary with the relative abundance of the two layers. It should be pointed out that the position and intensity of the composite peaks do not vary with the relative abundance of the constituent layers in a necessarily straight-line relationship.

The above illustrations will serve to show how a nonintegral series of reflections arises from a random mixing of layers. The mathematical theory of X-ray diffraction for such statistical structures has been discussed by Hendricks and Teller\(^{36}\) and later by Mering.\(^{37}\) Brown and MacEwan\(^{38}\) have very recently presented a further discussion of this matter and an extremely useful series of graphs, showing the expected basal reflections of mixtures of various proportions of a variety of layers. The reader is referred to these works for further details of mixed-layer structures.

**ADDITIONAL REFERENCES**


Brindley, G. W., and D. M. C. MacEwan, The Interpretation of Composite X-ray

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X-ray-diffraction Data


Many of the references given with Chap. 4 on Structure of the Clay Minerals also contain X-ray-diffraction data.
CHAPTER 6

Shape and Size—Electron Micrographs

GENERAL STATEMENT

The use of the electron microscope has permitted the precise determination of the shape of the particles of various clay minerals and has shed light on the range of particle size of the components of clay and on the degree to which the particle size can be reduced when the clay is worked mechanically with water. Numerous investigators have published electron micrographs of the clay minerals and discussed electron-microscopic techniques as applied to clay-mineral researches. Particularly worthy of mention are the contributions of Ardenne, Eitel, Middel, Humbert, Shaw, Marshall, Alexander, Moore, Bates, Kerr, and their various collaborators. For general details of technique, the works of these authors should be consulted, as well as the texts by Zworykin et al. and Cosslett.

Some of the electron micrographs presented herein are reproduced with permission from the report\textsuperscript{10} of Project 49 of the American Petroleum Institute. Other electron micrographs published in this volume were kindly obtained by Prof. T. A. Bates of Pennsylvania State College expressly for this volume. It is desired to acknowledge the great kindness and courtesy of Professor Kerr and the American Petroleum Institute in permitting the reproduction of their micrographs and of Professor Bates for supplying and permitting the publication of his work.

In electron microscopy, the image formation is due to the scattering of electrons as the electron beam passes through the sample. In the early work, the clay-mineral particles were mounted directly in the electron beam without any treatment. In later work the shadow method of preparing samples has been used frequently in order to show the thickness of the units better and to increase the contrast of the particles against the background. In the shadow method, mounted specimens are placed in a metal evaporator, where some metal, frequently uranium or beryllium, is evaporated onto the specimen mounts obliquely. The angle of deposition of the metal is varied according to the thickness of particles in the sample. Angles of about 10° are used for thin particles, while angles up to 30° are used for thicker particles. Direct magnifications of from 3,000 to 15,000 are obtained, and these are increased from three to five times by photographic enlargement.

Both positive and negative prints are used in this volume. The positive prints cast white shadows, and the negative prints cast black shadows.

In electron microscopy the specimens become heated by energy absorption. Since heating to low temperature (60° to 100°C) causes dehydration reactions of some of the clay minerals, \textit{e.g.,} halloysite, vermiculite, and montmorillonite, care must be taken to register the original character of these minerals.

Hast\textsuperscript{13} has applied the replica technique to the study of clay. In his method, a replica peel of cellulose nitrate is obtained from a freshly fractured surface of the clay. The peel is obtained by coating the surface of the clay with cellulose nitrate dissolved in amyl acetate and allowing the acetate to evaporate. The peel is coated with vaporized beryllium or aluminum 25 to 50 Å thick, after which the cellulose nitrate film is dissolved away in amyl acetate. The metal replica is then mounted in the electron beam. Applying the technique to bentonites, Hast\textsuperscript{13} has found evidence of a "thread-like" stacking arrangement of the montmorillonite particles. Further work is necessary before the apparent results yielded by the method can be evaluated.

Allophane. As would be expected, this amorphous material is found in particles without any definite and regular shape. The electron micrograph of the sample from Indiana (Fig. 22) shows a rounded nodular appearance which is perhaps characteristic of that developed by amorphous material on drying. Occasional holes are to be seen in the rounded masses; these may be attributed to shrinkage on drying. The sample from Woolwich, England (Fig. 23) shows particles somewhat rounded, but in general with an irregular shape.

Kaolinite. Electron micrographs of well-crystallized kaolinite (Fig. 24) show well-formed six-sided flakes, frequently with a prominent elongation (Fig. 26) in one direction. The elongation is parallel to either (010) or (110). Certain of the edges of the particles are beveled instead of being at right angles to the flake surface. Occasionally the particles appear to be twinned. In poorly crystallized kaolinite, the particles show less distinct six-sided flakes. The edges of the flakes are somewhat ragged and irregular, and the hexagonal outline is only crudely shown (Fig. 25).

Anauxite from the type locality (Fig. 27) is in hexagonal flakes, which are frequently somewhat ragged and irregular.

Electron micrographs of various kaolinite samples have shown particles with maximum dimensions of flake surfaces from 0.3 to about 4 microns and thicknesses from 0.05 to about 2 microns. This does not mean that larger particles of kaolinite are not present in some clays, since such larger particles may have been split or otherwise reduced in size in the preparation of the sample for the electron microscopy. It does mean, however, that kaolinite particles are easily reduced to this size but are not reduced to smaller sizes except with difficulty, e.g., after much mechanical working.

In general, poorly crystallized kaolinite occurs in smaller particles than the well-crystallized mineral. It does not always follow that kaolinite with a very small particle size has a low degree of crystallinity. For example, the kaolinite component of some so-called flint clays is extremely fine-grained and extremely well crystallized.

Dickite. Dickite occurs in well-formed, six-sided, flake-shaped particles frequently showing a definite elongation in one direction (Fig. 28). Samples which have been examined show flake surface dimensions ranging from about 2.5 to 8 microns and thickness dimensions of 0.07 to 0.25 micron. Dickite particles are often large enough to be studied with the light microscope.

Nacrite. Electron micrographs of a few samples of nacrite show somewhat irregular, rounded, flake-shaped units. In some particles a crude
FIG. 22. Electron micrograph of allophane, Lawrence County, Indiana, from Kerr.
Fig. 34. Electron micrograph of nontronite, Sandy Ridge, North Carolina, from Bates.

Fig. 35. Electron micrograph of saponite, Death Valley, California, from Kerr.
Some of the magnesium-rich members of the montmorillonite group appear to be composed of equidimensional flake-shaped units about like those of the aluminum-rich montmorillonites. The saponite from Death Valley, California, illustrates such material (Fig. 35). However, hectorite, the fluorine-bearing magnesium-rich montmorillonite, is found in thin laths, which often lose their identity when gathered into aggregates (Fig. 36). The laths attain a length of about 1 micron and a width of about 0.1 micron. The thinnest laths appear to be only 12 to 18 A thick. Some of the particles are terminated by edges intersecting the long edges at distinct angles which, however, are not of uniform size.

Sauconite (Fig. 37) appears to occur in broad laths, which are approximately 50 A thick. The particles in Fig. 37 show a variety of habits, and some of them may be other montmorillonite clay minerals.

Illite. The electron micrograph of Fithian illite (Fig. 38) shows small, poorly defined flakes, commonly grouped together in irregular aggregates. Some of the flakes have a distinct hexagonal outline. The thinnest flakes are approximately 30 A thick. Many of the flakes have a diameter of 0.1 to 0.3 micron. Some other illites (see, for example, Fig. 39) show no evidence of flakes with hexagonal outlines. Such flakes have irregular but well-defined outlines and are characterized by a uniform thickness. The electron micrographs of illite resemble those of some montmorill-

Fig. 39. Electron micrograph of illite (brammallite), South Wales, from Bates.

Fig. 40. Electron micrograph of illite, Skytop, Pennsylvania, from Bates.
I lonites. The particles of illite are, however, larger and thicker and have better-defined edges.

Figure 40 shows lath-shaped particles of illite obtained in studies by Dr. C. E. Weaver of Pennsylvania State College. With the exception of morphology, this material has all the attributes of other illites. It occurs in the -1-micron fraction of a sandstone. The hexagonal flakes associated with the laths are probably kaolinite. The significance of an elongate form of illite has not been determined.

Vermiculite and Chlorite. No information is available regarding the electron micrography of the vermiculite and chlorite clay minerals. It appears probable from structural considerations that electron micrographs of these minerals would be similar to those of the illites, except that vermiculite might occur in thinner flakes.

Attapulgite-Sepiolite-Palygorskite. Attapulgite is shown by electron micrographs (Fig. 41) to occur in single laths and bundles of laths. There appears to be no evidence of a tubular form like that found for halloysite. The laths attain a maximum length of about 4 to 5 microns, a maximum thickness of 50 to 100 A, and a width only two or three times the thickness. There appears to be a tendency for two or three laths to form a parallel bundle or for a great many laths to form thick bundles.

16 Weaver, C. E., manuscript in preparation.
Fig. 42. Electron micrograph of alpha sepiolite, Little Cottonwood, Utah, from Kerr.
Fig. 43. Electron micrograph of beta sepiolite, Baldissero, Italy, from Kerr.

Fig. 44. Electron micrograph of mixed-layer metabentonite, Oak Hill, Pennsylvania, from Bates.
Some sepiolites are elongate and fibrous like attapulgite (Fig. 42), and this type has been called alpha-sepiolite or parasepiolite by Fersmann. Other sepiolites, called beta-sepiolite by Fersmann, are composed of extremely small flake-shaped units of irregular outline (Fig. 43). In some cases the elongate variety appears to have a tubular character, but this attribute has not yet been definitely established. The sepiolite fibers are about the same size as those of attapulgite. The dimensions of the flaky variety are not well known, but the maximum dimension is less than about 1 micron. The cause of the difference between the two types is not known definitely, but it may be that the flake shape results from some replacement of magnesium by aluminum in the structure.

Mixed-layer Minerals. Adequate data for any generalizations on the electron micrography of mixed-layer minerals are not available. Figure 44 was obtained from a metabentonite composed of a random interstratification of about 80 per cent illite (nonexpanding, dioctahedral) and 20 per cent expandable clay mineral. The micrograph shows thin flakes with irregular but well-defined outlines. The flakes are quite thin, and there is rather little tendency for them to aggregate.

ADDITIONAL REFERENCES


hexagonal outline can be seen (Fig. 29). In these samples, the flakes are generally less than about 1 micron in diameter, and the thickness is about 0.025 to 0.15 micron.

**Halloysite.** Numerous investigators have shown that the morphology of halloysite is quite different from that of kaolinite, the former being elongate instead of flake-shaped (Figs. 30 and 31). Primarily because of the work of Bates, halloysite is now known to appear in electron micrographs as elongate tubular particles. Convincing evidence of the tubular development is furnished by the doughnut forms, believed to be the ends of tubular particles, that are seen in some electron micrographs. Sometimes it is difficult to determine if the halloysite particles are actually tubes or flake-shaped units which have curled and rolled up at their edges. Bates states his belief that the rolling-up process is possible in very thin flakes where the number of silicate layers is so few that the strain produced by the misfit of silicon-oxygen and aluminum-hydroxyl sheets in each layer is not overcome by the cumulative effect of interlayer bonds between a large number of successive layers.

Bates has determined the dimensions of the halloysite tubes from the electron micrographs of many samples. The outside diameters were found to range from 0.04 to 0.19 micron with a median value of 0.07 micron. Inside diameters were found to have a median value of 0.04

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FIG. 24. Electron micrograph of kaolinite, Macon, Georgia, from Kerr.
Fig. 25. Electron micrograph of kaolinite, Mesa Alta, New Mexico, from Kerr.

Fig. 26. Electron micrograph of kaolinite, Zetlitz, Czechoslovakia, from Bates.
FIG. 27. Electron micrograph of anauxite, Bilin, Czechoslovakia, from Kerr.
Fig. 28. Electron micrograph of dickite, San Juanito, Mexico, from Kerr.

Fig. 29. Electron micrograph of nacrite, Brand, Saxony, from Kerr.
Fig. 30. Electron micrograph of halloysite, British Guiana, from Bates.

Fig. 31. Electron micrograph of halloysite, Wendover, Utah, from Bates.
micron with a range from 0.02 to 0.1 micron. The average wall thickness was found to be 0.02 micron. Figure 31 shows a high degree of uniformity of size among the halloysite particles; this feature is not characteristic of many halloysites from other localities.

Some of the electron micrographs of halloysite (2H₂O) show split ends and partially unrolled tubes. This phenomenon appears to develop as a consequence of the change from the 4H₂O to the 2H₂O form of the mineral.

**Montmorillonite.** Numerous electron micrographs of montmorillonite (Figs. 32 and 33) show irregular fluffy masses of extremely small particles. Frequently, details concerning the individual particles are not revealed, but in some cases the larger masses appear to be stackings of flake-shaped units without regular outlines. Some of the individual particles appear to be about 0.002 micron thick, from which it can be concluded that at least some montmorillonites break down relatively easily to flakes approaching unit-cell thickness. Accurate estimations of the areal dimensions of the flakes are difficult to obtain because of their irregularity but are probably of the order of 10 to 100 times the thickness.

Mathieu-Sicaud, Mering, and Perrin-BonneV have shown that variations in the exchangeable cation carried by montmorillonites are reflected in their appearance in electron micrographs. According to them, Na montmorillonite appears as a more or less continuous, nebulous, film-like assemblage, frequently showing cracks intersecting at 120°. H montmorillonite appears as a mosaic of aggregate masses with distinct hexagonal outlines, which are often 300 A in diameter and 50 to 80 A thick. Ca montmorillonite appears as irregular aggregates, which increase in size as the preparatory suspension is aged. At concentrations of Ca⁺⁺ at least equal to the cation-exchange capacity, the aggregates grow in thickness as well as laterally. According to Mathieu-Sicaud et al. these differences are due to variations in the attraction between the montmorillonite particles and in the relative strength of the attractive forces at the edges of the particles and on their basal planes.

Electron micrographs of nontronite show that the iron-rich member of the montmorillonite group tends to occur in elongate lath-shaped units (Fig. 34), although flakes, needles, and rods of varying size are also evident. In some samples the particles appear to show striations parallel to the maximum dimension. The length of the laths may reach several microns and is frequently about five times the width dimension. The thickness of the laths has a minimum dimension of the order of one or a few unit cells.

FIG. 32. Electron micrograph of montmorillonite, Yavapai County, Arizona, from Bates.

FIG. 33. Electron micrograph of montmorillonite, Upton, Wyoming, from Kerr.
DATA FOR THE CLAY MINERALS

**Allophane.** As would be expected, this amorphous material is found in particles without any definite and regular shape. The electron micrograph of the sample from Indiana (Fig. 22) shows a rounded nodular appearance which is perhaps characteristic of that developed by amorphous material on drying. Occasional holes are to be seen in the rounded masses; these may be attributed to shrinkage on drying. The sample from Woolwich, England (Fig. 23) shows particles somewhat rounded, but in general with an irregular shape.

**Kaolinite.** Electron micrographs of well-crystallized kaolinite (Fig. 24) show well-formed six-sided flakes, frequently with a prominent elongation (Fig. 26) in one direction. The elongation is parallel to either (010) or (110). Certain of the edges of the particles are beveled instead of being at right angles to the flake surface. Occasionally the particles appear to be twinned. In poorly crystallized kaolinite, the particles show less distinct six-sided flakes. The edges of the flakes are somewhat ragged and irregular, and the hexagonal outline is only crudely shown (Fig. 25).

Anauxite from the type locality (Fig. 27) is in hexagonal flakes, which are frequently somewhat ragged and irregular.

Electron micrographs of various kaolinite samples have shown particles with maximum dimensions of flake surfaces from 0.3 to about 4 microns and thicknesses from 0.05 to about 2 microns. This does not mean that larger particles of kaolinite are not present in some clays, since such larger particles may have been split or otherwise reduced in size in the preparation of the sample for the electron microscopy. It does mean, however, that kaolinite particles are easily reduced to this size but are not reduced to smaller sizes except with difficulty, e.g., after much mechanical working.

In general, poorly crystallized kaolinite occurs in smaller particles than the well-crystallized mineral. It does not always follow that kaolinite with a very small particle size has a low degree of crystallinity. For example, the kaolinite component of some so-called flint clays is extremely fine-grained and extremely well crystallized.

**Dickite.** Dickite occurs in well-formed, six-sided, flake-shaped particles frequently showing a definite elongation in one direction (Fig. 28). Samples which have been examined show flake surface dimensions ranging from about 2.5 to 8 microns and thickness dimensions of 0.07 to 0.25 micron. Dickite particles are often large enough to be studied with the light microscope.

**Nacrite.** Electron micrographs of a few samples of nacrite show somewhat irregular, rounded, flake-shaped units. In some particles a crude
micron with a range from 0.02 to 0.1 micron. The average wall thickness was found to be 0.02 micron. Figure 31 shows a high degree of uniformity of size among the halloysite particles; this feature is not characteristic of many halloysites from other localities.

Some of the electron micrographs of halloysite ($2H_2O$) show split ends and partially unrolled tubes. This phenomenon appears to develop as a consequence of the change from the $4H_2O$ to the $2H_2O$ form of the mineral.

**Montmorillonite.** Numerous electron micrographs of montmorillonite (Figs. 32 and 33) show irregular fluffy masses of extremely small particles. Frequently, details concerning the individual particles are not revealed, but in some cases the larger masses appear to be stackings of flake-shaped units without regular outlines. Some of the individual particles appear to be about 0.002 micron thick, from which it can be concluded that at least some montmorillonites break down relatively easily to flakes approaching unit-cell thickness. Accurate estimations of the areal dimensions of the flakes are difficult to obtain because of their irregularity but are probably of the order of 10 to 100 times the thickness.

Mathieu-Sicaud, A., Mering, and Perrin-Bonnet have shown that variations in the exchangeable cation carried by montmorillonites are reflected in their appearance in electron micrographs. According to them, Na montmorillonite appears as a more or less continuous, nebulous, film-like assemblage, frequently showing cracks intersecting at 120°. H montmorillonite appears as a mosaic of aggregate masses with distinct hexagonal outlines, which are often 300 A in diameter and 50 to 80 A thick. Ca montmorillonite appears as irregular aggregates, which increase in size as the preparatory suspension is aged. At concentrations of Ca++ at least equal to the cation-exchange capacity, the aggregates grow in thickness as well as laterally. According to Mathieu-Sicaud et al., these differences are due to variations in the attraction between the montmorillonite particles and in the relative strength of the attractive forces at the edges of the particles and on their basal planes.

Electron micrographs of nontronite show that the iron-rich member of the montmorillonite group tends to occur in elongate lath-shaped units (Fig. 34), although flakes, needles, and rods of varying size are also evident. In some samples the particles appear to show striations parallel to the maximum dimension. The length of the laths may reach several microns and is frequently about five times the width dimension. The thickness of the laths has a minimum dimension of the order of one or a few unit cells.

Fig. 22. Electron micrograph of allophane, Lawrence County, Indiana, from Kerr.
Fig. 34. Electron micrograph of nontronite, Sandy Ridge, North Carolina, from Bates.

Fig. 35. Electron micrograph of saponite, Death Valley, California, from Kerr.
Some of the magnesium-rich members of the montmorillonite group appear to be composed of equidimensional flake-shaped units about like those of the aluminum-rich montmorillonites. The saponite from Death Valley, California, illustrates such material (Fig. 35). However, hectorite, the fluorine-bearing magnesium-rich montmorillonite, is found in thin laths, which often lose their identity when gathered into aggregates (Fig. 36). The laths attain a length of about 1 micron and a width of about 0.1 micron. The thinnest laths appear to be only 12 to 18 A thick. Some of the particles are terminated by edges intersecting the long edges at distinct angles which, however, are not of uniform size.

Sauconite (Fig. 37) appears to occur in broad laths, which are approximately 50 A thick. The particles in Fig. 37 show a variety of habits, and some of them may be other montmorillonite clay minerals.

Illite. The electron micrograph of Fithian illite (Fig. 38) shows small, poorly defined flakes, commonly grouped together in irregular aggregates. Some of the flakes have a distinct hexagonal outline. The thinnest flakes are approximately 30 A thick. Many of the flakes have a diameter of 0.1 to 0.3 micron. Some other illites (see, for example, Fig. 39) show no evidence of flakes with hexagonal outlines. Such flakes have irregular but well-defined outlines and are characterized by a uniform thickness. The electron micrographs of illite resemble those of some montmoril-
Fig. 37. Electron micrograph of sauconite, Friedensville Ridge, Pennsylvania, from Bates.

Fig. 39. Electron micrograph of illite (brammallite), South Wales, from Bates.

Fig. 40. Electron micrograph of illite, Skytop, Pennsylvania, from Bates.
Illites. The particles of illite are, however, larger and thicker and have better-defined edges.

Figure 40 shows lath-shaped particles of illite obtained in studies by Dr. C. E. Weaver\(^{16}\) of Pennsylvania State College. With the exception of morphology, this material has all the attributes of other illites. It occurs in the -1-micron fraction of a sandstone. The hexagonal flakes associated with the laths are probably kaolinite. The significance of an elongate form of illite has not been determined.

Vermiculite and Chlorite. No information is available regarding the electron micrography of the vermiculite and chlorite clay minerals. It appears probable from structural considerations that electron micrographs of these minerals would be similar to those of the illites, except that vermiculite might occur in thinner flakes.

Attapulgite-Sepiolite-Palygorskite. Attapulgite is shown by electron micrographs (Fig. 41) to occur in single laths and bundles of laths. There appears to be no evidence of a tubular form like that found for halloysite. The laths attain a maximum length of about 4 to 5 microns, a maximum thickness of 50 to 100 A, and a width only two or three times the thickness. There appears to be a tendency for two or three laths to form a parallel bundle or for a great many laths to form thick bundles.

\(^{16}\) Weaver, C. E., manuscript in preparation.
Fig. 42. Electron micrograph of alpha sepiolite, Little Cottonwood, Utah, from Kerr.
Fig. 43. Electron micrograph of beta sepiolite, Baldissaro, Italy, from Kerr.

Fig. 44. Electron micrograph of mixed-layer metabentonite, Oak Hill, Pennsylvania, from Bates.
Some sepiolites are elongate and fibrous like attapulgite (Fig. 42), and this type has been called alpha-sepiolite or parasepiolite by Fersmann. Other sepiolites, called beta-sepiolite by Fersmann, are composed of extremely small flake-shaped units of irregular outline (Fig. 43). In some cases the elongate variety appears to have a tubular character, but this attribute has not yet been definitely established. The sepiolite fibers are about the same size as those of attapulgite. The dimensions of the flaky variety are not well known, but the maximum dimension is less than about 1 micron. The cause of the difference between the two types is not known definitely, but it may be that the flake shape results from some replacement of magnesium by aluminum in the structure.

Mixed-layer Minerals. Adequate data for any generalizations on the electron micrography of mixed-layer minerals are not available. Figure 44 was obtained from a metabentonite composed of a random interstratification of about 80 per cent illite (nonexpanding, dioctahedral) and 20 per cent expandable clay mineral. The micrograph shows thin flakes with irregular but well-defined outlines. The flakes are quite thin, and there is rather little tendency for them to aggregate.

ADDITIONAL REFERENCES


hexagonal outline can be seen (Fig. 29). In these samples, the flakes are generally less than about 1 micron in diameter, and the thickness is about 0.025 to 0.15 micron.

**Halloysite.** Numerous investigators have shown that the morphology of halloysite is quite different from that of kaolinite, the former being elongate instead of flake-shaped (Figs. 30 and 31). Primarily because of the work of Bates, halloysite is now known to appear in electron micrographs as elongate tubular particles. Convincing evidence of the tubular development is furnished by the doughnut forms, believed to be the ends of tubular particles, that are seen in some electron micrographs. Sometimes it is difficult to determine if the halloysite particles are actually tubes or flake-shaped units which have curled and rolled up at their edges. Bates states his belief that the rolling-up process is possible in very thin flakes where the number of silicate layers is so few that the strain produced by the misfit of silicon-oxygen and aluminum-hydroxyl sheets in each layer is not overcome by the cumulative effect of interlayer bonds between a large number of successive layers.

Bates has determined the dimensions of the halloysite tubes from the electron micrographs of many samples. The outside diameters were found to range from 0.04 to 0.19 micron with a median value of 0.07 micron. Inside diameters were found to have a median value of 0.04

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Bates, T. F., Personal Communication.
Fig. 24. Electron micrograph of kaolinite, Macon, Georgia, from Kerr.
FIG. 25. Electron micrograph of kaolinite, Mesa Alta, New Mexico, from Kerr.

Fig. 27. Electron micrograph of anauxite, Bilin, Czechoslovakia, from Kerr.
Fig. 28. Electron micrograph of dickite, San Juanito, Mexico, from Kerr.

Fig. 29. Electron micrograph of nacrite, Brand, Saxony, from Kerr.

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Fig. 32. Electron micrograph of montmorillonite, Yavapai County, Arizona, from Bates.

Fig. 33. Electron micrograph of montmorillonite, Upton, Wyoming, from Kerr.
**DATA FOR THE CLAY MINERALS**

**Allophane.** As would be expected, this amorphous material is found in particles without any definite and regular shape. The electron micrograph of the sample from Indiana (Fig. 22) shows a rounded nodular appearance which is perhaps characteristic of that developed by amorphous material on drying. Occasional holes are to be seen in the rounded masses; these may be attributed to shrinkage on drying. The sample from Woolwich, England (Fig. 23) shows particles somewhat rounded, but in general with an irregular shape.

**Kaolinite.** Electron micrographs of well-crystallized kaolinite (Fig. 24) show well-formed six-sided flakes, frequently with a prominent elongation (Fig. 26) in one direction. The elongation is parallel to either (010) or (110). Certain of the edges of the particles are beveled instead of being at right angles to the flake surface. Occasionally the particles appear to be twinned. In poorly crystallized kaolinite, the particles show less distinct six-sided flakes. The edges of the flakes are somewhat ragged and irregular, and the hexagonal outline is only crudely shown (Fig. 25).

Anauxite from the type locality (Fig. 27) is in hexagonal flakes, which are frequently somewhat ragged and irregular. Electron micrographs of various kaolinite samples have shown particles with maximum dimensions of flake surfaces from 0.3 to about 4 microns and thicknesses from 0.05 to about 2 microns. This does not mean that larger particles of kaolinite are not present in some clays, since such larger particles may have been split or otherwise reduced in size in the preparation of the sample for the electron microscopy. It does mean, however, that kaolinite particles are easily reduced to this size but are not reduced to smaller sizes except with difficulty, e.g., after much mechanical working.

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ADDITIONAL REFERENCES


CHAPTER 7

Ion Exchange

The clay minerals have the property of sorbing certain anions and cations and retaining these in an exchangeable state; i.e., these ions are exchangeable for other anions or cations by treatment with such ions in a water solution [the exchange reaction also takes place sometimes in a nonaqueous environment (see page 141)]. The exchange reaction is stoichiometric. The exchangeable ions are held around the outside of the silica-alumina clay-mineral structural unit, and the exchange reaction generally does not affect the structure of the silica-alumina packet. A simple and well-known example of the ion-exchange reaction is the softening of water by the use of zeolites, permutites, or carbon exchangers.

The property of exchange capacity is measured in terms of milliequivalents per gram or more frequently per 100 g. One equivalent of Na⁺ expressed as Na₂O would be a combining weight of 31 and 1 meq per 100 g would be equal to 0.031 per cent Na₂O. Exchange capacity is determined at neutrality, i.e., pH 7.

Vastly more information is available regarding cation exchange than anion exchange, and although they will be considered separately, an elaborate discussion of all the aspects of anion exchange is not possible at this time. In clay materials the commonest exchangeable cations are Ca⁺⁺, Mg⁺⁺, H⁺, K⁺, NH₄⁺, Na⁺, frequently in about that order of general relative abundance. The common anions in clay materials are SO₄²⁻, Cl⁻, PO₄³⁻, NO₃⁻. The general relative abundance of the anions is not yet known.

IMPORTANCE OF ION EXCHANGE

The property of ion exchange and the exchange reaction are of very great fundamental and practical importance in all the fields in which clay materials are studied and used. The significance of exchange reactions in many fields has not always been appreciated even by those actively working in these fields. Therefore, some significant applications of ion exchange will be given so that its importance will be apparent.

In the field of soils, plant foods are frequently held in the soils as exchangeable ions, and consequently their persistence in the soil and their
availability for plant growth depends on exchange reactions. For example, the retention and availability of potash added in fertilizers depends on cation exchange between the potash salt and the clay mineral in the soil. Further, the tilth of the soil is frequently determined by the character of the exchangeable ion, and it may be controlled by an exchange reaction. Thus the presence of appreciable Na⁺ in a soil makes it unsuitable for agriculture. The replacement of the Na⁺ by another ion, usually Ca⁺⁺, will generally make the soil suitable for agriculture.

In the field of geology many examples could be given, but two will suffice. Weathering processes involve the liberation of alkalies and alkaline earths, which may or may not be retained in the secondary material, depending on exchange reactions. The nature of the weathering product depends to a very great extent on whether or not the alkalies and alkaline earths are retained and on which of them are preferentially retained. Weathering is not simply the breakdown of the primary minerals followed by leaching.

Variations in the amount and kind of certain ions in the environment of accumulation of sedimentary rocks must be reflected in the exchangeable-ion composition of argillaceous sediments. Therefore, exchangeable-ion data should be of significance in determining the environment of accumulation of ancient sediments.

In oceanography the concentration of sodium in sea water is to a considerable extent a consequence of the cation-exchange properties of clay materials which have accumulated in the sea. The relative exchangeability of the common cations brought to the sea and the property of some clay minerals to fix K⁺ would lead to a concentration of sodium (see pages 144–152).

Ion exchange is of very great importance in all the applied arts where clay materials are used, or where the properties of clays are important, because the physical properties of clay materials are frequently dependent to a large extent on the exchangeable ions carried by a clay. Again many examples of the great importance of this fact could be given, but a few will suffice. In general the plastic properties of a clay or soil will be very different depending on whether Na⁺ or Ca⁺⁺ is the exchangeable cation. The ceramist, therefore, can change the plastic characteristics of many clays to meet his needs by carrying out a base-exchange reaction. Thus, it is common practice in the brick industry to add soda ash to the plastic clay to improve its properties. The construction engineer, also, can sometimes vary to suit his needs the property of a soil material on which, through which, or with which he proposes to work.

Sometimes the construction engineer inadvertently causes an ion-exchange reaction, by a shift of water table, emplacement of a mass of
concrete, etc., with an unexpected change in the properties of the soil. If the changes in the plastic, compaction, and shrinkage properties resulting from such exchange reactions are not foreseen, the consequences may be disastrous.

Bentonite clay is widely used for many purposes. For certain uses it must form thixotropic suspensions in water. Only bentonites composed of the clay mineral montmorillonite carrying Na$^+$ as the exchangeable ion mix with water to give suspensions of pronounced thixotropic character.

CATION EXCHANGE

History. According to Kelley,$^1$ who reviewed the history of cation exchange in detail, the discovery that soils have the power of exchanging cations with solutions containing other cations was the outgrowth of observations dating back into the remote past. For example, it has been known for centuries that liquid manures become decolorized and deodorized when filtered through soils. Thompson$^2$ is generally credited with being the first person who systematically studied cation exchange. The term base exchange was used to describe the reaction for many years, even long after it was established that the hydrogen ion may take part in the exchange reaction. In experiments begun in 1845 and published 5 years later, Thompson showed that, when soils were mixed with ammonia and then leached with water, the greater part of the ammonia was held back.

Following Thompson, Way$^{3,4}$ began a detailed study of the phenomenon and began to publish his results in 1850. Way showed that cation exchange in soils was restricted to the clay fraction and that it was connected with the silicate compounds in the soil. Also in 1850 Forschamer$^5$ showed that calcium and magnesium are released from soil by leaching with sea water. Following the pioneering labors of Thompson, Way, and Forschamer, a large number of investigators, particularly in the field of soil chemistry, have studied all aspects of the exchange reaction.

Cation-exchange Capacity. The range of the cation-exchange capacity of the clay minerals is given in Table 14.

It follows from a consideration of the factors influencing cation-

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exchange capacity (see pages 132–136) that there is no single capacity value that is characteristic of a given group of clay minerals. A range of capacities must be shown for each group. Since the cation-exchange capacity of a given mineral type may vary with so many factors, capacity values are rigorously comparable only if they have been obtained by the same standard procedure on material of comparable textural and structural attributes.

**Table 14. Cation-exchange Capacity of Clay Minerals, in Milliequivalents per 100 G.**

<table>
<thead>
<tr>
<th>Clay Mineral</th>
<th>Capacity (Milliequivalents)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>3-15</td>
</tr>
<tr>
<td>Halloysite 2H₂O</td>
<td>5-10</td>
</tr>
<tr>
<td>Halloysite 4H₂O</td>
<td>40-50</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>80-150</td>
</tr>
<tr>
<td>Illite</td>
<td>10-40</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>100-150</td>
</tr>
<tr>
<td>Chlorite</td>
<td>10-40</td>
</tr>
<tr>
<td>Sepiolite-attapulgite-palygorskite</td>
<td>20-30</td>
</tr>
</tbody>
</table>

The cation-exchange capacities in Table 14 are taken at pH 7. Titration curves showing the relation between pH and milliequivalents of added NaOH are given in Figs. 45 to 48. Marshall, Mukherjee, Mitra, and others have considered in detail the significance of such titration curves. At relatively low and high pH values, attack of acids and alkalis on the clay-mineral structure is the factor largely controlling the shape of the curves. It can be seen from Figs. 45 to 50 that the character of the clay mineral, its concentration, and the base used also affect the nature of the curves. Other attributes to be discussed later (see pages 132 and 137), such as variations in degree of crystallinity and particle size, also affect the shape of the curves.

Marshall and others have shown that a single cation may be sorbed by a clay mineral with a wide range of bonding energies, and that this is fundamentally related to the position on the silica-alumina packet at

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FIG. 45. Titration curves for hydrogen-illite, after Marshall and Krinbill.

FIG. 46. Titration curves for hydrogen-kaolinite, after Marshall and Krinbill.

FIG. 47. Titration curves for hydrogen-montmorillonite (Wyoming bentonite), after Marshall and Krinbill.

FIG. 48. Titration curves for hydrogen-montmorillonite (Indian bentonite), after Mukherjee and Mitra.
which the cation is sorbed, *e.g.*, whether it is held between the sheets of the layered minerals or around their edges. According to these workers, this is an important cause of the variation in titration curves. The possible positions for sorbed cations vary with the lattice structure of the minerals, and consequently the variation of bonding energy for a given cation would not be expected to be the same for all types of clay minerals (see page 134).

It can be seen from Figs. 45 to 48 that the cation-exchange capacity of montmorillonite may vary with the concentration of the clay, particularly at relatively high concentrations. Thus the cation-exchange capacity based on \( \text{NaOH} \) for an Indian bentonite (montmorillonite) calculated at the inflection point of its potentiometric-titration curve is shown to vary from 81 to 103 meq per 100 g as the clay concentration increased from 0.25 to 8.80 per cent. The variation with clay concentration is considerably less for kaolinites and illites than for montmorillonites.

The exchange capacity may vary also with the nature of the cation. Figures 49 and 50, showing titration curves for kaolinite and montmorillonite with cations of different valence, illustrate the relatively great possible differences for monovalent and divalent cations. In both cases the exchange capacity is considerably larger when determined with \( \text{Ca}^{++} \) than with \( \text{Na}^+ \). As will be shown (pages 137–144), other factors such as particle size, lattice distortion, clogging of exchange positions, etc., may also affect the cation-exchange capacity.

**Other Minerals with Cation-exchange Capacity.** The clay minerals are not the only components of clay materials that have cation-exchange capacity. All inorganic minerals of extreme fineness have a small cation-
exchange capacity as a result of broken bonds around their edges. This capacity increases as the particle size decreases, but even in the small size in which nonclay minerals occur in clays, the exchange capacity is generally insignificant. Zeolite minerals, which are occasionally found in some clays, have cation-exchange capacities of the order of 100 to 300 meq per 100 g.

Some organic materials have cation-exchange capacity, and values ranging from 150 to 500 meq per 100 g are reported\textsuperscript{12,13} for the organic fraction of some soils. In general, organic material with high exchange capacity is restricted to Recent sediments and to soils. The organic material in ancient sediments which has undergone even a small amount of metamorphism is not likely to have significant cation-exchange capacity.

\textbf{Causes of Cation Exchange.} There are three causes of the cation-exchange capacity of the clay minerals:

1. \textit{Broken bonds} around the edges of the silica-alumina units would give rise to unsatisfied charges, which would be balanced by adsorbed cations. The broken bonds would tend to be on noncleavage surfaces and hence on the vertical planes, parallel to the $c$ axis, of the layer clay minerals and on horizontal planes, perpendicular to the $c$ axis, of the sepiolite-palygorskite-attapulgite minerals.

The number of broken bonds and hence the exchange capacity due to this cause would increase as the particle size decreased. Also lattice distortions would tend to increase broken bonds, and the exchange capacity would be expected to increase as the degree of crystallinity decreased.

In the kaolinite and halloysite minerals broken bonds are the major cause of exchange capacity. In the illite, chlorite, and sepiolite-palygorskite-attapulgite minerals, broken bonds are an important cause of exchange capacity, and when these minerals are well crystallized and have relatively low capacity, it may be the major cause. Substitutions within the lattice, particularly in poorly crystalline examples of illite, chlorite, and sepiolite-palygorskite-attapulgite, may partially explain their exchange capacity.

In montmorillonites and vermiculites, broken bonds are responsible for a relatively small portion (20\% ±) of cation-exchange capacity, the remainder probably resulting from substitutions within the lattice. Johnson\textsuperscript{14} has recently argued that the total exchange capacity of

\textsuperscript{13} Francis, M., Sur la matière organique dans les argiles, \textit{Verre silicates ind.}, \textbf{14}, 155–158 (1949).
montmorillonites results from broken bonds, but his evidence is not convincing.

2. **Substitutions within the lattice structure** of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium, for trivalent aluminum in the octahedral sheet result in unbalanced charges in the structural units of some clay minerals. Sometimes such substitutions are balanced by other lattice changes, *e.g.*, OH for O, or by filling more than two-thirds of the possible octahedral positions, but frequently they are balanced by adsorbed cations.

Exchangeable cations resulting from lattice substitutions are to be found mostly on cleavage surfaces, *e.g.*, the basal cleavage surfaces of the layer clay minerals. Since the charges resulting from substitutions in the octahedral sheet would act through a greater distance than the charges resulting from substitutions in the tetrahedral sheet, it would be expected that cations held because of the latter substitutions would be bonded by a stronger force than those held by forces resulting from substitutions in the octahedral sheet. In some cases, cations held by forces due to substitutions of aluminum for silicon seem to be substantially nonexchangeable, *e.g.*, the potassium in the micas. In the clay minerals, replacements in the octahedral layer are probably the major substitutions causing cation-exchange capacity.

In montmorillonite and vermiculite, substitutions within the lattice cause about 80 per cent of the total cation-exchange capacity. In a montmorillonite with a cation-exchange capacity of about 100 meq per 100 g (1 equivalent per 1,000 g) and a molecular weight of about 720, substitutions of less than one-sixth of the aluminum by magnesium or one-twelfth of the silicon by aluminum would account for the capacity if there were no internal balancing of charges.

3. *The hydrogen of exposed hydroxyls* may be replaced by a cation which would be exchangeable. Some hydroxyl groups would be exposed around the broken edges of all the clay minerals, and cation exchange due to broken bonds would, in part at least, be replacement of the hydrogens of exposed hydroxyls. This cause of exchange capacity would be important for kaolinite and halloysite because of the presence of the sheet of hydroxyls on one side of the basal cleavage plane.

Edelman and Favejee have suggested structures for montmorillonite and halloysite, and McConnell has suggested an alternative structure for montmorillonite which would have hydroxyls in basal plane cleavage surfaces. On the basis of these structural concepts a considerable amount

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of the cation-exchange capacity of these minerals would be due to this cause. However, neither of these suggested structures have been generally accepted.

**Position of Exchangeable Cations.** In the clay minerals in which the cation exchange results from broken bonds, the exchangeable cations are held around the edges of the flakes and elongate units. In the clay minerals where the exchange is due to lattice substitutions, the cations are mostly on the basal plane surfaces. Thus in kaolinite and halloysite the cations are at the edges, whereas in montmorillonite and vermiculite about 80 per cent are on basal plane surfaces, with the remainder on the edges. In the case of the illite, chlorite, and sepiolite-palygorskite-attapulgite minerals, most of the cations are at edges with a relative few on cleavage surfaces.

In a montmorillonite with a cation-exchange capacity of 100 meq per 100 g and a unit-cell weight of 720, and assuming that 80 per cent of the exchange positions are on basal plane surfaces, there would be 1 equivalent for 1/34 unit cells. With a basal surface area of 92.26 Å² per unit cell, there would be a total surface area per exchange position of about 160 Å², or an area per exchange position on each basal plane surface of about 80 Å².

In masses of clay with relatively small amounts of adsorbed water, i.e., with no more water than is required to develop plasticity, it is likely that the adsorbed cations around the edges of the flakes are held directly in contact or at least very close to the clay-mineral surface. Brown\(^{17}\) has present X-ray data based on Fourier syntheses indicating that, for montmorillonite under such conditions of clay-water concentration, the adsorbed cations between the basal plane surfaces are held midway between the clay-mineral surfaces.

In clay-water systems in which the amount of water is at least greater than that required for the plastic state, the exchangeable cations may be at greater distances from the clay-mineral surfaces and separated from them by water molecules. In any given system of this kind, the position of all the exchangeable cations with respect to the clay-mineral surface is not the same, and even the relative positions of all of the same sort of cation probably will not be the same; some cations of a given type will be closer to the clay-mineral surface than others. Very careful investigation of the ionization of exchangeable cations by Marshall\(^6\) and his colleagues\(^{18}\) has thrown much light on this problem. Only a portion of the adsorbed

---


cations are likely to be ionized, and the percentage ionized depends on the particular clay mineral, the amount of water, i.e., the concentration of the clay-water system, the nature of the cations, the relative concentration of the cations, and the nature of the adsorbed anions.

Marshall\textsuperscript{19} has shown that, for alkali cations and for constant concentration of cations, the order of ionization is kaolinite > montmorillonite > illite. An investigation of Na\textsuperscript{+}, K\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+} showed that the order of these three cations is not consistently the same, although NH\textsubscript{4}\textsuperscript{+} generally shows a lower fraction active. Attapulgite appears to give a higher degree of ionization than kaolinite. With decreasing concentration of a given clay the fraction active falls, and some data suggest that there is a reversal at very low concentrations. Recent data from Marshall\textsuperscript{19} in Table 15 show the fraction of monovalent cations active in relation to clay mineral, clay concentration, degree of saturation, and monovalent cation employed.

The divalent ion Ca\textsuperscript{++} shows a lesser fraction ionized than Na\textsuperscript{+}, and less than K\textsuperscript{+} by a considerable factor. This factor is about \(\frac{1}{2}\) for kaolinite and \(\frac{1}{2}\) to \(\frac{1}{2}\) for clays of the montmorillonite groups. Chatterjee and Marshall\textsuperscript{20} have recently arrived at the following conclusions regarding the ionization of Ca\textsuperscript{++}, Ba\textsuperscript{++}, and Mg\textsuperscript{++} for kaolinite, illite, and montmorillonite: For these divalent ions, illite > montmorillonite, with kaolinite varying in its relative position according to the nature of the cation and the extent of neutralization. Recent data from Marshall\textsuperscript{19} are given in Table 16, showing fraction active of Mg\textsuperscript{++}, Ca\textsuperscript{++}, and Ba\textsuperscript{++} in relation to clay mineral, degree of saturation, clay concentration, and divalent cation employed. These data show, for example, that at 50 per cent concentration the fraction of Ca\textsuperscript{++} active is slightly less for kaolinite than for montmorillonite and considerably less than for illite. At 100 per cent concentration, the fraction of Ca\textsuperscript{++} active varies as follows: illite < montmorillonite < kaolinite. At 50 per cent concentration, the fraction of Mg\textsuperscript{++} active varies in the order kaolinite < montmorillonite < illite, whereas at 100 per cent concentration the order is montmorillonite < illite < kaolinite.

Data are not at hand for the ionization characteristics of the other clay minerals. The complete structural implications of ionization studies have not yet been worked out, but it seems clear that a single cation can be held by a given clay mineral with different bonding energies. The bonding energy is dependent in part on the position of the adsorbed cation on the clay-mineral unit. Thus, cations between the basal plane.


\textsuperscript{20} Chatterjee, B., and C. E. Marshall, Studies in the Ionization of Mg\textsuperscript{++}, Ca\textsuperscript{++}, Ba\textsuperscript{++} Clays, J. Phys. & Colloid Chern., 54, 671–681, (1950).
surfaces are likely to be held more strongly than those around the edges of units. This would account in part for the variations in ionization shown by the clay minerals. It does not, however, fit all of Marshall's data, and it must be concluded that the significance of many of these data is not yet clear.

**Table 15. Ionization of Some Exchangeable Univalent Cations for Several Clay Minerals**

(After Marshall)

<table>
<thead>
<tr>
<th>Clay</th>
<th>Concentration, %</th>
<th>Assumed</th>
<th>Cation</th>
<th>Fraction active</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>meq/100 g</td>
<td></td>
<td>Saturation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50%</td>
<td>75%</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2.8</td>
<td>100</td>
<td>Na</td>
<td>0.377</td>
</tr>
<tr>
<td>(Wyoming bentonite)</td>
<td>3.3</td>
<td>100</td>
<td>K</td>
<td>0.295</td>
</tr>
<tr>
<td>Illite</td>
<td>10.0</td>
<td>28</td>
<td>Na</td>
<td>0.073</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>10.0</td>
<td>2.75</td>
<td>Na</td>
<td>0.263</td>
</tr>
</tbody>
</table>

**Table 16. Cationic Fractions Active in Relation to Clay Mineral, Degree of Saturation, and Divalent Cation Employed**

(After Marshall)

<table>
<thead>
<tr>
<th>Clay</th>
<th>Concentration, %</th>
<th>Assumed</th>
<th>Cation</th>
<th>Fraction active</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>meq/100 g</td>
<td></td>
<td>Saturation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50%</td>
<td>75%</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>1.04</td>
<td>100</td>
<td>Mg</td>
<td>0.0122</td>
</tr>
<tr>
<td>(Wyoming bentonite)</td>
<td>1.07</td>
<td>100</td>
<td>Ca</td>
<td>0.0175</td>
</tr>
<tr>
<td>Illite</td>
<td>4.9</td>
<td>28</td>
<td>Mg</td>
<td>0.047</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>9.0</td>
<td>2.75</td>
<td>Mg</td>
<td>0.0100</td>
</tr>
</tbody>
</table>

**Rate of the Exchange Reaction.** The rate of cation exchange varies with the clay mineral, the concentration of the cations, and the nature and concentration of the anions. In general the reaction for kaolinite
Ion Exchange

is most rapid, being almost instantaneous. It is slower for montmorillonites and for attapulgite and requires an even longer time, perhaps hours, to reach completion for illites. Apparently exchange on the edge of the particles, as in kaolinite, can take place quickly, but penetration between the sheets of montmorillonite or in the channels of attapulgite requires more time. In the case of illite a small part of the exchange is between basal flake surfaces firmly held together, and this is likely to be slow, causing a long time to complete the reaction.

Chloritic clay minerals are likely to have a rate of exchange similar to the illites. Vermiculite is likely to be similar to montmorillonite, except that it may be somewhat slower because of the larger areal size of the flakes of vermiculite, so that more time is required for penetration between them.

Exchange in some of the zeolite minerals is even slower than that in the clay minerals, many hours being required for completion. Apparently much time is required to penetrate the channel-like openings of some of these minerals.

**Variation Due to Particle Size.** As shown in Tables 17 and 18, the cation-exchange capacities of kaolinite and illite increase as the particle size decreases. It has generally been considered that the cation-exchange capacity of montmorillonite does not change substantially with particle size, and Hauser and Reed\(^2\) have shown that there is no variation in the

---

**Table 17. Variations in the Cation-exchange Capacity of Kaolinite with Particle Size**

<table>
<thead>
<tr>
<th>Particle size, microns</th>
<th>10-20</th>
<th>5-10</th>
<th>2-4</th>
<th>1-0.5</th>
<th>0.5-0.25</th>
<th>0.25-0.1</th>
<th>0.1-0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation-exchange capacity, meq/100 g</td>
<td>2.4</td>
<td>2.6</td>
<td>3.6</td>
<td>3.8</td>
<td>3.9</td>
<td>5.4</td>
<td>9.5</td>
</tr>
</tbody>
</table>

**Table 18. Variations in the Cation-exchange Capacity of Illite with Particle Size**

<table>
<thead>
<tr>
<th>Particle size, microns</th>
<th>1-0.1</th>
<th>0.1-0.05</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation-exchange capacity, meq/100 g</td>
<td>Sample A</td>
<td>Sample B</td>
<td>Sample C</td>
</tr>
<tr>
<td>Sample A</td>
<td>18.5</td>
<td>21.6</td>
<td>33</td>
</tr>
<tr>
<td>Sample B</td>
<td>13.0</td>
<td>20.0</td>
<td>27.5</td>
</tr>
<tr>
<td>Sample C</td>
<td>20.0</td>
<td>30.0</td>
<td>41.7</td>
</tr>
</tbody>
</table>

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Clay Mineralogy

87- to 14-μm particle range. Caldwell and Marshall (see Table 19) show no variation in the cation-exchange capacity of nontronite in the particle range from 2 to 0.05 micron, but they do show a slight increase in this same range for saponite. The same authors show a slight increase for attapulgite with decreasing particle size.

TABLE 19. VARIATION IN THE CATION-EXCHANGE CAPACITY OF NONTRONITE, ATTAPULGITE, AND SAPONITE WITH PARTICLE SIZE
(After Caldwell and Marshall)

<table>
<thead>
<tr>
<th>Particle size, microns</th>
<th>2-1</th>
<th>1-0.5</th>
<th>0.5-0.2</th>
<th>0.2-0.05</th>
<th>&lt;0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation-exchange capacity, meq/100 g</td>
<td>Nontronite</td>
<td>60.8</td>
<td>61.0</td>
<td>64.3</td>
<td>57.0</td>
</tr>
<tr>
<td></td>
<td>Attapulgite</td>
<td>18.0</td>
<td>19.0</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Saponite</td>
<td>69.3</td>
<td>76.0</td>
<td>81.5</td>
<td>86.3</td>
</tr>
</tbody>
</table>

In minerals such as kaolinite and illite, in which the exchange capacity is due primarily to broken bonds, an increase is to be expected with decreasing particle size. In the case of expanding-lattice minerals, where most of the exchange is on accessible basal plane surfaces, it seems that particle size should make little difference. However, it would be expected that, in some montmorillonites, perhaps because of the location of lattice substitutions, nature of exchangeable ion, areal size of the flakes, etc., the accessibility of the basal plane surfaces would increase with decreasing particle size, and therefore some types of montmorillonite would be expected to show moderate variation of cation-exchange capacity with particle size. Johnson has recently presented data showing a variation of cation capacity with particle size for several montmorillonites and concludes that the capacity is entirely derived from broken bonds. This conclusion, however, does not necessarily follow from Johnson’s data.

Effect of Grinding. Kelley and Jenny showed that grinding of the clay minerals, as well as many nonclay minerals, caused an increase in cation-exchange capacity, as is shown in Table 20. The experiments of these investigators were carried out in a rubber-lined ball mill, using polished agate balls. The grinding causes a variation in particle size, an increase in surface, and an increase in the number of broken bonds. X-ray examination of the ground material showed a progressive broadening and diffuseness of the diffraction bands, with their final disappearance.


Ion Exchange

**Table 20. Cation-exchange Capacity, in Milliequivalents per 100 g, in Relation to Grinding**

(After Kelley and Jenny[25])

<table>
<thead>
<tr>
<th>Minerals</th>
<th>100 mesh</th>
<th>Ground 48 hr</th>
<th>Ground 72 hr</th>
<th>Ground 7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite</td>
<td>10.5</td>
<td>...</td>
<td>76.0</td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td>3.0</td>
<td>62.0</td>
<td>72.5</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>8.0</td>
<td>57.5</td>
<td>70.4</td>
<td>100.5</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>126</td>
<td>...</td>
<td>238.0</td>
<td></td>
</tr>
</tbody>
</table>

...after very long grinding indicating a gradual breaking down of the structure.

Recently Laws and Page[26] have found that there is little further increase in the cation-exchange capacity of kaolinite after 96 hr of grinding, and they present evidence to indicate that the kaolinite structure has been destroyed at this point and that a new permutite-like structure has developed. Perkins[27] has shown that only 48 hr of grinding is enough to seriously disrupt the structure of both kaolinite and muscovite.

**Relation to Temperature.** According to Kelley[1] the temperature effect of cation exchange is generally small. Wiegner[28] has reported a small negative temperature coefficient, and various other workers[29] have found that the exchange reaction is accelerated somewhat by raising the temperature. Chapman and Kelley[30] point out that the disadvantages of heating may outweigh the advantage because of the increased solubility of certain constituents at the higher temperatures.

The change in cation-exchange capacity of montmorillonite saturated with Ca++, Na+, and Li+ on heating to various temperatures is given in Table 21. The exchange capacity is reduced on heating, but the reduction is not uniform and varies with the cation present. Thus the Ca montmorillonite shows a gradual loss of cation-exchange capacity on heating to 300°C (93 to 41 meq per 100 g) and an abrupt drop from 41 to 12 meq between 300° and 390°C, which is the temperature interval during which inner crystalline swelling is lost. Na montmorillonite, unlike the calcium variety, shows only a slight drop in exchange capacity up to 300°C (95 to 90 meq), and a moderate drop from 300° to 390°C.

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### TABLE 21. EFFECT OF HEATING ON THE CATION-EXCHANGE CAPACITY OF MONTMORILLONITE AND ILLITE
(After Hofmann and Klemen³²)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Heating temperature, °C</th>
<th>Drying time, days</th>
<th>d(001), Å</th>
<th>Water content* over 35% H₂SO₄</th>
<th>Exchangeable cations, meq/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Drying clay</td>
<td>Wetted clay</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca montmorillonite</td>
<td>105</td>
<td>2</td>
<td>10.2</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2</td>
<td>9.8</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>14</td>
<td>9.6</td>
<td>9.6</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>490</td>
<td>14</td>
<td>9.6</td>
<td>9.6</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>2</td>
<td>9.6</td>
<td>9.6</td>
<td>4.7</td>
</tr>
<tr>
<td>Na montmorillonite</td>
<td>105</td>
<td>2</td>
<td>9.8</td>
<td>30</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2</td>
<td>9.8</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>14</td>
<td>9.6</td>
<td>21</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>490</td>
<td>14</td>
<td>9.6</td>
<td>9.6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>2</td>
<td>9.6</td>
<td>9.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Li montmorillonite</td>
<td>20</td>
<td>1.2</td>
<td>10.2</td>
<td>30</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>2</td>
<td>10.5</td>
<td>30</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Illite, Sárospatak, Hungary.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>2</td>
<td></td>
<td></td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2</td>
<td></td>
<td></td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>2</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>2</td>
<td></td>
<td></td>
<td>9</td>
</tr>
</tbody>
</table>

* Computed on dry basis on heating to 900°C.

Between 390°C and 490°C the reduction is only to 39 meq, even though the property of inner crystalline swelling is lost in this temperature interval. At 700°C, following the loss of lattice OH water from the Na montmorillonite, the exchange capacity drops to 3.4 meq. For Li montmorillonite, the exchange capacity is reduced to 56 meq on heating to only 105°C, which is below the point of loss of the swelling characteristic. Swelling of this montmorillonite is lost at 125°C, with a drop in exchange capacity to 31 meq per 100 g.

The data of Hofmann and Endell³¹ and Hofmann and Klemen³² show that the exchange capacity of montmorillonite is reduced to a considerable extent by heating before the swelling property is lost. The amount of reduction is large for montmorillonite saturated with Li⁺ and Ca⁺⁺ and

small when it is saturated with Na+. Complete loss of swelling follows the reduction in exchange capacity. Hofmann and Endell interpret their data to mean that, when the clay is heated, the exchangeable cations tend to move inside the montmorillonite lattice. Since Li is a small ion, it can fit easily into the structure, possibly in vacancies in the octahedral sheet, and consequently only a low temperature is required for the shift into the structure. The move into the lattice is followed by a loss of swelling. Because the Na ion is a large one, it would fit with great difficulty into the structure, and a high temperature would be required for the move. The exchange capacity and swelling of Na montmorillonite would persist, therefore, to a relatively high temperature.

In the case of nonexpanding clay minerals the available data indicate a gradual reduction in cation-exchange capacity with increasing temperature of heating.

Environment of the Exchange Reaction. Cation exchange usually takes place in an aqueous environment, and the ions generally have considerable solubility. However, it has been shown that clays may take ions from water suspensions of very insoluble substances and resistant minerals by means of ionic sorption reactions, and it is probable that the reaction can take place in suspensions of high concentration, i.e., in the presence of relatively little water. Indeed this is a means of the natural disintegration of minerals that is important and is not generally appreciated. Thus, Bradfield found that sodium-saturated clays were able to take enough barium from barium sulfate to fill about one-fifth of the exchange positions of the clay. Graham has shown that H clay will extract calcium from anorthite by cation exchange. This exchange has been explained as follows: The resistant minerals in water suspensions are in equilibrium with traces of ions which dissolve from their surfaces. The clays destroy this equilibrium by sorbing the ions, and if the equilibrium is to be maintained, ions must move from the resistant mineral into the solution.

It was suggested, by Kelly and by Jenny and Overstreet, and shown later, by Jenny and his coworkers, using tracer elements, that ion

---

exchange can take place directly between plant roots and clays without the intermediate solution of the ions. The cation moves directly from the clay to the plant in return for another ion, which moves directly from the plant to the clay. This probably requires that ions be able to migrate on clay-mineral surfaces from exchange spot to exchange spot. Jenny postulated that exchangeable ions are in a continuous state of thermal agitation, and when neighboring zones of agitation overlap, there should be an opportunity for a given cation to jump from one spot to another, provided that there is another ion of like charge simultaneously jumping in the opposite direction. It may well be that direct exchange can take place between clay minerals and inorganic materials as well as between clay minerals and plants.

Buswell and Dudenbostel have shown that H montmorillonite will react with dry NH₃ gas to form NH₄ montmorillonite. Cornet has shown the same thing and has gone further to indicate that some of the NH₃ is taken up between the basal plane surfaces of the montmorillonite. The present use of dry gaseous ammonia as a fertilizer makes use of this sorption of NH₃ by the clay minerals.

Magistad and Burgess have shown that the cation-exchange reaction can take place in alcohol.

**Hydrogen Clays.** It has been shown by Paver and Marshall, Chatterjee and Paul, Mukherjee and others that hydrogen montmorillonites and hydrogen kaolinites are in reality hydrogen-aluminum systems. It is substantially impossible to prepare a clay in which all the exchange positions are occupied by H⁺, since Al³⁺ moves from the lattice to exchange positions before saturation with H⁺ becomes complete. These conclusions are probably applicable to the other clay minerals as well and apply to the greatest degree to the expanding-lattice minerals and sepiolite-attapulgite-palygorskite. Kaolinite is affected to the least

---

degree, with the illite and chlorite minerals showing an intermediate effect.

Paver and Marshall\textsuperscript{43} have shown that the electrolysis of clays removes not only the mobile cations, although this predominates in the earlier stages, but also basic constituents, such as iron and magnesium, which are frequently found at the anode, while silicic acid moves in considerable quantity with the bulk of the bases to the cathode. Electrolyzed clays, on treatment with neutral salts, liberate aluminum, and the amount increases with the concentration of the salt to a maximum which is approximately equivalent to the exchange capacity of the clay.

Mukherjee and his colleagues\textsuperscript{46,47} have studied in detail the changes which occur when the clay minerals undergo repeated desaturation and treatment with barium chloride. With montmorillonite, repeated cycles of desaturation and neutral salt treatment caused a steady decrease in the aluminum and a smaller decrease in the hydrogen released by exchange. After four cycles the ratio of hydrogen to aluminum released becomes very large. Successive treatments caused a large reduction in the cation-exchange capacity of the montmorillonite, indicating considerable decomposition, which was confirmed by the appearance of soluble silica in the earlier desaturations. With kaolinite, aluminum and hydrogen were similarly brought into solution by the neutral salt treatment, but there was no reduction in cation-exchange capacity, and no soluble silica was found. Probably the attack on kaolinite is restricted to the aluminum exposed on external surfaces. It is likely that the sepiolite-palygorskite and vermiculite minerals would act like the montmorillonite and that illites and chlorites would be intermediate, but more like the kaolinite.

Unpublished work by Michelson\textsuperscript{48} suggests that the movement of aluminum from positions in the lattice to exchange positions is facilitated by drying. So long as the sample is not dried, the amount of movement is relatively small. Michelson's work was done on montmorillonite, but it probably applies also to the other clay minerals.

The fact that hydrogen clays are in reality hydrogen-aluminum systems is of great importance in clay and soil investigations. The failure to recognize this fact has caused many erroneous conclusions to be reported and much confusion in interpreting results. For example, numerous studies have been made of the physical properties of supposedly


\textsuperscript{47} Mukherjee, J. N., B. Chatterjee, and A. Ray, Liberation of $H^+$, $Al^{+++}$ and $Fe^{+++}$ Ions from Pure Clay Minerals on Repeated Soil Treatment and Desaturation, J. Colloid Sci., 3, 437-446 (1946).

\textsuperscript{48} Michelson, G., personal communication.
monoionic clays prepared by treating hydrogen clays with various cations. Actually in many cases monoionic clays were not attained, and the reported results are to a considerable extent a consequence of the presence of Al$^{3+}$ and not, as supposed, of the cation with which the clay was treated. Further it makes extremely difficult the study of the properties of calcareous clays, since the carbonate cannot readily be removed without damaging the clay-mineral component and altering its properties.

Clogging of Cation-exchange Positions. It has just been pointed out that the development of aluminum on exchange positions reduces the exchange capacity of montmorillonite clays. This is in part due to damaging of the montmorillonite lattice, but also in part to clogging of the exchange positions by aluminum. Dion$^{49}$ has pointed out that Fe$_2$O$_3$ alone or in the hydrated form may serve to reduce the cation-exchange capacity of clay minerals by a clogging action.

A somewhat similar effect may be produced by organic ions. Hendricks$^{50}$ has pointed out that large, flat organic ions adsorbed on the basal surface of montmorillonite may be of sufficient size to blanket more than one exchange position and thereby seem to reduce the exchange capacity of the montmorillonite. Organic molecules with an area greater than about 80 $\AA^2$ and flat-lying could spread over more than one exchange position.

Other effects may serve to reduce the exchange reaction. Sulfur compounds may form on the adsorbing surface$^{51}$ of the clay minerals, which would serve to reduce exchange. This matter is not well understood, but studies of clay-mineral catalysts reveal that they can be poisoned by sulfur, probably because of sulfur compounds which form on the clay-mineral surface and reduce the sorption activity.

Replaceability of Exchangeable Cations. Very early studies of cation exchange showed that under a given set of conditions, various cations were not equally replaceable and did not have the same replacing power. Way$^4$ concluded that the replacing power of the common ions was Na < K < Ca < Mg < NH$_4$, which means, for example, that in general Ca$^{++}$ will more easily replace Na$^+$ than Na$^+$ will replace Ca$^{++}$.

As the cation-exchange reaction was studied, it became obvious that there was no single universal replaceability series. The series varied depending on the experimental conditions, on the cations involved, and

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on the kind of clay material. Gedroiz\textsuperscript{52} in 1922, for example, gave the following order of replacing power based on the replacement of Ca\textsuperscript{++} by 0.01 \textit{N} solution of chlorides: Li < Na < K < Mg < Rb < NH\textsubscript{4} < Co < Al. In the replacement of Ba\textsuperscript{++} by 0.1 \textit{N} solution, using the same soil material, Gedroiz found Li < Na < NH\textsubscript{4} < K < Mg < Rb < Ca < Co < Al.

The matter of cation replaceability is of very great importance, and a very large amount of research on the problem has been reported. Replaceability is not yet completely understood, but it is known that it is controlled by a considerable number of factors, and much has been learned about the nature and the influence of each of the factors. In the following discussion of the factors involved, no attempt is made to place them in an order of importance.

\textit{Effect of Concentration.} Kelley and Cummins\textsuperscript{53} found that the replacement of Ca\textsuperscript{++} and Mg\textsuperscript{++} by Na\textsuperscript{+} in the Yolo soil of California increased as the concentration of Na\textsuperscript{+} in the solution increased. Gedroiz\textsuperscript{52} pointed out that the replacement of Ca\textsuperscript{++} and Mg\textsuperscript{++} by NH\textsubscript{4}\textsuperscript{+} in a Chernozem soil increased as the concentration of NH\textsubscript{4}\textsuperscript{+} increased. This is to be expected, since cation exchange is a stoichiometric reaction and the laws of mass action would hold. In general, therefore, increased concentration of the replacing cation causes greater exchange by that cation.

Gedroiz\textsuperscript{52} in his experiments found that the increased replacement of Ca\textsuperscript{++} and Mg\textsuperscript{++} by NH\textsubscript{4}\textsuperscript{+} was not in direct proportion to the concentration and that the ratio of Ca\textsuperscript{++} to Mg\textsuperscript{++} was also not in direct proportion. That is to say, the concentration of replacing cation is important, but it is not the sole factor. Schachtschabel\textsuperscript{54} demonstrated conclusively that the effects of concentration depend on the kind of cation that is being replaced and also on the valence of the cation, as well as on other factors.

The complexity of this factor of concentration is shown by the following data brought out by Kelley:\textsuperscript{1} "With cation pairs of about similar replacing power and of the same valence such as K\textsuperscript{+} vs. NH\textsubscript{4}\textsuperscript{+} or Ca\textsuperscript{++} vs. Ba\textsuperscript{++}, dilution has relatively little effect on exchange, while with cations of different replacing power and different valence, for example Na\textsuperscript{+} vs. Ca\textsuperscript{++} or NH\textsubscript{4}\textsuperscript{+} vs. Ca\textsuperscript{++}, dilution produces marked effect on exchange." Kelley points out that a fully satisfactory explanation of these facts cannot now be given.

\textsuperscript{52} Gedroiz, K., On the Absorptive Power of Soils. Translated by S. Waksman and distributed by U.S. Department of Agriculture (1922).
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Population of Exchange Positions. Jenny and Ayers\textsuperscript{55} and later Wiklander,\textsuperscript{56} in considerable detail, have shown that the ease of release of an ion depends not only on the nature of the ion itself but also upon the nature of the complementary ions filling the remainder of the exchange positions, and on the degree to which the replaced ion saturates the exchange spots. Thus, Wiklander shows that, as the amount of exchangeable calcium on the clay mineral becomes less, the calcium becomes more and more difficult to release. Sodium, on the other hand, tends to become easier to release as the degree of saturation with sodium ions becomes less. Magnesium and potassium are not affected by the degree of saturation to the same extent as calcium and sodium.

Nature of Anion in Replacing Solution. Numerous investigators have found that the replaceability of a given ion varies with the nature of the anion which may be present. Thus Neznayko\textsuperscript{57} found considerable variation in the replaceability of Na\textsuperscript{+} from montmorillonite by Ca\textsuperscript{++} depending on whether calcium hydroxide or calcium sulfate was used. Marshall\textsuperscript{6} reports that considerable variation in the cation-exchange capacity is obtained by leaching with different neutral salts of a given ion. The whole matter of the effect of anions is complicated by the possibility of the formation of “basic” salts with the clay and a soluble anion, e.g., clay-(ZnOH)\textsuperscript{+},\textsuperscript{58} and, at relatively high concentration of anions, by the probability of reactions with the clay mineral, altering its structure and forming new compounds.

Nature of the Ion. Other things being equal, the higher the valence of the ion, the greater its replacing power and the more difficult it is to displace when already present on the clay. Hydrogen is an exception since for the most part it behaves like a divalent or trivalent ion.

Kelley\textsuperscript{1} points out that the replacing power increases qualitatively with atomic number in ions of the same valence.

Also, in ions of the same valence, replacing power tends to increase as the size of the ion increases; i.e., the smaller ions are less tightly held than the larger ions. An exception to the effect of ion size occurs in those ions which have almost exactly the correct size to fit into the hole in the basal oxygen sheet of the layer clay minerals. Thus potassium, as pointed out by Page and Baver,\textsuperscript{59} has an ionic diameter of 2.66 Å, which is about


\textsuperscript{57} Neznayko, M., personal communication.


the same as the diameter of the cavity in the oxygen layer, so that the potassium ion can just fit into one of these cavities. As a consequence the potassium ion is relatively very difficult to replace.

Wiegner and Jenny suggested that the size of the hydrated ion, rather than the size of the nonhydrated ion, controls replaceability. According to Wiegner, for ions of equal valence, those which are least hydrated have the greatest energy of replacement and are the most difficult to displace when already present upon the clay. Thus, lithium, although a very small ion, is considered to be highly hydrated and, therefore, to have a very large hydrated size. The low replacing power of Li⁺ and its ready replaceability are said to be a consequence of this large hydrated size.

The magnitude of the computed hydration of the various ions varies with the base chosen for comparison. Hydration values suggested by several investigators and obtained in different ways are given in Table 22 to show the order of magnitude of the hydration generally given for the common ions.

The matter of the hydration of the adsorbed ions in clay-water systems is a matter of much controversy at the present time. Wiegner and Jenny and later Alten and Kurmies have presented strong evidence that all the common cations are hydrated and that hydration is important in exchange reactions. The evidence is based on investigations carried out in alcohol rather than water. It is stated that alcohol, in which the ions would not be hydrated, reverses the usual lyotropic replacement series, so that ions are held in the order of their true ionic size and not in the order of their hydrated size.

Bernal and Fowler some years ago presented data that threw doubt on the hydration of some of the cations. Bar and Tenderloö have enumerated difficulties encountered by explanations of clay properties based on cation hydration, and Baver has summarized experimental data on the swelling and heat of wetting of soil colloids that do not fit well with cation hydration. Recently, Hendricks and his col-

References:

TABLE 22. ION SIZES AND IONIC HYDRATION

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radii, Å</th>
<th>Hydration, moles H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not hydrated</td>
<td>Hydrated</td>
</tr>
<tr>
<td>Li</td>
<td>0.68</td>
<td>0.78</td>
</tr>
<tr>
<td>Na</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>K</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>NH₄</td>
<td>1.43</td>
<td>5.37</td>
</tr>
<tr>
<td>Rb</td>
<td>1.49</td>
<td>3.6</td>
</tr>
<tr>
<td>Cs</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.89</td>
<td>0.78</td>
</tr>
<tr>
<td>Ca</td>
<td>1.17</td>
<td>1.06</td>
</tr>
<tr>
<td>Sr</td>
<td>1.34</td>
<td>1.27</td>
</tr>
<tr>
<td>Ba</td>
<td>1.49</td>
<td>1.43</td>
</tr>
<tr>
<td>Al</td>
<td>0.79</td>
<td>0.57</td>
</tr>
<tr>
<td>La</td>
<td>1.30</td>
<td>1.22</td>
</tr>
</tbody>
</table>

D and F. Pallman, H., Bodenk und Forsch., 6, 21 (1938).

Lehmanns⁶⁶ have presented compelling evidence, based on careful dehydration studies, that Na⁺, H⁺, and K⁺ and the trivalent ions are not hydrated when adsorbed by the clay minerals. According to them, Ca⁡⁺⁺ and Mg⁡⁺⁺ are hydrated to 6H₂O, and Li⁺ is hydrated to 3H₂O. This is directly contrary to conclusions of those favoring the hydration concept, who consider Li⁺ and Na⁺ to be among the most highly hydrated ions.

According to Bar and Tenderlo⁶¹ replaceability is related to the polarization of the ion, with increasing polarization being accompanied by increasing difficulty of exchange. Also, highly polar ions are thought to be held closer to the adsorbing surface. Polarization increases as the valence increases and as the size of the ion decreases.

**Effect of Heating.** The work of Hofmann and J. Endell⁶⁴ has indicated that heating to moderate temperatures not only reduces the cation-exchange capacity but changes the relative replaceability of the cations.

Ion Exchange

Thus, for montmorillonite, heating to 125°C tends to fix Li⁺ in an unreplaceable form and not to affect the replaceability of Na⁺, whereas at ordinary temperatures Li⁺ is more easily replaced than Na⁺. The extensive and excellent work of Marshall and his colleagues in developing and using clay membranes as electrodes to measure ion activity also has shown the great variation of ion replaceability with increasing temperatures. Andrews and Maldonado have shown that the relative amounts of the cations which are replaceable change when the clay fraction of the Crowley silt loam soil is heated up to 100°C. They found that the relative amounts of replaceable K⁺, Ca++, and H⁺ decreased on prolonged heating, whereas Na⁺ and Mg++ increased.

It seems likely that the change in replaceability of cations when heated would be relatively greater for the expanding-lattice minerals than for those minerals in which the capacity is due largely to broken bonds. In the former case, most of the adsorbed cations are held between the basal layers, and the change in replaceability is probably largely in these ions. At elevated temperatures, when there is little or no water present between basal layers in addition to the sorbed cations, the size of the ion and its geometrical fit into the structure of the oxygen layers are probably major factors in determining replaceability.

Nature of the Clay Mineral. Early investigations of many soils suggested that the replaceability of various cations varied with the nature of the adsorption complex, all other factors being equal. The work of Jarusov, Bar and Tenderloo, and Gieseking and Jenny particularly showed this to be true, and the careful work on pure kaolinite, muscovite, and montmorillonite by Schachtschabel clearly demonstrated that there was not a single replaceability series characteristic of all clay materials, but separate replaceability series for the various clay minerals.

The replaceability of NH₄⁺ from kaolinite, montmorillonite, and muscovite by various cations at various concentrations is shown in Figs. 51 to 53, taken from Schachtschabel. These data show, for example, that, for NH₄ montmorillonite, H⁺ and K⁺ are about equally exchangeable, that all the univalent cations except Rb⁺ and Cs⁺ are more exchangeable than the divalent ions, and that all the divalent ions have about the same replaceability. For NH₄ kaolinite the exchangeability of the cations is about the same as for NH₄ montmorillonite. NH₄⁺, however, is more

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lightly held by kaolinite. For NH₄ muscovite, H⁺ and K⁺ are more lightly held than the divalent ions, and NH₄⁺ is even more lightly held than in kaolinite. When a mixture of montmorillonite and muscovite is treated with mixtures of calcium and ammonium acetate, the mica adsorbs relatively much more of the NH₄⁺, and the montmorillonite adsorbs relatively more of the Ca²⁺. Also Ca²⁺ in competition with equivalent concentrations of K⁺ would be taken up preferentially by montmorillonite, while the opposite is the case for muscovite. Schachtschabel⁴⁴ used this latter behavior as the basis for an analytical method for the determination of the relative abundance of montmorillonite and the mica-like clay minerals when mixed together in soils.

Hendricks and Alexander⁷¹ have also studied the relative acceptance of Ce³⁺ and H⁺ by montmorillonite and illite and have found that the illites preferentially take up H⁺, while the montmorillonites take up much more Ce³⁺. They use this difference as the basis for a method of estimating the amount of montmorillonite present in mixtures of these two minerals.

Barshad⁷² has recently investigated the cation-exchange characteristics of vermiculite and has shown that the exchange process is reversible between Na⁺, Ca²⁺, Mg²⁺, and K⁺ but is not completely reversible between K⁺, NH₄⁺, Rb⁺, and Cs⁺. The latter ions tend to become fixed and relatively nonreplaceable. Walker and Milne⁷³ have also investigated the replaceability of the exchangeable cations of vermiculite with much the same results. They show that K⁺ and NH₄⁺ replace Mg²⁺ with difficulty, whereas Mg²⁺ is readily replaced by Li⁺ and Na⁺. However,

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Ion Exchange

Fig. 52. NH₄ montmorillonite; ionic exchange with alkali and alkaline-earth chlorides, after Schachtschabel.⁶⁴

Fig. 53. NH₄ muscovite; ionic exchange with alkali and alkaline-earth chlorides, after Schachtschabel.⁶⁴
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A vermiculite prepared with Li⁺ or Na⁺ readily loses these ions by replacement with K⁺ or NH₄. Any difference in replaceability between vermiculite and montmorillonite is of interest, since the only major difference between these two minerals seems to be in the size of the layers in the a and b crystallographic directions.

Allaway⁷⁴ has investigated the replaceability of Ca⁺⁺ in various clay minerals by determining its availability to plants. He finds that for Ca⁺⁺ the availability series is peat > kaolinite > illite > montmorillonite and that the availability increases as the saturation of the Ca⁺⁺ increases.

Marshall's⁶ work on the ionization of the cations sorbed by the clay minerals has also shown a difference in relative cation replaceability for the various clay minerals (see pages 134–136). In general the higher the degree of ionization, the greater the ease of replaceability.

Fixation of Cations. It is well known by soil investigators that certain cations may be sorbed by the clay minerals in a nonexchangeable or difficultly exchangeable state. Potassium is the commonest ion that is “fixed” to a considerable degree and the ion that has been most studied because of its importance in soil fertilization. Wood and DeTurk,⁷⁵ Bray and DeTurk,⁷⁶ Stanford,⁷⁷ and others have shown that illite will fix potassium, and most of the K⁺ fixed in soils is probably due to the action of this clay mineral. Volk⁷⁸ showed that potash fixation is often accompanied by the formation of mica in the soil. The potassium fixation in illite occurs by the replacement of K⁺ between the basal surfaces of the mineral in the positions normally occupied by K⁺ in this mineral. Much illite, particularly in soils which are undergoing leaching, is somewhat degraded, i.e., it is potash-deficient in that leaching has removed some K⁺ from positions between the layers. On the addition of potassium to such material, K⁺ goes back into these normal positions, and the illite is rebuilt. Under natural soil conditions, fixation appears to be completed in a matter of months following its addition as fertilizer.

Wiklander⁷⁹ has shown that the amount of fixation in illite-type material

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Ion Exchange

varies with the cations already adsorbed. Thus fixation is relatively high for materials saturated with Ca$^{++}$ and Na$^{+}$ and low for those saturated with H$^{+}$ and NH$_{4}^{+}$. Stanford$^{77}$ also has shown that the presence of H$^{+}$, Fe$^{3+}$, and Al$^{3+}$ tends to block the fixation of K$^{+}$ by illite. Drying tends to increase the fixation by illite.

According to Raney and Hoover$^{80}$ and others, montmorillonite has some power to fix potassium, but less than illite. Other investigators, notably Stanford,$^{77}$ state that K$^{+}$ is fixed in montmorillonite only if the material is dried. Barshad$^{72}$ has shown that vermiculite can fix some potassium. In the case of montmorillonite and vermiculite, as with illite, any fixation of K$^{+}$ would take place on the basal planes between the unit layers.

Kaolinite has substantially no power to fix K$^{+}$ either in a moist condition or after drying. Joffe and Levine$^{81}$ have reported K$^{+}$ fixation by very finely ground kaolinite, but the grinding may well have destroyed the kaolinite structure.

Bray and DeTurk$^{76}$ and Wood and DeTurk,$^{75}$ working with illitic Prairie soils, have shown that the K$^{+}$ is held in various degrees of replaceability and availability to plants and that some substantially non-replaceable K$^{+}$ may be available to plants. These authors have shown that an equilibrium exists in such soils between the exchangeable and nonexchangeable potassium.

NH$_{4}^{+}$ is very similar to K$^{+}$ in its ion-exchange properties, and Chaminade,$^{82}$ Page and Baver,$^{83}$ and Stanford and Pierre$^{84}$ have demonstrated the fixation of NH$_{4}^{+}$ by clays in difficultly exchangeable form. The latter workers have concluded that the ammonium ion and the potassium ion are fixed in soils by the same mechanism.

Barshad$^{72}$ has recently investigated vermiculite and has found that this clay mineral can fix at least a part of any adsorbed Rb$^{+}$ or Cs$^{+}$. Although the matter has not been established experimentally, it seems likely that Mg$^{2+}$ could in some conditions be fixed by “degraded chlorite” by a mechanism similar to that operating for K$^{+}$ and “degraded illite.”


82 Chaminade, R., Fixation d’ion NH$_{4}$ par les colloides argileux des sols sous forme non exchangeable, *Compt. rend.*, 210, 264-266 (1940).


Also the synthesis experiments of Caillere, Henin, and Mering indicate that Mg\(^{++}\) can be fixed by montmorillonite with the development of a chlorite type of structure under certain conditions of concentration of the Mg\(^{++}\).

The fixation of magnesium and potassium is of considerable importance in diagenetic processes in sediments accumulating at the present time (see pages 351–352).

**Theory of Cation Exchange.** Numerous attempts have been made to develop a theory of cation exchange which would permit the quantitative expression of exchange data by an equation. Kelley, Marshall, and Du Rietz have reviewed this matter in detail and have commented on the deficiencies of the theories that have been proposed.

Equations based on three considerations have been suggested. Wiegner and Jenny, and Vageler and Woltersdorf derived empirical equations from, or connected with, adsorption isotherms. The general basis of these theories is Freundlich’s adsorption equation or modifications of it. Thermodynamic arguments involving more or less crude approximations have led to various mass-action equations by Kerr, Vanselow, and Rothmund and Kornfeld. Davis has criticized these latter formulations, and Kelly in turn has objected to some of Davis’s remarks. A third approach to the problem based on kinetic considerations has been made by Gapon and Jenny. Davis has recently attempted to improve Jenny’s equation.

As Kelley has shown, none of these equations is completely satisfactory, and indeed they cannot be universally applied because of the large number of variations dependent on the nature of the clay mineral, nature of ion, concentration of ion, concentration of clay, etc. The

application of any such equations would probably need to be restricted to
similar kinds of exchange material, to a given range of concentrations,
and perhaps to other factors.

Determination of Cation-exchange Capacity and Exchangeable Cations. It should be obvious from the foregoing discussion of the factors controlling cation exchange in clay minerals that accurate determinations of cation-exchange capacity and exchangeable cations are very difficult to accomplish. Literally dozens of methods have been suggested, and a tremendous amount of time has been spent on this problem. Kelley\textsuperscript{1} and Peech et al.\textsuperscript{96,95} have considered in detail the various methods and have pointed out various pitfalls.

The determination of cation-exchange capacity is at best a more or less arbitrary matter, and no high degree of accuracy can be claimed. The measurement is generally made by saturating the clay with NH\textsubscript{4} or Ba\textsuperscript{2+} and determining the amount held at pH 7. In the absence of water-soluble or slightly soluble salts, and for a clay mineral which itself is not moderately soluble, the determination is not very difficult. However, even for such materials, if the clay mineral is degraded illite or degraded chlorite, it is difficult frequently to separate exchangeable from non-exchangeable ions. Also in acid clays the presence of Al\textsuperscript{3+}, or in fer­ruginous clays the presence of Fe\textsuperscript{3+}, tends to partially clog some of the exchange positions and make the determination difficult. The determination is particularly difficult for relatively soluble clay minerals, such as the high-magnesium montmorillonites and the palygorskites. Trust­worthy determinations of cation-exchange capacity can be accomplished only by a skilled analyst who is aware of the fundamental causes of the difficulties that beset the problem.

Determination of the exchangeable-cation composition is also a very difficult problem. It involves the complete replacement of all exchangeable cations by some cation which is not present in the sample, accurate analysis of the solution obtained, and determination of and suitable correction for the cations that pass into solution from any soluble substances that may be present or from the decomposition of some insoluble material in the sample. Again the problem is particularly difficult for clay minerals of relatively high solubilities, for acid clays, and for materials with a fairly high content of soluble or moderately soluble salts. The use of the flame photometer for the analysis of the ions in the replacing solution has in recent years provided satisfactory data in a very short time, particularly for some of the alkali ions and calcium.


ANION EXCHANGE

It has been shown by Mattson,97 Ravikovitch,98 Scarseth,99 Toth,100 and many others101,27 that the constituent minerals of many soil clays exhibit anion-exchange reactions. The investigations of anion exchange in clay materials have been to a considerable extent associated with studies of the adsorption of phosphate by soils.

The investigation of anion-exchange reactions in soils is very difficult, primarily because of the possibility of the decomposition of the clay minerals in the course of the reaction. Thus, in studies of the adsorption of phosphate by kaolinite, there has been considerable argument as to whether many of the results observed are due to adsorption, to replacement of OH ions in the kaolinite lattice by phosphate ions, or to a reaction between the phosphate and alumina produced by the destruction of the kaolinite lattice.

There seem to be two, and possibly three, types of anion exchange in the clay minerals, as follows:

1. Replacement of OH ions, as has been suggested by many authors for the phosphate adsorption by kaolinite. Buswell and Dudenbostel40 presented strong evidence, based on infrared absorption, that this can take place, and recently McAuliffe and coworkers,102 using deuterium-tagged hydroxyls, have shown conclusively that the OH ions of clay-mineral surfaces can enter into exchange reactions.

Dickman and Bray103 have presented very clear evidence for the replacement of hydroxyls by fluorine in kaolinite. They showed that the liberation of hydroxyls caused a well-marked increase in the alkalinity of the suspensions. The OH and fluorine ions are of about the same size, and the exchange would involve no lattice rearrangement. In the case of exchange due to replacement of OH ions, the extent of the reaction depends on the accessibility of the OH ions, and in general the only factor

preventing complete substitution is the fact that many OH ions are within the lattice and, therefore, not accessible.

2. Hendricks\textsuperscript{104} has suggested that another factor in anion exchange is the geometry of the anion in relation to the geometry of the clay-mineral structure units. Anions such as phosphate, arsenate, borate, etc., which have about the same size and geometry as the silica tetrahedron, may be adsorbed by fitting on to the edges of the silica tetrahedral sheets and growing as extensions of these sheets. Other anions such as sulfate, chloride, nitrate, etc., because their geometry does not fit that of the silica tetrahedral sheets, cannot be so adsorbed.

In the case of both types 1 and 2 listed above, anion exchange would take place around the edges of the clay minerals. In contrast to cation exchange, as in montmorillonite, there would be substantially no anion exchange on the basal plane surfaces of any of the clay minerals. For these types of anion exchange, and in the case of the clay minerals like kaolinite in which cation exchange is due to broken bonds, the cation- and anion-exchange capacities should be substantially equal, and Dean and Rubins\textsuperscript{107} have shown this to be the case. In the case of montmorillonite and vermiculite, in which cation exchange is due mostly to lattice substitutions, anion capacity should be only a small fraction of the cation-exchange capacity. In the case of illite, chlorite, and the sepiolite-palygorskite minerals, anion-exchange capacity should be slightly less than cation-exchange capacity.

Dean and Rubins\textsuperscript{101} have shown that anion-exchange capacity of the clay mineral in the Sassafrass soil is proportional to the surface area. In addition, anion-exchange capacity would be expected to vary with the degree of crystallinity of the clay minerals. Thus, there should be a difference in the anion-exchange capacity between well-crystallized and poorly crystallized kaolinite. In the latter, because of imperfections in the stacking of the alumina-silica layers, there would be considerably more exposed OH ions available for anion exchange.

Schofield\textsuperscript{105, 106} has suggested a third manner of anion exchange. According to Schofield, the clay minerals may have anion-exchange spots, as well as cation-exchange spots, on basal plane surfaces. Such active anion-exchange positions would be due to unbalanced charges within the lattice, e.g., an excess of aluminum in the octahedral positions. It is difficult to see how this could be, since positive and negative deficiencies would tend to balance each other, unless they recurred at considerable

\textsuperscript{104} Hendricks, S. B., personal communication.
distances from each other. That is to say, there would be either positive or negative deficiencies, but not both. Schofield has indicated that in strongly acid solutions clays can take up both potassium and chloride ions, the former greatly predominating, and that both the K⁺ and Cl⁻ are exchangeable for other cations and anions. Mattson, on the other hand, has interpreted experiments on the Donnan equilibrium in such a way as to show an apparent negative adsorption of chloride and sulfate. Further experimentation is necessary to resolve this matter, and indeed much remains to be learned about the whole subject of anion exchange in the clay minerals.

A further factor complicating anion-exchange studies is that any free or exchangeable iron, aluminum, or alkaline earths present in the clay may form insoluble salts with the anions, and it is very difficult to separate the effects due to such reactions from those which may be due to reaction with the clay minerals.

**Phosphate Fixation.** Students of soils have known for a long time that some of the phosphate added to soils in fertilizers is frequently converted to an insoluble form and fixed in the soil. Such fixation can be due to the formation of insoluble salts of iron, aluminum, or the alkaline earths. The formation of phosphates of aluminum and iron probably explains to a considerable extent the results of soil-phosphate fixation experiments carried out at low pH, and the formation of phosphates of alkaline earths probably accounts for many of the results obtained at a high pH.

Black, Murphy, Scarseth, and Stout have shown that phosphate fixation also is carried out by the clay minerals, and this probably accounts for the phosphate that is fixed at about neutrality. The fixation power of the various clay minerals is relatively low, and it would seem from the work of Murphy that kaolinite, or possibly halloysite, has the highest power of all the clay minerals for phosphate fixation. Data presented by Steele indicate that the phosphate retained at pH 7 for a montmorillonitic soil is about 0.03 millimole per gram. For a kaolinitic soil it is about 0.07 millimole per gram. The other clay minerals would probably retain about as much phosphate as the montmorillonites.

In the case of kaolinite, phosphate fixation increases with decreasing

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particle size, and Stout\textsuperscript{110} has shown that fixation greatly increases in finely ground kaolinite. However, it may well be that the fine grinding of the kaolinite has so disrupted its structure that the results obtained are not a simple matter of clay-mineral fixation.

The manner in which phosphate fixation takes place in clay minerals is probably a matter of sorption of the phosphate ion in the way developed in discussing anion exchange, with the portion that is fixed being adsorbed in relatively inaccessible positions in the clay-mineral structure.

**ADDITIONAL REFERENCES**


CHAPTER 8
Clay-Water System

This chapter is concerned with water which can be held by clay materials only at relatively low temperatures and is driven off by heating to about 100° to 150°C. The OH lattice water which is lost at temperatures above about 300°C is considered elsewhere (Chap. 9). The nature of the low-temperature water and the factors that control its characteristics are of great importance, since they largely determine the plastic, bonding, compaction, suspension, and other properties of clay materials, which in turn frequently control their commercial utilization. Thus, an understanding of this low-temperature water in relation to the clay minerals must precede an understanding of the plastic and many other properties of clay materials.

The water lost at low temperatures may be classed in three categories, depending on its relation to the mineral components and to the texture of the clay materials, as follows: (1) the water in pores, on the surfaces, and around the edges of the discrete particles of the minerals composing the clay material; (2) in the case of vermiculite, montmorillonite, and the hydrated form of halloysite, the interlayer water between the unit-cell layers of these minerals (this is the water which causes the swelling of montmorillonite); and (3) in the case of the sepiolite-attapulgite-palygorskite minerals, the water which occurs within the tubular opening between the elongate structural units. Type 1 water requires generally very little energy for its removal, and drying at only a little above ordinary room temperatures is adequate for its substantially complete elimination. Water of types 2 and 3 requires definite energy for its complete removal. In the case of the hydrated form of halloysite, drying at room temperature is adequate to remove most of the interlayer water, but higher temperatures (see pages 217–218) are required for total removal. In the case of the vermiculite and montmorillonite minerals, temperatures at least approaching 100°C are necessary for substantially complete elimination of interlayer water. At this temperature some little time is required for complete removal of this water, whereas at somewhat higher temperatures it is driven off rapidly. In the case of halloysite, the reaction is not reversible and the hydrated mineral ordinarily cannot be formed again. Vermiculites and montmorillonites rehydrate with
difficulty if the dehydration is absolutely complete, but easily if only a
trace of water is allowed to remain between the unit layers. The water
in the channels of the sepiolite-attapulgite-palygorskite minerals is lost
at about the same temperature as the interlayer water of the layer clay
minerals. The channel water is regained readily if removal is by drying
only at low temperatures. The energy necessary for dehydration and the
precise temperatures at which it occurs are shown for the various clay­
mineral groups by differential thermal and dehydration analyses in
Chap. 9.

NATURE OF ADSORBED WATER

Langmuir,1 Terzaghi,2 Hardy,3 Baver,4 Winterkorn,5 and many others6
have presented evidence to show that the water held directly on the
surfaces of the clay particles is in a physical state different from that of
liquid water. It has frequently been considered to be denser and more
viscous than ordinary liquid water. The specific characteristics of this
water which delimit it from ordinary water would probably be restricted
ordinarily to relatively short distances from the clay-particle surfaces,
distances generally of the order of three to ten molecular layers of water,
i.e., 8 to 28 Å. The possible thickness of the nonordinary water can vary
a good deal even for a given clay mineral, and the transition from non­
ordinary water to ordinary water can be abrupt or gradual, depending
on factors that will be considered presently.

It appears certain that the possible thickness of the nonordinary, or
so-called nonliquid, water is relatively small on irregular surfaces, such as
those around the edges of clay-mineral particles, and relatively large on
the flat surfaces of the clay minerals. The film of nonordinary water is
best developed and appears to reach its greatest thickness on the basal
plane surfaces of the expanding-lattice minerals of the montmorillonite
group. It follows that the water in pores would be substantially liquid
water, with nonliquid water forming only a thin film on the surface of the
pores and where adjacent clay-mineral particles come together.

1 Langmuir, I., The Constitution and Fundamental Properties of Solids and Liquids,
2 Terzaghi, K., The Physical Properties of Clays, Tech. Eng. News MIT, 9, 10, 11,
36 (1928).
3 Hardy, W. B., Friction, Surface Energy, and Lubrication, “Colloid Chemistry,”
4 Baver, L. D., and H. W. Winterkorn, Sorption of Liquids by Soil Colloids, II,
115 (1943).
Clay-Water System

Terzaghi and many others have explained the initially adsorbed water on the basis of the dipole character of the water molecule; the latter possesses positive and negative charges, the centers of which do not coincide. Since the surface of the clay particle is normally negatively charged, the positive ends of the water molecules are considered to lie toward the clay surface with the negative ends extending outward. The initial layer of water is believed to consist of water molecules all oriented in the same direction. According to this concept, the first layer of oriented-dipole water molecules forms another surface of negative charges on which can be built another layer of completely oriented water molecules. This process of building up layers could be continued indefinitely were it not for the fact that the water molecules possess thermal energy and tend to be in a state of continuous motion. In accordance with classical concepts of colloidal theory, the motion due to thermal energy will oppose the regular orientation. Therefore, at any given instant and at a certain distance from the surface some of the molecules will be oriented at right angles to the surface. An instant later these molecules will have moved, but others will have become oriented in their place. At the actual clay-mineral surface the molecules will be highly oriented, and the degree of orientation will decrease going outward, as the relative effect of thermal movement becomes greater. Macey has pointed out difficulties encountered by this concept, particularly in view of the facts that the clay-mineral surface is not a uniformly charged plane and that the water molecules strictly do not act as little rods with positive and negative ends.

Earlier investigations, mainly by Bernal and Fowler and Bernal and Megaw, of the hydrogen bond and of the distribution of charges about a water molecule led Hendricks and Jefferson to a concept of the nature of the initially adsorbed water that is based on an orientation of water molecules with a structure tied to the configuration of the oxygens or hydroxyls in the basal surface layers of the unit cells of the clay minerals. In the language of Hendricks and Jefferson, a water layer is composed of water molecules joined into hexagonal groups of an extended hexagonal net, as shown in projection in Fig. 54. This arrangement is partly a result of a tetrahedral distribution of charge about a water molecule; two

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corners of the tetrahedron being occupied by hydrogen atoms and the
other two corners by an excess of electrons. Each side of the hexagon
(Fig. 54) must correspond to a hydroxyl bond, the hydrogen bond of one
water molecule being directed toward the negative charge of a neighboring
molecule. One-fourth of the hydrogen atoms, or a hydrogen atom of
half of the water molecules, are not involved in bonding within the net
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(K, M, and O of Fig. 55). The net is tied to the surface of the clay minerals by the attraction between those hydrogen atoms not involved in bonding within the net and the surface oxygen layer of the clay-mineral unit (Figs. 55 and 56). When the surface of the clay mineral contains hydroxyl groups (e.g., halloysite and kaolinite), part of the hydroxyls are free for bonding through hydrogen to oxygen atoms in the water layer.

![Diagram of Clay-Water System]

**Fig. 56.** Configuration of water net proposed by Hendricks and Jefferson,\(^9\) showing the binding through hydrogens to the adjacent clay-mineral surfaces.

The suggested\(^9\) superposition of the water net and basal layers of oxygens and hydroxyls, together with the type of bonding between them, is shown in Figs. 57 and 58, respectively.

The net has just the \(a\) and \(b\) dimensions of the silicate layer minerals, if the separation of the oxygen atoms of the water molecules is about 3.0 \(\text{Å}\) in projection. It is assumed that the oxygen atoms are in one plane. In this configuration, there is relatively loose packing of the water molecule, there being four water molecules per molecular layer per unit cell of the clay mineral instead of six, as would be the case in close packing.

The stability of the layer of water molecules arises from the geometrical
Fig. 57. Superposition of water net on the basal oxygen layer of vermiculite, suggested by Hendricks and Jefferson. Large dashed circles (A, B, C, etc.) are oxygen atoms of clay-mineral surface, 2.73 Å below plane of water molecules.

Fig. 58. Superposition of water net on the basal hydroxyl layers of two-layer clay minerals and the type of bonding between hydroxyl groups and water layers, after Hendricks and Jefferson. At L, N, and P hydrogens of hydroxyl groups are free for binding to oxygens of water molecules.
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relationship to the oxygen atoms or hydroxyl groups of the silicate framework. The presence of the first layer would favor the formation of a second layer, and the water structure would thus be propagated away from the clay-mineral surface. At some distance from the surface the dissociation pressure of successive layers, considered as hydrates, would finally approach the vapor pressure of water at the temperature of observation, and the oriented water net would cease to develop.

In the Hendricks and Jefferson\textsuperscript{10} configuration every other water molecule lies about over an oxygen of the surface layer of the three layer clay minerals (Fig. 57). Since half of the water molecules have hydrogen available for vertical bonding, the directly superimposed oxygens and water molecules may be assumed to be tied together through these hydrogen bonds. As successive molecule layers develop, the exterior layer can be tied to the layer next below by a hydrogen from every other water molecule. According to this scheme no hydrogens would be available for tying together series of water layers growing outward from two neighboring clay-mineral surfaces, unless the directly adjacent water layers of two water envelopes were tied together by relatively fewer bonds. A plane or planes of relatively weakly bonded water molecules would exist, therefore, at the junction of two water envelopes.

The Hendricks and Jefferson\textsuperscript{10} concept of the structure of the adsorbed water has been criticized by Hofmann and Hausdorf,\textsuperscript{11} Mackenzie,\textsuperscript{12} and Walker,\textsuperscript{13} because it neglects the probable influence of adsorbed cations, which in many cases are to be found directly on or at least very close to the oxygen surface on which the water configuration develops. Further, some of these cations are hydrated and, therefore, would probably significantly influence the arrangement of the water molecules directly adjacent to them. Mackenzie has particularly emphasized this point and has indicated that the matter of cation hydration would be particularly important in the part of the adsorbed water net closest to the clay-mineral surfaces. In the case of montmorillonite, there would be about one monovalent cation for each two hexagonal configurations of water in the first molecular water layer. According to Mackenzie, there is a space problem in fitting such a number of ions into the water net. Mackenzie presents computations of the energy of hydration of the sheet surface of montmorillonite carrying various ions; these data are in accord with his suggestion that, at low water contents, water sorption depends primarily on the exchangeable ion present, the sheet surface being of


subsidiary importance. Others, notably Williamson,\textsuperscript{14} have objected to the Hendricks and Jefferson concept, because of their feeling that the sorption forces are strong enough to cause a dense packing of at least the initially adsorbed water molecules.

\begin{itemize}
\item Oxygen layers forming surface of silicate
\item Oxygen atoms of ice
\end{itemize}

Fig. 59. (a) Superposition of the ice lattice on the surface oxygen layer of the clay minerals, after Macey.\textsuperscript{7} (b) Structure of ice.

Macey,\textsuperscript{7} arguing from the similarity between the structure of ice and of the oxygen atoms exposed at a sheet surface of the layer clay minerals, has postulated that the initially adsorbed water has the structure of ice. He considers that it fits on top of the oxygen net of the basal plane of

the three-layer clay minerals, as shown in Fig. 59A. The fit of the water molecules with the oxygen net as suggested by Macey is different from that suggested by Hendricks and Jefferson. According to the Macey concept, the distance between oxygens in the water layer would be 4.52 Å, and the packing would be even looser than that suggested by Hendricks and Jefferson.\textsuperscript{10} There would be three molecules of water per unit cell per molecular layer. Such loose packing of water in a given layer would be predicated on hydrogen binding to additional water not in the layer under consideration. As illustrated in Fig. 59B, showing the structure of ice, other water molecules would be just out of the plane in contact with the silicate structure, and there is no epitaxial arrangement between them and the silicate surface. In the Hendricks and Jefferson concept, the ice structure is stretched so that the offset water molecules come into the same plane and there is no change in the hydrogen binding. Also the stretch permits a complete epitaxial arrangement of all the water molecules and the silicate surface. The same objections raised against the Hendricks and Jefferson structure can be raised against the Macey structure. However, the space problem caused by the presence of adsorbed cations might be less acute. Forslind\textsuperscript{15} has reported electron-diffraction data which seem to indicate a structure at least similar to ice in the initially adsorbed water of montmorillonite. Very recently DeWit and Arens\textsuperscript{16} have published some density measurements that seem to be in agreement with the Macey concept.

Barshad\textsuperscript{17} has very recently suggested another concept of the nature of the adsorbed water on the basis of careful dehydration determinations. According to him, at very low states of hydration for montmorillonite, the water molecules tend to form tetrahedrons with the oxygens of the top layer of the linked silica tetrahedrons of the lattice. This type of packing would give rise to hexagonal rings of water molecules which are similar to the hexagonal rings of oxygens of the vertices of the linked silica tetrahedrons of the individual silicate sheets. In Fig. 60, a to f represent such water molecules forming tetrahedral units with oxygens of the underlying silica tetrahedral network. The packing in this configuration would be loose, as there would be only four molecules of water per unit cell per molecular layer, and the height added for a single layer of water molecules would be 1.78 Å, according to Barshad. It appears that this value

should be 2.1 Å, using Barshad's value of 2.55 Å for the water molecules, which reduces the agreement of Barshad’s computed and analytical data for c dimensions at certain stages of hydration. Barshad postulates that at higher states of hydration the water adsorbed by montmorillonite tends to form hexagonal rings of water molecules; these are similar to the hexagonal rings of the oxygens of the montmorillonite basal plane which forms the bases of the linked silica tetrahedrons. In Fig. 60, 1 to 6 represent such water molecules. In this configuration the packing is more dense, and there are six molecules of water per unit cell per layer of water molecules. The height added for a single water layer would be about 2.55 Å, since the water molecules would be directly superimposed on the oxygens. At still higher states of hydration, it is believed that water molecules fill even the centers of these hexagonal water rings and the centers of the hexagonal oxygen rings of the linked silica tetrahedrons not occupied by exchangeable ions. Such water layers would consist of closely packed water molecules, and there would be eight water molecules per unit cell per molecular layer. Barshad states that adsorption does not progress beyond the state of two molecular layers until dense packing is accomplished. It must be pointed out that Barshad's interpretations are based on dehydration data, which require extremely pure monomineral material. They would be subject to another interpretation if the montmorillonite and vermiculite investigated consisted of mixed layers with hydration layers of different thicknesses. Investigations by Hendricks and Mering suggest the possibility of this alternative explanation.

Thus, Mering has suggested that, in Ca montmorillonite, the initially adsorbed water is packed octahedrally about the Ca²⁺ and that, with increasing available water, a double water layer of superimposed water molecules first develops, followed by successive layers of superimposed water molecules. In Na montmorillonite, increasing amounts of water

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develop successive layers of superimposed water molecules. It appears that Barshad's concept is not substantiated geometrically as well as those of Mering and Hendricks et al.

It is obvious that students of clay mineralogy are not in agreement regarding the precise nature of the configuration of the initially adsorbed water. There is, however, general agreement that this adsorbed water has some sort of definite configuration.

DENSITY OF INITIALLY ADSORBED WATER

As indicated in discussing the configuration of the adsorbed water molecules on the clay-mineral surfaces, rather large differences in the denseness of packing are possible. The density of the adsorbed water would vary, of course, depending on the nature of the packing. Accurate determinations of the density of adsorbed water would provide evidence for or against a particular configuration. Unfortunately, the determination of the density of the adsorbed water is a very difficult problem experimentally, and although numerous determinations have been published, none are completely satisfactory. Indeed the very wide variation in the results obtained emphasizes their unsatisfactory nature.

Tscapek 20 has arrived at a value of 1.7, and Hauser and Le Beau, 21 studying bentonite suspensions, present values greater than 1, suggesting a dense packing. On the other hand Nitzsche 22 has presented determinations giving values less than 1, and recently DeWit and Arens 14 have obtained values as low as 0.73 for the density of the first few molecular layers of water adsorbed by montmorillonites. The configurations which have the greatest similarity in geometry to that of the oxygen layer of the surface of the clay minerals, namely, those of Hendricks and Jefferson 10, Macey 7, and the low-hydration types of Barshad 17 require a specific gravity less than 1.

EVIDENCE FOR THE CRYSTALLINE STATE OF THE INITIALLY ADSORBED WATER

There is abundant evidence for some sort of definite configuration of the water molecules initially adsorbed on the surfaces of the clay minerals. The characteristics of water molecules themselves afford evidence for a

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grouping into a definite network. Gieseking$^{23}$ has summarized this
point as follows:

The oxygen atom in water according to the work of Bernal and Fowler$^8$ and of
Cross et al.$^{24}$ tends to direct its attractive forces toward the four corners of a
regular tetrahedron. In the water molecules, most of the attractive force of the
oxygen atom will be directed towards the two corners of the tetrahedron where the
hydrogen atoms will reside, but a small residual force will be directed towards
the two other corners of the tetrahedron. The total positive attractive force on
the two hydrogen atoms should exactly equal the total negative attractive force
on the divalent oxygen atom. For steric reasons according to Bernal and Fowler,
the two hydrogens cannot exactly neutralize the four spots on the oxygen atoms
so that the spots where the hydrogen atoms reside will carry a slight residual
positive charge and the other two corners of the tetrahedron should carry an
equally small residual negative charge. Water molecules, therefore, tend to
attract or sorb each other. In this way a molecule of water is subjected to less
strain if the residual positive side of the molecules has this positive charge neutral­
ized by the negative side of a neighboring molecule. This process, whereby
residual positive hydrogen rich spots of one molecule neutralize residual nega­
tive spots in neighboring molecules is called hydrogen bonding. According to
Bernal and Fowler, hydrogen bonding does not stop with the union of only two
molecules of water in the liquid phase, but from X-ray diffraction patterns of
water Fowler and Bernal$^{25}$ have concluded that a few tens or hundreds of water
molecules tend to be hydrogen bonded. . . . The oxygen ions in the surface of
the clay mineral crystals, like the oxygen atoms in the water molecules, will also
be weakly charged. These layers of oxygen atoms will direct most of their forces
backward into the crystal towards the positive silicon or metallic ions in the
interstitial spaces of the clay mineral crystal. Weak residual negative charges
will result on the outside layer of oxygen atoms in the clay mineral crystals,
which will be free to take part as donors in hydrogen bonding. Each oxygen if
free from other sorbed substances could attract the hydrogenated or positive side
of a water molecule.

The oxygen atoms in the clay-mineral surface have a definite pattern, and
consequently there would be a pattern of charges on this surface that
could be carried over into the adsorbed water molecules. Therefore, the
natures of the clay-mineral surface and of the water molecules both favor
the development of a definite configuration in the initially adsorbed water.

Strong evidence that the character of initially adsorbed water is
different from that of liquid water comes from a study of the properties
of clay-water systems. Thus Grim and Cuthbert$^{26}$ have suggested a

$^{24}$ Cross, P. C., P. Burnham, and P. A. Leighton, The Raman Spectrum and the
$^{25}$ Fowler, A. H., and J. D. Bernal, Notes on the Pseudo Crystalline Structure of
$^{26}$ Grim, R. E., and F. L. Cuthbert, The Bonding Action of Clays, I, Clays in Green
theory of the bonding action of clay and water in molding sands, based on the nonliquid nature of initially adsorbed water, which accounts for the strength and other properties of such materials and explains many of their attributes which heretofore have not been understood. Grim and many others have shown that the plastic properties of clays are difficult or impossible to account for without postulating some change in the physical state of the adsorbed water. Thus, in the case of sand-clay-water mixtures, the maximum bonding force is developed when the sand and clay are wet with an extremely restricted amount of water. With a very small amount less or more than the optimum amount of water, the bond is greatly reduced. This can readily be explained by considering that the maximum bond is developed when the mixture contains the maximum amount of water that can develop a definite configuration. Additional water will, at least in part, partake of the nature of liquid water and greatly weaken the bond between the sand grains. Similarly, clays develop optimum plasticity when a definite amount of water is added to a dry clay. If water is added in small increments to a dry powdered clay, almost no experience is necessary to determine just when enough water has been added to the clay to develop plasticity. Again this phenomenon is readily explained by considering that plasticity develops when just enough water is added to satisfy the requirements of all available surfaces for water with a definite configuration plus a little more water which would develop little or no definite configuration of water molecules. For a further discussion of this point, see Grim.

Russell has pointed out that the structural characteristics of soils require that the initially adsorbed water be in a nonliquid state.

The investigators of the phenomenon of heat of wetting in clay materials (see page 186) have generally attributed it, at least in part, to a change in the nature of the water adsorbed on the surfaces of the clay-mineral particles. Many soil investigators have shown that the freezing point of the initially adsorbed water in soils is depressed. In other words the soil contains a certain amount of water in a physical state that makes it difficult to freeze. Bodman and Day have shown that montmorillonite depresses the freezing point to a greater degree than kaolinite, which is in accordance with the high water-sorption powers of montmorillonite.

On the basis of an analysis of the phase relations of water, Winterkorn has concluded that the water held directly on the clay-mineral surfaces

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must be solid and not liquid and that the change in state of the water with
distance from the clay-mineral surface is an exponential one.

THICKNESS OF ADSORBED NONLIQUID WATER

Because of the kinetic nature of the water molecules, adsorbed water
with a definite configuration of water molecules could be expected to
extend for only a limited distance from the clay-mineral surface. Numerous attempts have been made to estimate the thickness of adsorbed
water with definite nonliquid characteristics, without very good agree­
ment. However, the values probably do indicate the correct order of
magnitude.

Houwink has arrived at a value of 25 A, which is equivalent to about
10 molecular layers of water, and Mattson has given the figure of 40 A,
equal to about 16 water layers. Grim and Cuthbert, from their study
of the relation of bonding strength to water content, concluded that, for
montmorillonite with Na⁺ as the exchangeable cation, the nonliquid
water has a thickness of three molecular layers and, for Ca montmoril­
onite, the thickness is four molecular layers, or about 10 A. These same
authors also suggest that for Na montmorillonite there is a gradual
transition to liquid water beyond the 7.5-A thickness, whereas in Ca
montmorillonite the transition to liquid water is abrupt. In Na mont­
orillonite some orientation of water molecules may persist to a distance
of a hundred or more angstroms from the montmorillonite surface,
whereas in Ca montmorillonite little or none persists beyond about 15 A.
An explanation of the variation in physical properties due to variations
in the exchangeable cations seems to require that the cations influence
the thickness of the oriented layers of water molecules as well as the per­
fection of the arrangement, and perhaps also the actual nature of the
configuration of the water molecules. It is a well-known fact that, other
things being equal, Na clays require less water to develop plasticity than
do Ca clays. This may be explained by the reduced thickness require­
ment for oriented water when Na⁺ is the dominant adsorbed cation.

In contrast to the relatively small thickness of nonliquid water sug­
gested by the previous authors, Jaeger and later Spiel have concluded

30 Houwink, R., "Elasticity, Plasticity and Structure of Matter," Cambridge, New
York (1937).
31 Mattson, S., Laws of Soil Colloidal Behavior, VII, Form and Function of Water,
32 Jaeger, F. M., Viscosity of Liquids in Connection with Their Chemical and
Natuurk., Sec. II, 16 (1938).
33 Spiel, S., Effect of Adsorbed Electrolytes on the Properties of Monodisperse
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that the thickness of adsorbed water at optimum plasticity for kaolinite clays is of the order of several hundred angstroms. Opposed to these very large values, DeWit and Arens\(^\text{16}\) have recently concluded that the thickness of adsorbed water held by kaolinite is to be measured in a very few molecular layers.

Reasoning on structural grounds and from the properties of clay-water systems, it would seem unlikely that kaolinite would adsorb water with a definite configuration to a greater thickness than would montmorillonite. The low values for the thickness of the nonliquid water for kaolinite therefore seem most reasonable. It seems likely that the illite, chlorite, and possibly also the vermiculite minerals would yield values similar to kaolinite. No information is available on this characteristic for the palygorskite-attapulgite-sepiolite minerals.

TIME FACTOR

Grim and Cuthbert\(^\text{34}\) have shown that, when rammed samples of sand, water, and certain clays are allowed to stand under certain conditions, there is an increase in the compression strength without any loss of water. This “air-set” strength is explained by them on the basis that a certain amount of time is required for the water to penetrate to some of the surfaces of the clay-mineral particles and for the water molecules to assume their orientation. According to them, the compressive strength is dependent on the development of nonliquid water.

These authors\(^\text{6}\) emphasize the general fact that the properties of clay-water systems may change with time without a change in water content because of a change in the nature of the water. This is a matter of very great importance in certain fields of the utilization of clays. For example, in engineering practice, it makes it difficult to translate laboratory findings on strength, sensitivity, etc., to actual field application because of the difficulty of duplicating field conditions and of evaluating the time factor. Engineers are aware of this factor in their constant use of undisturbed samples with carefully retained natural moisture content for their laboratory tests. Its significance is illustrated by the very different values obtained for such properties as compressive strength and plasticity on undisturbed and remolded samples.

INFLUENCE OF CATIONS AND ANIONS

The ions adsorbed on the surfaces of the clay minerals may affect the adsorbed water in several ways:

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1. A cation may serve as a bond to hold the clay-mineral particles together or to limit the distance to which they can be separated.

In general, multivalent cations have a greater tendency than univalent cations to tie clay-mineral flakes together. The potassium ion is an exception, probably because its size permits it to fit snugly in the hexagonal perforation of the oxygen net of the surface of the three-layer clay minerals and because its coordination number is favorable. The ammonium ion acts like the potassium ion. In the case of other common monovalent cations, there would probably be little tendency for the ion to tie the particles together, and under some conditions it might enhance the repulsive force between the particles.

2. Certain of the adsorbed cations may become hydrated. The hydrated ions would be enclosed in an envelope of water molecules probably having some sort of configuration. This configuration and its relation to the arrangement of water molecules on adsorbing surfaces some distance from the hydrated ions would influence the over-all nature of the arrangement of the water molecules and the thickness to which the orientation could develop. It is of interest and importance that the hydrated calcium and magnesium ions apparently restrict the thickness of the adsorbed water with a well-developed configuration, whereas in the case of the sodium ion, which may not be hydrated, oriented water can grow to very great thicknesses. However, the lithium ion, which is also hydrated, permits oriented water of great thickness to develop. According to Hendricks et al., Li⁺ is surrounded by only three molecules of hydration water, whereas Ca⁺⁺ and Mg⁺⁺ are surrounded by six molecules of hydration water. Because of this difference in the amount of hydration and perhaps also because of the small size of the lithium ion, it would be expected to influence the normal net of water molecules to a smaller degree than would calcium and magnesium ions.

3. The size of the adsorbed ions is of importance, as has been emphasized by Sullivan, Forslind, and others. Forslind, for example, has suggested that small ions, which would fit into the net of water molecules without disrupting it, would be expected to have a tightening effect on the net which would enhance its development. Ions which would not fit into the water net, because of their size, would be expected to retard or even prevent its development.

4. The geometry of the adsorbed ions is probably also of importance, in relation to the possible fit of the adsorbed ions into the water net

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and resulting disruption or weakening of the water configuration. It seems that, in the case of some anions, such as the phosphate ion, this matter of geometry is of particular importance. For example, it is well known in the drilling-mud art that an extremely small amount of the phosphate ion may greatly influence some of the thixotropic characteristics of montmorillonite-water suspensions. The probable explanation resides in the similarity between the tetrahedral nature of the phosphate ion and the configuration of the water molecules; this similarity would permit the phosphate tetrahedrons to almost fit into the water structure. They would fit without completely disrupting the water structure but would cause some strain and weakening of the water configuration, which would account for the alteration of the thixotropic characteristics of the system.

Hendricks, Nelson, and Alexander have made a very careful study of the water adsorbed by montmorillonite saturated with various cations. They have determined the amount of water adsorbed at various relative humidities, the resulting variation in the c-axis spacing of the mineral, and the corresponding differential thermal curves. The differential thermal curves show an endothermic peak due to the energy necessary to drive off the adsorbed waters from the montmorillonite. Some of the results of the work of Hendricks and his colleagues are shown in Figs. 61 and 62. The endothermic peak due to loss of adsorbed water is single, double, or triple for certain of the cations prepared at certain relative humidities. These workers interpret the composite nature of the multiple peaks—and their interpretation is in accord with their other data—as follows: In the case of dual peaks of samples prepared at comparatively low relative humidities, the larger of the maxima is attributed to the dehydration of the cation, and the lesser of the maxima to the loss of water from the surface of the clay mineral away from the hydrating cation. At higher relative humidities the dual peaks may become triple, and the third maximum is attributed to the development of an additional layer of oriented water molecules. Thus Mg montmorillonite shows a dual peak after adsorbing water at 5 per cent relative humidity and a triple peak after being treated at only 10 per cent relative humidity. Ba and Li montmorillonites show no evidence of the development of a second water layer unless the relative humidity is at least 40 per cent.

Certain of the univalent ions, e.g., Na+, K+, and Cs+, show a single peak after treatment at low relative humidities, and this is interpreted to mean that these ions are not hydrated. As has been mentioned elsewhere, there is other evidence for the nonhydration characteristics of these cations.

Hendricks, Nelson, and Alexander conclude from their investigation
Fig. 61. Thermal-analysis curves, amounts of adsorbed water, and values of the apparent cleavage space of magnesium, calcium, strontium, and barium salts of Mississippi montmorillonite, after Hendricks, Nelson, and Alexander.
FIG. 62. Thermal-analysis curves, amounts of adsorbed water, and values of the apparent cleavage space of lithium, hydrogen, potassium, and cesium salts of Mississippi montmorillonite, after Hendricks, Nelson, and Alexander.18
that, for montmorillonite carrying magnesium and alkaline-earth ions, the first step of water sorption is the hydration of the cation with six molecules of water; this is followed by completion of a water layer having a hexagonal type of structure. An additional water layer of similar structure is taken up at higher relative humidities. Similar results were obtained for Li montmorillonite, except that only three molecules of water were required for the hydration of the lithium ion. In montmorillonites carrying sodium, potassium, and cesium, the cation apparently was not hydrated. Mackenzie has recently questioned the interpretation of the single endothermic peak of Na montmorillonite as evidence for the nonhydration of the sodium ion. According to him, all the water molecules in a single molecular water layer of Na montmorillonite could be tied to the sodium ion and, therefore, could be expected to yield a single endothermic peak.

Barshad's concept (see page 169) of a change in the configuration of the water molecules as the amount of water sorbed increases, provides another possible explanation for the multiple nature of the differential thermal endothermic peaks resulting from the loss of adsorbed water. Mering has presented evidence suggesting that, at low relative humidities (below about 30 per cent relative humidity), a Ca montmorillonite does not form a single water layer but instead a skeletal double layer, corresponding to the octahedral coordination of hydration water about the Ca++, and that the thickness of such a water layer is about 4.4 A. At relative humidities between 30 and 80 per cent, two complete water layers develop, and the thickness of the water layer increases to about 5.9 A. Mering has shown that saturation of about 30 per cent of the base-exchange capacity with Ca++ is adequate to produce the hydration characteristics of a Ca montmorillonite. Walker has suggested a similar hydration sequence for Mg vermiculite. It is clear from the foregoing that further investigation is required before the detailed steps in the sorption of water by montmorillonite with various adsorbed cations is well understood.

Numerous investigations have brought out the interesting fact that Na montmorillonite, on drying at room temperature, tends to develop a single water layer between the silicate layers and that Ca montmorillonite under the same conditions tends to develop two water layers, whereas, at high relative humidities and in the presence of an abundance of water, Na montmorillonite sorbs by far the larger quantity of water.

Clay-Water System

Barshad\(^{38}\) has studied the sorption of water by vermiculite. According to him, vermiculite saturated with Mg\(^{++}\), Ca\(^{++}\), Ba\(^{++}\), H\(^{+}\), Li\(^{+}\), or Na\(^{+}\) shows, when immersed in water, total sorption between the silicate layer equal to only two molecular water layers. When vermiculite saturated with K\(^{+}\), NH\(_4\)^{+}, Rb\(^{+}\), or Cs\(^{+}\) is immersed in water, there is no expansion of the lattice, indicating no water sorption between the silicate layers.

Siefert\(^{39}\) has presented the results, shown in Table 23, for the sorption of water by kaolinite. These data show the relative influence of the various cations on water sorption by this clay mineral.

**Table 23. Influence of Cations on Water Sorption of Kaolinite**

<table>
<thead>
<tr>
<th>Relative humidity, per cent</th>
<th>Order of decreasing sorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Ca &gt; H = Na = K</td>
</tr>
<tr>
<td>81.5</td>
<td>H = Ca &gt; Na &gt; K</td>
</tr>
<tr>
<td>99.9</td>
<td>H = Ca = Na &gt; K</td>
</tr>
</tbody>
</table>

Mackenzie\(^{12}\) has recently suggested that a given ion like Na\(^{+}\) might hydrate to a different degree on different clay minerals and even on the same type of clay mineral if the bonding force holding the ion varied. Thus, in montmorillonite the degree of hydration of Na\(^{+}\) might vary depending on whether the charge holding it derived from a substitution within the tetrahedral or the octahedral sheet.

**Stepwise Hydration of Montmorillonite**

Careful study by Bradley, Clark, and Grim\(^{40}\) of a hydrogen montmorillonite produced by electrodialysis of a Wyoming bentonite indicated that the swelling of the lattice during hydration took place in a stepwise fashion. A series of four apparently definite and discrete hydrates were found, having cell heights of 12.4, 15.4, 18.4, and 21.4 Å. Near the range where any given hydrate is stable, successive orders of (00l) reflections appear for it alone. In intermediate ranges two suites of (00l) reflections appear simultaneously, one to be identified with the hydrate next higher in the sequence and one with the hydrate next lower.

In their study, Bradley et al.\(^{40}\) used oriented aggregates in which the basal cleavages were substantially parallel. Hofmann,\(^{41}\) working with

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powders, failed to check the conclusions of Bradley et al., but later Hofmann and Hausdorf, using oriented aggregates, also concluded that the hydration of montmorillonite took place by the formation of successive monomolecular layers of water. The latter investigators, and later Hendricks and Jefferson, have shown theoretically that powder diffraction should indicate that the c-axis-dimension spacing varies continuously but not uniformly with water content, and that this apparently would be a result of an averaging effect from a lattice that contains various numbers of water layers in different parts. That is, the apparently continuous change in the c dimension results from a random alternation of successive discrete hydrates.

Mering and others have shown that the development of discrete monomolecular water layers probably does not hold precisely at low moisture contents when the clay carries an adsorbed ion that hydrates, e.g., Ca$^{++}$ or Mg$^{++}$. In these cases, the hydration net around the cation prevents the orderly development of the initial hydration layers.

**STABILITY OF MONTMORILLONITE HYDRATION**

A considerable body of evidence, largely unpublished, shows that montmorillonite clays, when subjected for long periods of time to substantially uniform moisture conditions, develop hydration characteristics of considerable stability. Such materials resist change in the degree of hydration, but when the hydration is changed even to a very slight degree, the stability may be abruptly and completely lost. Thus a high-swelling bentonite sample carefully collected to preserve its natural hydration can be placed in water without any slaking, even when moderately stirred. However, if such a bentonite is dried only a very small amount, it will slake and swell immediately when placed in water. Apparently, if hydration layers develop with a high degree of uniformity of thickness and distribution, they have considerable stability, which is not present if there is even a very minor variation in thickness from layer to layer.

This matter of stability of hydration is of great practical importance. In soil mechanics, for example, tests run on samples with the natural moisture carefully retained (as is the usual procedure) are likely to give results completely misleading if applied to the materials as used in the field, where some loss of water may take place.

A further point in regard to the stability of montmorillonite hydration is worthy of note. When the dried mineral is placed in water, it may rapidly adsorb water up to a certain point and then become a thick pasty mass. No more water is sorbed unless the mass is stirred vigorously. Adsorption tends to stop at a given point, and an equilibrium is developed at a very high moisture content. This characteristic is shown particularly by the Na montmorillonite in the bentonite from the Wyo-
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It is of considerable commercial utility in that it permits the mineral to be used for water impedance.

INFLUENCE OF ADSORBED ORGANIC MOLECULES

Gieseking\textsuperscript{42} reported that montmorillonite clays lost their tendency to swell by water sorption when saturated with a variety of organic cations. These cations are adsorbed on the basal plane surfaces of the montmorillonite (see Chap. 10). Hendricks\textsuperscript{43} has shown that the amount of water adsorbed by montmorillonite carrying certain adsorbed amine ions approaches closely the quantity expected from the difference between the total extent of the surface and the probable part of the surface covered by the amine ions. Hendricks has also pointed out that the reduction in water sorption should not be exactly correlative with the size of the organic ion, since the shape of the organic ion may be such as to destroy the configuration of water molecules in the adsorbed water layer.

Grim, Allaway, and Cuthbert\textsuperscript{44} have shown that water adsorption of kaolinite clays is reduced after their treatment with organic ions and that the decrease in water adsorption is relatively less for kaolinite than for montmorillonite. It appears certain that similar results would be obtained for the other clay minerals and that the values would be intermediate between those for montmorillonite and kaolinite.

HEAT OF WETTING

A dry clay material evolves heat when placed in water, and this phenomenon is known as the heat of wetting. Heat is also evolved when clay materials are placed in some liquids other than water, as, \textit{e.g.}, alcohols and various organic liquids. Janert\textsuperscript{45} has shown that heat of wetting may be higher for organic liquids, and that values generally are higher for polar than for nonpolar liquids. Janert has also shown that there is no direct correlation between polarity and heat of wetting, so that polarity is not the sole determining factor. Figure 63, giving data for the heat of wetting for water and for carbon tetrachloride as developed by a "brick clay," illustrates the kind of difference in values for water


and some other liquids. The heat of wetting decreases as the moisture content of the clay increases at the time of making the determination (Fig. 63). Miller et al. 46 present heat-of-wetting values for attapulgite obtained with water and several organic liquids (Table 24). The organic liquids used by them also gave lower values than water, and for a series of normal alcohols the values decreased markedly as the chain length of the alcohol increased.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Dried raw clay</th>
<th>Clay dried at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>400°C</td>
</tr>
<tr>
<td>Water</td>
<td>10.6</td>
<td>17.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>4.2</td>
<td>...</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>...</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Heat of wetting is measured in calories per gram of dried clay, with the drying being done usually at 110°C.

Values for Heat of Wetting. Heat-of-wetting values for kaolinite and montmorillonite saturated with various cations and for an illite sample are given in Table 25. Values for attapulgite, given in Table 24, are only slightly lower than those of montmorillonite.

TABLE 25. HEAT-OF-WETTING VALUES FOR KAOLINITE, MONTMORILLONITE, AND ILLITE, IN CALORIES PER GRAM

<table>
<thead>
<tr>
<th>Reference</th>
<th>Kaolinite</th>
<th>Montmorillonite</th>
<th>Illite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Natural</td>
<td>Ca++</td>
<td>H+</td>
</tr>
<tr>
<td>Siefert</td>
<td></td>
<td>1.45</td>
<td>1.40</td>
</tr>
<tr>
<td>Endell, Loos, et al.</td>
<td></td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Parmelee and Frechette</td>
<td></td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>

Values for the other clay minerals are not yet available, but they will undoubtedly range between those for montmorillonite and kaolinite. Chlorite will probably yield values closer to those for illite, and vermiculite closer to those for montmorillonite.

Pate, Anderson, Janert, and others have shown that the heat of wetting varies with the adsorbed cation and that it is generally higher for divalent than for univalent cations. Janert gives the order Ca > Mg > H > Na > K.

Harmon and Fraulini have presented data showing an increase in heat of wetting for kaolinite as the particle size of the kaolinite decreases (Table 26). This is an expected relationship, since heat of wetting

TABLE 26. HEAT OF WETTING OF KAOLINITE IN RELATION TO PARTICLE SIZE AND CATION-EXCHANGE CAPACITY

<table>
<thead>
<tr>
<th>Particle size, microns</th>
<th>10-20</th>
<th>5-10</th>
<th>.2-.4</th>
<th>.1-0.5</th>
<th>0.5-0.25</th>
<th>0.25-0.1</th>
<th>0.10-0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of wetting, cal/g</td>
<td>0.95</td>
<td>0.99</td>
<td>1.15</td>
<td>1.38</td>
<td>1.42</td>
<td>1.87</td>
<td></td>
</tr>
<tr>
<td>Exchange capacity, meq/100</td>
<td>2.40</td>
<td>2.60</td>
<td>3.58</td>
<td>3.76</td>
<td>3.88</td>
<td>5.43</td>
<td>9.50</td>
</tr>
</tbody>
</table>


should increase as the surface area increases with decreasing particle size. It should apply equally well to the other nonexpanding clay minerals. In the case of expanding-lattice minerals, such as montmorillonite and vermiculite, there should be no strict correlation with particle size, since the total surface is theoretically available to water sorption regardless of the size of the particles. However, in the case of large units, as in vermiculite, there would probably be some variation in the ease of wetting of the particle surfaces, so that some variation of heat of wetting with particle size probably would be found. Also, the surfaces of montmorillonites carrying certain adsorbed ions, e.g., K\(^+\), are not completely available for water adsorption, and some correlation with particle size would be expected for such montmorillonites.

Anderson and Mattson,\(^5\) Baver,\(^4\) and others have pointed out a relation between cation-exchange capacity and heat of wetting for a series of natural soils. Montmorillonites with a very high cation-exchange capacity yield high values for heat of wetting; kaolinites with low cation-exchange capacity yield low heat-of-wetting values; and illites give intermediate values. Soils composed of one or a mixture of these common clay minerals would show some correlation between cation-exchange capacity and heat of wetting. It is doubtful if a close correlation would exist between these two characteristics in a series of natural soils—certainly it would not be a straight-line relationship—since other factors, such as particle size and nature of adsorbed cation, would influence the heat evolved on wetting.

**Cause of Heat of Wetting.** Behrends\(^5\) has narrated early ideas offered to explain heat of wetting, such as the compression of water at the adsorbing surface, capillary condensation, etc. It is now generally agreed that the phenomenon is due to two factors: (1) a change in state of the water directly adjacent to the adsorbing surface, and (2) the possible hydration of adsorbed ions. Baver and Winterkorn\(^6\) have emphasized the importance of the development of orientation of the water molecules in the adsorbed water as a cause of heat of wetting.

Janert\(^4\) has shown that the heat of wetting, calculated per equivalent, is only a fraction of the values usually assigned to the total heat of hydration of various cations in dilute solutions. This is explained on

the basis that the ion is not completely free and is, therefore, capable of only partial hydration. According to Janert, the ratios of the heat of wetting to the heat of hydration for various ions are as follows: for H clays 1:11.5, for Mg clays 1:9, for Ca clay 1:7, for K clays 1:5.1, and for Na clays 1:4.9. Janert was of the opinion that ion hydration is a major cause of the heat of wetting.

Siefert computed the heat evolved per milliequivalent of cation and found that a given cation adsorbed by kaolinite evolves more heat than when adsorbed by montmorillonite. Since, in montmorillonite, there is little surface aside from that occupied by the cation, Siefert concluded that the heat of wetting due to the surface is greater than that due to cation hydration.

It seems likely that the relative importance of surface and cation hydration would vary for different clay minerals and for various adsorbed cations. It is probably incorrect to assume that either factor is always the more important cause.

**Heat of Wetting in Solutions of Electrolytes.** Siefert has shown that when hydrogen kaolinite is wetted in 0.1 N NaOH or 0.015 N Ca(OH)₂ solutions, there is an increase in heat evolved of 0.2 cal/g over that of pure water; this is probably due in part to the neutralization of the clay acid by the base. However, Na kaolinite wetted in NaOH and K kaolinite wetted in KOH showed a similar increase in heat evolved in comparison to that developed in water. Somewhat similar results were obtained by Siefert for montmorillonite clays. The explanation for this phenomenon is not clear, but it may be merely the result of the better dispersion of the clay in the alkaline solution.

**Effect of Firing.** The data given in Fig. 64, after Parmelee and Frechette, show the relation of heat of wetting to firing temperature for montmorillonite, kaolinite, and illite. In the case of the montmorillonite, there is a sharp drop in heat of wetting after firing at the temperature where hydroxyl water is lost from the lattice. The illite shows a slight increase in heat of wetting on firing up to about 450°C and a reduction in heat of wetting after temperatures somewhat above that required for the loss of hydroxyl water. The kaolinite shows a slight reduction in the amount of heat evolved when heated to temperatures somewhat in excess of that required for the loss of hydroxyl water. Data given by Miller et al. (Table 24) show the heat of wetting of attapulgite to increase greatly on firing up to about 550°C and then decrease, so that after firing at 900°C the same value as that for the unfired mineral is obtained. The reason for the changes in heat of wetting of the various clay minerals when heated to these particular temperatures is not clear. Additional experimental data are needed before heat-of-wetting values for fired clays can be understood.
ADDITIONAL REFERENCES


Clay-Water System


Kapp, L. C., The Approximate Size of Soil Particles at Which the Heat of Wetting is Manifest, Soil Sci., 401-412 (1930).


Kiefe, C., Sur les possibilités de liaisons et d'orientation des molecules d'un liquide sur un solide. Epitaxie entre la kaolinite et l'eau, mimeographed, Paris (1947).


Schwarz, F., Heat of Wetting of Clays, Sprechsaal, 82, 24-25 (1949).


CHAPTER 9

Dehydration, Rehydration, and the Changes Taking Place on Heating

Dehydration involves the loss of any water, adsorbed, interlayer, or lattice OH water, held by the clay minerals. A study of dehydration is concerned with the amount of water lost, rate of water loss, temperature of dehydration, and energy involved. Dehydration frequently involves significant changes in the structure of the clay minerals, and consequently changes taking place during the heating of the clay minerals cannot be considered apart from dehydration. Changes taking place in the clay minerals on heating to relatively high temperatures are not necessarily related to dehydration reactions, but for the sake of uniformity and continuity, such changes will also be considered in this chapter.

Certain of the clay minerals take up water again on cooling after being heated to moderately high temperatures. Such rehydration characteristics will also be considered here.

METHODS OF STUDY

Various methods are available for studying the hydration properties of the clay minerals. Since some of the methods supplement each other, it is frequently desirable to use more than one procedure. This is particularly true where phase changes are important. For such studies, a combination of X-ray diffraction and some other method is necessary.

Vapor-pressure—Water-content Determinations. This method has been used by Thomas,¹ Puri,² Kuron,³ Alexander and Haring,⁴ and many other investigators of soils. Air-dried samples are allowed to absorb moisture at various relative humidities, and curves are plotted of water content.

Dehydration content versus vapor pressure. It is likely, as Nagelschmidt has pointed out, that the exchangeable ions are of greater importance than the clay minerals themselves in causing the variations in moisture content as determined. Only very limited application of the method has been made to monomineral samples, and its contribution to the knowledge of clay minerals remains for future studies.

Dehydration Curves. In this method the loss in weight of the material upon heating to higher and higher temperatures is recorded and plotted against the temperature. There are several variations of the method as follows:

The sample may be heated at a given temperature until no loss in weight occurs; it is then heated to a higher temperature and held at that temperature until no loss in weight takes place. This procedure is repeated until a temperature is reached at which there is no further loss in weight. This procedure has been used by Nutting, Ross and


Fig. 65. Dehydration curves, from Nutting. The weight at 800°C is taken as the base weight in plotting the curves. (A) Halloysite, Liège, Belgium; (B) kaolinite, Ione, California; (C) anauxite, Mokelumne River, California.
Kerr, Kelley, and many others. Results for the various clay minerals are given in Figs. 65 to 69. Various investigators have plotted their data somewhat differently, as illustrated in Figs. 65 to 69.

The sample may be heated continuously at a constant rate, which has varied in the experiments of different investigators from 5°C/hr to 10°C/min, and the loss in weight is recorded at successively higher temperatures. The samples are weighed while they are hot. Migeon 12

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Fig. 66. Dehydration curves, after Nutting. The weight at 700° to 900°C is taken as the base weight in plotting the curves. (A) Penninite, Paradise Range, Nevada; (B) chlorite, Danville, Virginia; (C) palygorskite (mountain leather), Montana; (D) sericite, Prince Rupert, British Columbia; (E) vermiculite, North Carolina; (F) illite, Fithian, Illinois; (G) glauconite, Lyons Wharf, Maryland; (H) sepiolite, Asia Minor.

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Dehydration

and Longchambon\textsuperscript{13} particularly have used this procedure, and results for some of the clay minerals are shown in Fig. 70. In this method equilibrium conditions are not reached at any given temperature.

In both the above procedures, the actual humidity of the air in contact with the sample should be kept constant, since variations will affect the results. Nagelschmidt\textsuperscript{5} has pointed out that it is generally assumed that

\[
\begin{align*}
\text{Loss of Water in Per Cent} & = f(T) \\
\text{Temperature } ^\circ \text{C} & = g(T)
\end{align*}
\]

the loss in weight of one mineral upon heating is not affected by the presence of a second mineral and that the dehydration curve of a mixture would be equal to the superposition of curves of the separate minerals in the mixture. This assumption has not been proved, and, indeed, data from differential thermal analyses (see page 210) show that it is likely to be true only in some mixtures and not in others.

In the case of natural clays which are not pure clay minerals, the loss

in weight which is measured is not necessarily due entirely to a loss of water. It may be due to the loss of CO$_2$ from carbonates and to the loss of volatile constituents which may be present in nonclay-mineral components. Also, if divalent iron and/or manganese are present, their oxidation would tend to cause an increase in weight and thereby to reduce the apparent water loss. Variations in the specific characteristics of the minerals being studied, such as grain size, crystallinity, nature of adsorbed ions, etc., affect dehydration results. These factors also influence differential thermal results, and they will be considered in some detail, as well as in the discussion of the dehydration properties of the individual minerals.

**Differential Thermal Analyses.** The method of differential thermal analysis determines, by suitable apparatus, the temperature at which
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thermal reactions take place in a material when it is heated continuously to an elevated temperature, and also the intensity and general character of such reactions. In the case of the clay minerals, differential thermal

analyses show characteristic endothermic reactions due to dehydration and to loss of crystal structure and exothermic reactions due to the formation of new phases at elevated temperatures. The method is, therefore, useful for clay-mineral researches as a means of studying high-temperature reactions, in addition to its value in the investigation of hydration phenomena.
The method is not restricted to clays and, in fact, has been applied to a wide variety of materials, such as carbonates, hydrates, sulfides, organics, etc. It is applicable to any material which experiences thermal reactions on heating which begin abruptly and are completed in a relatively short temperature interval.

Differential thermal results are plotted in the form of a continuous curve in which the thermal reactions are plotted against furnace temperatures, with endothermic reactions conventionally shown as downward deflections and exothermic reactions as upward deflections from a horizontal base line. The amount of divergence of the difference curve from the base line reflects the difference in temperature between the sample and the furnace at any given temperature and is, therefore, a measure of the intensity of the thermal reaction. Differential curves for the various clay minerals are given in Figs. 71 to 76.

History of Method. Le Chatelier in 1887, in an investigation of the components of clays, appears to have been the first person to set up simple apparatus to measure and record thermal reactions taking place in a material when it is heated and to have used such data as analytical criteria to study the material. Little use was made of the method by mineralogists until about

\[\text{Ref.}\]

\[\text{Le Chatelier, H., De l'action de la chaleur sur les argiles, Bull. soc. franç. minéral., 10, 204-211 (1887).}\]
Dehydration

FIG. 72. Differential thermal curves: Scale A. (A) Montmorillonite, Otay, California; (B) montmorillonite, Tatatilla, Mexico; (C) montmorillonite, Upton, Wyoming; (D) montmorillonite, Cheto, Arizona; (E) montmorillonite, Pontotoc, Mississippi; (F) montmorillonite, Palmer, Arkansas; (G) nontronite, Howard County, Arkansas; (H) hectorite, Hector, California.

FIG. 73. Differential thermal curves: Scale A. (A) Biotite, University of Illinois collections; (B) muscovite, University of Illinois collections; (C) muscovite, Bryman, California (minus one micron fraction); (D) illite, Fithian, Illinois; (E) illite, Grundy County, Illinois; (F) illite, Thebes, Illinois; (G) glauconite, New Jersey; (H) glauconite, Washington.
1910, when several investigators used it in a study of clays. In these early studies the procedure generally followed was to place the material in a small platinum crucible with a single thermocouple junction in the center of the material. The whole mass was placed in a furnace and heated at a rapid and relatively uniform rate. The thermocouple was attached to a galvanometer which was read periodically at short intervals or recorded photographically. Thermal reactions in the material caused variations in the galvanometer record as compared to that obtained when the furnace contained no sample. The record obtained showed the thermal reactions of the material superimposed on the heating curve of the furnace. Examples of such records are shown in Fig. 77.

In 1899 Roberts-Austen devised the differential-thermocouple method for measuring temperature differences between a material and a reference unit, and in 1908 Burgess suggested simple, adaptable, and usable differential-thermocouple circuits. After the work of Roberts-Austen, the difference thermocouple was widely used by metallurgists, but Fenner in 1913, in his study of the stability relations of the silica minerals, appears to have been the first to apply it outside of the field of metallurgy. The technique devised by Fenner is substantially that used today in differential thermal analyses with some elaboration and refinement. Following Fenner’s work, the method was used sporadically in the study of high-temperature phase changes by Kracek and others and frequently in the study of the constituents of clays by various investigators.

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Fig. 74. Differential thermal curves: Scale A. Illite associated with chlorite: (A) maquoketa shale, Illinois; (B) Minford silt, Ohio. Illite with mixed layers of montmorillonite: (A) Bear River, Wyoming; (B) Sirospatak, Hungary (sarospattite); (C) Noyant Allier, France (bravaisite); (D) Decorah shale, Wisconsin.

In 1899 Roberts-Austen devised the differential-thermocouple method for measuring temperature differences between a material and a reference unit, and in 1908 Burgess suggested simple, adaptable, and usable differential-thermocouple circuits. After the work of Roberts-Austen, the difference thermocouple was widely used by metallurgists, but Fenner in 1913, in his study of the stability relations of the silica minerals, appears to have been the first to apply it outside of the field of metallurgy. The technique devised by Fenner is substantially that used today in differential thermal analyses with some elaboration and refinement. Following Fenner’s work, the method was used sporadically in the study of high-temperature phase changes by Kracek and others and frequently in the study of the constituents of clays by various investigators.

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Fig. 75. Differential thermal curves:
(A) prochlorite, Chester, Vermont; (B) clinohlore, Brewster, New York; (C) vermiculite and chlorite, Lenni, Pennsylvania; (D) vermiculite, North Carolina, natural; (E) vermiculite, North Carolina, Ca\(^{++}\); (F) vermiculite, North Carolina, Na\(^{+}\); (G) vermiculite, North Carolina, NH\(_4\); (H) vermiculite, North Carolina, K\(^{+}\). Curves C to H from Barshad;\(^{82}\) vertical scale slightly less than for other curves. Scale B for curves A and B.

Fig. 76. Differential thermal curves:
Scale A. (A) Attapulgite, Atapulgus, Georgia; (B) sepiolite, Salinelles, France; (C) palygorskite, North Africa; (D) palygorskite, from Caillere;\(^{84}\) (E) vermiculite, Arizona; (F) pyrophyllite, North Carolina; (G) talc, Vermont; (H) quartz, University of Illinois collections.
tors. In 1933 and 1935 excellent reports by Orcel and Caillere emphasized clearly the applicability of the method to clay-mineral researches, and since that time it has been used in the study of clays by many different investigators in many different countries. More recently, the method has become popular with investigators of other materials such as carbonates, sulfates, hydrates, etc.

**Description of Method.** In the method as generally used today, the sample to be studied is placed in one hole of a specimen holder, and an inert material that experiences no thermal reaction when heated to the temperature of the experiment, usually calcined aluminum oxide ($\alpha$-$\text{Al}_2\text{O}_3$), is placed in another hole of the specimen holder. One junction of the difference thermocouple (Fig. 78A) is placed in the center of the sample and the other junction in the center of the inert material. The holder and thermocouples are placed in a furnace so controlled as to

![Diagram](image_url)

**Fig. 77.** Thermal reactions in clay superimposed on furnace heating rate, as recorded by Wohlin. Curve $A$ is furnace heating curve. Curves $B$ to $D$ show furnace heating rate with thermal reactions for clays superimposed.
produce a uniform rate of temperature increase. The temperature of the inert material increases regularly as the temperature of the furnace increases. When a thermal reaction takes place in the sample, the temperature of the sample is greater or less than that of the inert material, depending on whether the reaction is exothermic or endothermic, for an interval of time until the reaction is completed and the temperature of the sample again comes to the temperature of the furnace. Consequently, for an interval of time the temperature of one junction of the difference couple is different from that of the other, and an emf is set up in the differential-thermocouple circuit which is recorded as a function of time or of the temperature of the furnace. The record may be made manually with a potentiometer or galvanometer, photographically with a galvanometer, or automatically with some electronic device. When no thermal reaction is taking place in the specimen, the temperatures at both junctions of the difference couple are the same, and no emf is set up. The direction of the emf in the circuit depends on whether the temperature of the sample is above or below that of the inert material, and consequently the recording mechanism moves in opposite directions for endothermic and exothermic reactions.

Figure 79 shows an idealized equilibrium dehydration curve and differential thermal curve for kaolinite. The endothermic reaction between about 500° and 700°C corresponds obviously to the dehydration of the mineral. A comparison of the curves illustrates that the differential method is a dynamic rather than a static one. The thermal reactions are not instantaneous, and they are recorded as functions of time or as

![Diagram of thermocouple setup](image)

**Fig. 78.** (a) Thermocouple setup as used today; (b) thermocouple setup as used in early work and in some current work. (a) Platinum–10 per cent rhodium wire; (b) platinum wire.
functions of the furnace temperature, which is continuously increasing as the reaction takes place. The temperature at which the dehydration begins corresponds to the start of the endothermic reaction. The temperature of the peak of the endothermic deflection varies, depending on the details of the procedure followed, the character of the reaction involved, and the material being studied.

Attempts have been made by Spiel, Kerr and Kulp, and Arens to analyze mathematically the differential thermal method. It will be obvious from the discussion of the equipment used and the factors affecting the results that the method has certain quantitative limitations which restrict rigorous mathematical treatment. Currently an effort is being made by a subcommittee of the International Committee for the Study of Clays under the chairmanship of Dr. R. C. Mackenzie of Aberdeen.

Dehydration

Scotland, to determine the inherent limitations of the method and to standardize the procedure and equipment. The work of this committee should permit a better analysis of the method.  

Equipment Used. The specimen holder most widely used in the United States is a block of nickel drilled with holes to accommodate about 0.5 g of sample. Experience has shown that such blocks are serviceable and provide peaks on the thermal curves of adequate sharpness and intensity. Ceramic holders have been widely used in England, and Grimshaw claims that they are desirable, because they cause the peaks for the thermal reactions to be large and well defined as a result of the slow transfer of heat between the test sample and surrounding material due to the low heat conductivity of the ceramic material. Grimshaw used a holder composed of recrystallized alumina, bonded with a small amount of clay and fired to 1600°C. In the early work of Le Châtelier and others, platinum crucibles were used to hold the specimen, and recently Gruver has claimed advantages for thin-walled platinum containers, because the high heat conductivity of the metal permits the material to reach furnace temperature quickly and because the thin walls provide little heat capacity. In disagreement with Grimshaw, Gruver states that thick-walled holders with higher heat capacity act as heat reservoirs and tend to lower the intensity and sharpness of some reactions. Arens claims that ceramic holders give relatively sharper endothermic peaks and smaller exothermic peaks and that nickel holders give relatively smaller endothermic peaks and sharper exothermic peaks. It may, therefore, be desirable to use different types of sample holders for different materials.

The thermocouple circuit most widely used at the present time is shown in Fig. 78A, with an additional separate thermocouple to measure furnace temperature for calibration. The circuit first used by Fenner and still used by some investigators, particularly in Europe, is shown in Fig. 78B. In the latter circuit the sample temperature rather than the furnace temperature is taken as the reference temperature.

Mackenzie and later Arens claimed that measurement of furnace temperature in the clay sample has the advantage of providing more comparable peak temperatures and facilitating calculations. As will be shown, many things may cause a shift of the temperature of a reaction peak so that no advantage will necessarily be gained. It seems probable

that greater advantages will accrue from calibrations with the actual furnace temperature.

Early investigators used a platinum–platinum 10 per cent rhodium thermocouple, and such couples are widely used today. Chromel-alumel couples have been used satisfactorily for temperatures up to 1000°C for many materials, and they have the advantage over noble-metal couples of developing higher emf and thereby providing greater sensitivity. Kracek has used gold-palladium-platinum-rhodium thermocouples, which also have the advantage of developing high emf at elevated temperatures.

In order to maintain the horizontal position of the base line of the differential temperature curve, it is necessary to maintain thermocouple beads of constant size and to keep the beads in positions in the centers of the sample and reference material. The thermocouple wire should be relatively fine gauge, about 22, in order to reduce loss of heat by conduction through the wire.

The intensity of the thermal reactions varies greatly in different materials, and it is essential to have some means (e.g., a variable resistance in the difference-thermocouple circuit) of permitting some variation and control of the sensitivity of the apparatus.

The furnace itself must have sufficient capacity to permit the desired heating rate up to the maximum temperature and must be of sufficient size to provide a uniform hot zone for the specimen holder. A wide variety of furnaces, both horizontal and vertical, have proved satisfactory, the selection being largely a matter of preference of the operator.

A wide variety of homemade and automatic types of program controllers have been used to obtain a uniform heating rate. The use of an autotransformer, driven by a motor through a speed reducer in such a way as to increase the voltage into the furnace gradually and continuously, has been found quite satisfactory for furnaces with alloy windings. Various manufacturers of temperature-control equipment have supplied a variety of automatic controllers which have also proved satisfactory. In general the controller should be tailor-made for the furnace, and care must be taken with the on-off type that the on-off impulse does not get into the differential-thermocouple record.

The difference-thermocouple record may be obtained by manual reading of a galvanometer or potentiometer. However, it is desirable to obtain a continuous difference record, and that can be done photographically with a reflecting galvanometer or with various automatic recorders of commercial manufacturers. For use with noble-metal couples, it is necessary to obtain automatic recorders of adequate and variable sensitivity which at the same time have sufficient stability to produce good records. This is important because the temperature
differences measured are very small, and the emf produced by noble-metal couples is therefore very small. In several laboratories the photopen recorder used with a reflecting galvanometer has proved very satisfactory.

Grim and Rowland have constructed curves for their apparatus correlating the height of the thermal deflections with the temperature difference at the time of the reaction (Fig. 80). These curves were based on measurements of the swing of the galvanometer for known temperature differences. Use of these curves with the differential curves will measure the temperature difference represented by various peak heights.

**Experimental Factors and Variations in Material Which Influence Results.**

As has just been shown, variations in the equipment used may influence differential thermal results. Variations in the materials being studied and in experimental technique may also cause significant variations in differential thermal curves.

The temperatures at the junctions of the difference thermocouple depend to some extent on the coefficient of thermal diffusivity of the material in which they are embedded. The rate at which a point in a hot body will cool under definite surface conditions is known as thermal diffusivity and is equivalent to \( \frac{K}{dc_p} \), where \( K \) is conductivity, \( d \) the density, and \( c_p \) the specific heat. The diffusivity of the specimen may be different from that of the inert material, and, furthermore, the diffusivity of the specimen may change as it is heated because of the formation of new phases at high temperatures or because of shrinkage of the sample. The effect of such a change on the differential curve will be to produce a sloping base line, or a sharp offset in the curve, depending on the suddenness of the change. In the curve for quartz (Fig. 76) the base line is shifted upward after the inversion of \( \alpha \) to \( \beta \)-quartz because of a difference in diffusivity.

The inert material used should have substantially the same specific heat, heat conductivity, and thermal diffusivity as the sample studied.

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Also it should not experience any thermal reaction in the course of analysis. Calcined alumina ($\alpha$-Al$_2$O$_3$) has proved quite satisfactory as inert material. In an attempt to maintain uniformity between sample and inert material, calcined clay has been used occasionally as the inert material. However, calcined clay may well have different diffusivity from natural clay; hence little is gained by this procedure. Also, in some cases, the calcined clay may show thermal reactions due to phase changes.

It is general practice to pack the sample in the holder under moderate pressure, and it follows from the foregoing statements that the sample

Fig. 81. Variation of differential thermal curves for kaolinite with particle size, after Spiel et al.}\(^{27}\)
and inert material should be packed or prepared in the same way. The importance of packing varies with the kind of material. It is particularly important with light, fluffy material and, as shown by Gruver,\textsuperscript{32} is of very little importance for granular, relatively fine grained material with a considerable range of particle-size distribution so that it will pack naturally to a fairly dense mass.

So far as packing of the sample is concerned, the particle-size distribution of the sample is generally of no importance, unless the material is all relatively coarse (+60 mesh) or extremely fine grained (−2 microns). A range of particle size permitting dense packing is advantageous.

Spiel \textit{et al.}\textsuperscript{27} has shown that for some materials the thermal curve varies with the particle size of the component minerals, particularly when the maximum size is about 2 microns. In general (Fig. 81), the size of the thermal reaction and the temperature of the peak decrease as the particle size decreases. In some materials (see page 213) the decrease in particle size may be accompanied by a decrease in crystallinity, which is reflected in the differential thermal curve by lower intensity of reactions and a decrease in the temperature of the reaction peaks. According to Arens,\textsuperscript{29} if the size of particle is larger than about 20 microns, the surface area is too small for dehydration reactions to occur rapidly enough to yield pronounced effects on differential thermal records. Reactions due to phase changes would be largely independent of particle size.

Arens\textsuperscript{29} has investigated the effect on the differential thermal curve of the shape and size of the sample hole and the position of the thermocouple bead in the hole. According to him, the size and shape of the hole greatly affect the peaks for reactions accompanied by a change of weight, \textit{e.g.}, dehydration, and have little effect on peaks due to phase changes. For example, a deep, narrow hole will enhance the endothermic reaction for the dehydration of illite. In the low-temperature region, heat transfer occurs largely by conduction; in the high-temperature region, largely by radiation. Placement of the thermocouple junction deep in the sample yields curves with relatively strong endothermic peaks in the low-temperature range and flat endothermic peaks in the high-temperature range. Exothermic reactions are recorded best with deep placement of the thermocouple junction.

Norton\textsuperscript{34} and Spiel \textit{et al.}\textsuperscript{27} have shown that, in general, the slower the heating rate, the broader the peak and the lower the temperature of the peak (Fig. 82). Increasing the heating rate delays the attainment of the temperatures of both endothermic and exothermic peaks and increases the height of the peak and the temperature interval during which the reaction takes place. According to Spiel, the area under the curve for a

given reaction and the temperature at the start of the reaction seem to be independent of the rate of heating. Arens has not checked this conclusion, having found some variation in the area under curve with the heating rate. The experiences of many investigators have shown that a heating rate in the range of 10 to 15°C/min is most satisfactory. A slower heating rate unduly reduces the sharpness of the reactions, and a faster heating rate causes too much overlapping of reactions, particularly in samples which are mixtures. The heating rate must be uniform, for even small changes in the rate of heating are likely to be reflected in the differential curve.

In order to obtain reproducible results for many materials, the furnace atmosphere must be kept constant, and for materials subject to oxidation it is important that the samples be prepared and placed in the furnace in such a way that they always have the same ease of oxidation.
Dehydration

land and Jonas\textsuperscript{35} have shown how variations in particle size, packing, covering of block, and dilution of sample, in addition to furnace atmosphere, influence the ease of oxidation in siderite and hence the differential curves obtainable from this mineral (Fig. 83).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig83.png}
\caption{Differential thermal curves for siderite, after Rowland and Jonas.\textsuperscript{36} (A) Firmly packed without cover on sample holder; (B) firmly packed without cover and run in nitrogen atmosphere; (C) firmly packed with cover on specimen holder; (D) very finely ground, loosely packed, and without cover.}
\end{figure}

Arens\textsuperscript{29} has pointed out that an increase in the partial vapor pressure in the furnace may cause a significant delay in the occurrence of a dehydration reaction. Rowland and Lewis\textsuperscript{36} have shown the great effect of an atmosphere of CO\textsubscript{2} in changing the reaction temperatures of the carbonates.

In studying carbonaceous clays, it is common practice to use an inert gas in the furnace to suppress the oxidation reaction, which otherwise


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frequently produces an exothermic effect large enough and of sufficient
duration to mask all other thermal reactions.

Spiel et al.\textsuperscript{27} have presented a series of curves for kaolinite diluted by
various quantities of an inert material, showing that the size of the reac-
tion and the temperature of the peak decrease as the amount of material
decreases. The temperature of the peak, therefore, is not an absolute
value but depends among other things on the amount of material used or
present in a mixture.

Grim\textsuperscript{37} has shown that the characteristics of curves for mixtures of some
minerals depend somewhat on the intimacy of mixing of the components,
and that in clay minerals there is considerable difference between the
curves for mixtures of discrete particles several microns or more in
diameter and those for mixtures consisting of an intimate interlayering
of considerably smaller units, such as are frequently found in nature.
Arbitrary curves set up on the basis of dry mixtures of clay minerals,
therefore, are frequently of no value in evaluating curves for natural
clays. In general, the thermal reactions for the individual components
decrease in intensity and sharpness of reaction as the intimacy of mixing
increases.

Care in the preparation of material for analysis and in making the
analysis will provide reproducible curves, which frequently permit
quantitative interpretations. It is obvious from the foregoing discussion
of the method that its accuracy for quantitative analysis is limited. The
accuracy varies with the kind of material being analyzed, but for many
substances values within 2 to 5 per cent are obtainable. In general, the
quantitative evaluations are based on the area under the peaks that
correspond to the reactions of the individual components. In some
instances it is difficult to measure the area under the curve, because the
reaction does not start or end abruptly. Berkelheimer\textsuperscript{38} and Dean\textsuperscript{39}
have presented methods for measuring the areas that are workable for
reactions that are at least moderately sharp and intense.

The sensitivity of the method varies for different materials depending
on the intensity of their thermal reactions. For hydrates, such as
gibbsite, which yield intense abrupt thermal reactions, less than 5 per
cent can be detected, whereas in the case of the micas at least 10 to 15 per
cent is necessary for detection, because of the low intensity and lack of
abruptness in their thermal reactions.

\textsuperscript{27} Grim, R. E., Differential Thermal Curves of Prepared Mixtures of Clay Minerals,

\textsuperscript{28} Berkelheimer, L. H., Differential Thermal Analyses of Quartz, \textit{U.S. Bur. Mines
Rept. Invest.} 3763 (1944).

(1947).
Identification of High-temperature Phases. The identification of changes in phase on heating the clay minerals has been made almost entirely by means of X-ray-diffraction analyses. In early investigations the samples were heated to various temperatures, quenched or allowed to cool, and then studied. Currently the use of high-temperature X-ray-diffraction cameras has permitted the obtaining of diffraction patterns while the minerals are at the high temperatures. Also, in the author’s laboratory, a small furnace has been mounted on the diffraction unit, so that spectrometer traces are obtained while the minerals are at the elevated temperature. The latter techniques not only save a tremendous amount of time but remove the possible difficulties resulting from phase inversions on cooling. It seems likely that the high-temperature X-ray-diffraction technique will provide information of great value in studies of the formation of minerals at elevated temperatures and of transformations at high temperatures. Except for the use of the petrographic microscope, other possible methods of identifying high-temperature transformations have been given little consideration. An exception is the work of Comefero, Fischer, and Bradley, using the electron microscope to reveal the development of mullite in heated kaolinite. The petrographic microscope is adequate for identifying a new phase, if it is well developed and relatively abundant. If the phase forms slowly, the initially formed material is frequently not sufficiently abundant nor in large enough units for identification optically; hence the point of the beginning of the transformation cannot be fixed by microscopic study.

ALLOPHANE

Dehydration curves published by Ross and Kerr (Fig. 67) show a continuous loss of water, with no breaks or very prominent flexures but a gradual decrease in amount as the temperature is increased. Water of the order of 10 to 15 per cent is lost below about 110°C, and a roughly similar amount is lost at higher temperatures up to about 1000°C. These authors conclude that the dehydration curves of allophane are characteristic of a material in which the water is held in solution and not in chemical combination. Nutting has published curves for two allophane samples, one of which shows a gradual water loss, whereas the other shows a distinct flexure between about 550°C and 600°C.

Grim and Rowland have published differential thermal curves for two allophane samples (Fig. 71), both of which show distinct endothermic reactions at low temperatures, corresponding to the water loss below 110°C shown by the dehydration data. One of the differential thermal

curves also shows an endothermic reaction at a temperature suggestive of loss of OH lattice water. The significance of this reaction and the distinct flexure shown by Nutting's data might reflect some structural organization in this allophane, or possibly only the presence of a crystalline impurity. The curve for the other allophane sample shows only very slight reactions above 300°C.

No investigation appears to have been made of the high-temperature phases formed on heating allophane. Since the composition of allophane can vary widely, great latitude in the high-temperature phases developed in different samples would be expected. No information is available regarding the possible rehydration of allophane.

**KAOLINITE**

**Dehydration and Phase Changes on Heating.** Dehydration curves for kaolinite are given in Figs. 65 and 67, and differential thermal curves are given in Fig. 71. Ross and Kerr have pointed out that the dehydration curves are almost flat up to about 400°C, showing little loss of water at low temperatures, which is in accord with the absence of any thermal reactions in the low-temperature region of the differential thermal curves of many kaolinites. Differential curves for some poorly crystalline kaolinites (Fig. 71) show a small initial endothermic reaction, indicating that, when there is irregularity in the arrangement of the kaolinite units, a small amount of water may be present between the layers. This is in accord with the slightly greater c-axis spacing of poorly crystalline as compared to well-crystallized kaolinites.

A series of dehydration curves presented by Ross and Kerr show that most of the dehydration takes place between about 400° and 525°C. The precise temperature for the loss of this OH lattice water varies from kaolinite to kaolinite, and this variation may be explained by variations in particle size, since the dehydration temperature is known to decrease with decreasing particle size. It may also be explained by variations in crystallinity, since the poorly crystalline material loses its hydroxyl water somewhat more readily than well-crystallized kaolinite. A small amount (2 to 3 per cent) of water is retained at about 525°C, and this moisture is lost gradually up to about 750° to 800°C, where dehydration is essentially complete.

Ross and Kerr found no difference in the dehydration characteristics of kaolinite and anauxite, but they did find that the dehydration temperature for nacrite and dickite was slightly higher than that required for kaolinite. Nutting has published a few curves for kaolinite, showing a slightly higher dehydration temperature than those published by Ross and Kerr. Nutting also indicates that the dehydration temperature of
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anauxite is slightly lower than that of kaolinite. The apparent difference in the findings of these investigators may be explained by differences in the particle size of their samples and possibly also in degree of crystallinity.

DeKeyser\textsuperscript{41} has stated that kaolinite can be dehydrated completely at temperatures as low as 350°C with long heating times (200 hr), and indeed this is about the temperature of the very beginning of the break in the dehydration curves for the mineral. In general, very long time intervals are necessary to reach equilibrium for the clay minerals at temperatures where the loss of OH water is beginning.

Differential thermal curves of kaolinite show an intense, sharp endothermic reaction corresponding to the loss of OH water (Fig. 71). The reaction begins at about 400°C, and for well-crystallized kaolinite the peak is at about 600°C. The intensity of the reaction and hence the size of the peak, as well as the peak temperature, are reduced slightly as the particle size decreases and as the crystallinity decreases. The variation seems to be greater for the crystallinity factor than for the particle-size factor. According to Grimshaw \textit{et al.},\textsuperscript{31} the peak temperature is 20° to 30°C lower for poorly crystalline kaolinite than for the well-crystallized variety.

There seems to be no difference in the differential curves for kaolinite and anauxite. The temperature of the peaks for the reaction for loss of OH water is higher (about 100°C) for nacrite and dickite than for kaolinite.

The sections of the differential curves for poorly crystallized kaolinite lying between the peak for loss of hydroxyl water and the intense exothermic reaction at about 950°C are relatively flat, whereas those for well-crystallized kaolinite in this temperature range tend to have an upward slope, with a slight endothermic reaction just before the exothermic reaction. Grim and Bradley\textsuperscript{42} have concluded that the loss of OH water in poorly crystallized kaolinite is accompanied by a fairly complete loss of structure, but that in well-crystallized kaolinites some structural remnants persist along with some water, and that this remnant is lost at the time of the higher-temperature endothermic reaction.

Numerous investigators have debated the nature of the material immediately following the loss of OH lattice water from kaolinite. Insley and Ewell\textsuperscript{43} showed that the dehydrated kaolinite did not have the same chemical attributes, solubility in acid, etc., as mixtures of amorphous

\textsuperscript{41} DeKeyser, W., A Study of Kaolin and Some Belgian Clays, \textit{Ann. mines Belg.}, \textbf{40}, 711–806 (1939).


silica and alumina heated to similar temperatures. Comefero, Fischer, and Bradley\textsuperscript{40} showed that the diffraction bands of dehydrated kaolinite were more distinct than such bands from strictly amorphous solids; also, on the basis of electron micrographs, they showed that the hexagonal shape of the kaolinite was preserved above 600°C. All this work appears to have been done with well-crystallized kaolinite, and the conclusion seems definite that, on dehydration, such material is not strictly amorphous but still retains some degree of order. It also appears certain that, for poorly crystalline kaolinite, the degree of order is relatively less and the loss of structure is fairly complete.

The exothermic reaction shown by the differential thermal curves between about 900° and 1000°C is somewhat less intense and takes place over a slightly wider temperature interval for poorly crystallized kaolinite than for the well-crystallized mineral. The explanation for this exothermic reaction has been a matter of much dispute. Insley and Ewell\textsuperscript{43} and many others have attributed it to the formation of \( \gamma \)-\( \text{Al}_2\text{O}_3 \). When pure amorphous alumina is heated, \( \gamma \)-\( \text{Al}_2\text{O}_3 \) crystallizes over a long temperature interval and at a lower temperature. Furthermore, \( \gamma \)-\( \text{Al}_2\text{O}_3 \) has a structure unlike one which would be anticipated from the sharpness and high intensity of this exothermic reaction. Insley and Ewell\textsuperscript{43} attempt to explain these difficulties on the basis of some structural order in the dehydrated kaolinite which delays the formation of \( \gamma \)-\( \text{Al}_2\text{O}_3 \) until a relatively high temperature, with a consequent sudden reaction releasing much energy. Comefero, Fischer, and Bradley\textsuperscript{40} present cogent reasons for attributing the exothermic reaction to the formation of mullite in the sample of well-crystallized kaolinite that they studied. These investigators, using a combination of electron microscopy and X-ray diffraction, found mullite needles developing at first while the hexagonal outline of the kaolinite was preserved, and they conclude that, after the loss of OH water, there exists a uniquely organized compound which collapses into mullite nuclei.

Several investigators\textsuperscript{44,45} have reported both mullite and \( \gamma \)-\( \text{Al}_2\text{O}_3 \) in kaolinite heated to 1000°C, so that the exothermic reaction could be attributed to the formation of either or both of these compounds in some samples.

Richardson\textsuperscript{46} has recently published the results of X-ray-diffraction


analyses of a series of kaolinites heated for 20 hr at each 50°C temperature interval from 800° to 1350°C. His results indicate the presence of γ-alumina from 950° to above 1350°C. Richardson also investigated halloysite and found no mullite forming below 1100°C, and since halloysite shows the same exothermic peak as kaolinite, the author concludes that the exothermic reaction in kaolinite is probably due to the formation of γ-alumina.

Recent unpublished work by Glass suggests that the apparent discrepancy in results may be due to variations in the crystallinity of the material investigated and to the experimental conditions. According to Glass, well-crystallized kaolinite at 1000°C yields strong diffraction lines for γ-Al2O3 and weak lines for mullite. On further heating to higher temperatures, or on long-continued heating at 1000°C, mullite continues to develop. If the heating is rapid, as it is in a differential thermal analysis, little further mullite develops until about 1250°C, when it abruptly appears in abundance and is accompanied by an exothermic reaction. Cristobalite appears in abundance at about 1300°C. In the case of poorly crystallized kaolinite, at least in the samples studied by Glass, only γ-Al2O3 appears at 1000°C. Mullite appears abruptly at about 1200°C, accompanied by an exothermic reaction, and cristobalite appears in abundance at about 1300°C. Johns has recently shown that the high temperature exothermic reaction for kaolinite can be explained by a mullite nucleation which may be revealed by thermal data before it is clearly shown by diffraction data. Johns has also shown that the nucleation would vary somewhat with the crystallinity of the kaolinite.

Bertorelli and Williams have claimed that mullite formation is enhanced by heating in the presence of inert gases. Caillere, Henin, and Ture have shown that there is a great variation in the intensity of the exothermic reaction at about 950°C as a consequence of variations in the presence of a very small amount of impurities. Parmelee and Rodriguez have shown that zinc, lithium, magnesium, iron, manganese, cerium, and molybdenum markedly enhance the formation of mullite from kaolinite; boron and calcium enhance it slightly; sodium, potassium, titanium, and tin retard its formation; and the relative influence of these elements varies

with temperature. Crookston\textsuperscript{51} has found that the presence of potassium reduces the formation of cristobalite from kaolinite markedly; sodium reduces it slightly; and calcium, magnesium, and hydrogen have little effect. These data make it clear that the effect of small amounts of impurities is undoubtedly a significant factor in explaining the apparent variation in results obtained by different investigators on heating kaolinite.

Hyslop and McMurdо\textsuperscript{52} have presented expansion-contraction curves for the various clay minerals (Figure 84). Kaolinite shows an initial slight expansion up to about 500°C, followed by contraction to the limits of the experiments at 1100°C. The beginning of the contraction accompanies the loss of OH water. There is a flexure at about 900°C, corresponding to an interval of relatively reduced contraction; this is the temperature of the exothermic reaction that is attributed to the formation of $\gamma$-$\text{Al}_2\text{O}_3$ or mullite.

Harmon and Parmelee\textsuperscript{53} have stated that

\[\ldots\] only minor changes in true specific gravity take place up to the dehydration of the kaolinite. At this point the specific gravity drops suddenly as would be expected from the theory that dehydrated kaolinite is a mixture of amorphous alumina and silica. The specific gravity then slowly increases apparently indicating that a small amount of amorphous oxides are recombining to form a compound. The increase is suddenly increased at about 900°C.

Harmon and Parmelee did their work with ball clays in which the kaolinite crystallinity was probably low. Rieke and Mauve\textsuperscript{54} have presented


similar data (Table 27) for a kaolinite from Zettlitz in Czechoslovakia, which is well crystallized; their data are in essential agreement with those of Harmon and Parmelee.

**Table 27. Specific Gravity of Clay Minerals after Heating to Various Temperatures for 12 Hr**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Raw clay</th>
<th>400°C</th>
<th>450°C</th>
<th>500°C</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>950°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite, Zettlitz</td>
<td>2.64</td>
<td>2.64</td>
<td>2.49</td>
<td>2.47</td>
<td>2.50</td>
<td>2.53</td>
<td>2.60</td>
<td>2.62</td>
<td>2.69</td>
<td>2.74</td>
</tr>
<tr>
<td>Mica, Sarospatak</td>
<td>2.61</td>
<td>2.80</td>
<td>2.71</td>
<td>2.63</td>
<td>2.58</td>
<td>2.56</td>
<td>2.51</td>
<td>2.52</td>
<td>2.53</td>
<td>2.55</td>
</tr>
<tr>
<td>Halloysite</td>
<td>2.62</td>
<td>2.57</td>
<td>2.46</td>
<td>2.45</td>
<td>2.48</td>
<td>2.52</td>
<td>2.55</td>
<td>2.65</td>
<td>2.70</td>
<td>2.78</td>
</tr>
<tr>
<td>Muscovite</td>
<td>2.86</td>
<td>2.89</td>
<td>2.91</td>
<td>2.92</td>
<td>2.84</td>
<td>2.81</td>
<td>2.71</td>
<td>2.64</td>
<td>2.59</td>
<td>2.58</td>
</tr>
<tr>
<td>Montmorillonite, Wyoming</td>
<td>Could not be determined because of swelling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

According to Norton, kaolinites fuse from about 1650° to 1775°C. The fusion point is preceded by a vitrification interval, which may extend over several hundred degrees, during which a glassy component is an increasingly abundant phase. Small amounts of associated impurities may cause large changes in the determined fusion point and vitrification range.

Rehydration. Grim and Bradley have shown that well-crystallized kaolinite, after heating to 600°C slowly (70 hr), picks up a small but appreciable amount of OH water at room temperature, and that poorly crystallized kaolinite similarly heated apparently does not regain any OH water under the same conditions. They interpret this as evidence that, on dehydration of the well-crystallized mineral at 600°C, some structure remains which has sufficient regularity to take up at least minor amounts of hydroxyl water.

Van Nieuwenberg and Pieters have shown that after heating to 850°C kaolinite can be completely rehydrated under steam pressure of 100 atm. Schachtschabel states that after heating to 800°C kaolinite rehydrates slowly at 110°C, but that at 175° to 205°C under pressure it completely rehydrates in about 100 hr.

**HALLOYSITE**

Dehydration and Phase Changes on Heating. Dehydration curves published by Ross and Kerr and Nutting (Figs. 65 and 67) show...
significant loss of water below 100°C for some halloysites and not for others, depending, as is now known, on whether or not the halloysite is the hydrated form (4H₂O). The curves show that at temperatures between 100° and 400°C there is a very slight gradual loss of water, with the amount increasing somewhat between about 300° and 400°C. From 400°-430°C to 500°C the hydroxyl water is lost rapidly and abruptly. Above about 500°C there is again a gradual loss of water up to about 800°C, where dehydration is essentially complete. Ross and Kerr point out that halloysite loses its OH lattice water at a temperature 60° to 80° lower than that for kaolinite.

The water lost below 100°C is pore water and that occurring between basal plane surfaces of adjacent unit layers. Most of this interlayer water can be lost at room temperature under conditions of low humidity and over moderate periods of time. Brindley and Goodyear have shown that drying at room temperature does not completely remove all interlayer water, and that the formula for air-dried halloysite is Al₂O₃·2SiO₂·nH₂O with n = 2½ to 2¾, which is equivalent to about one layer of water to every four silicate layers. Drying to about 400°C is required to remove the interlayer water completely. The moisture gradually lost between 100° and 400°C undoubtedly corresponds to the residue of interlayer water, which is driven off with difficulty. Brindley and Goodyear have also shown that the complete loss of the interlayer water is not accompanied by a reorganization of the randomly displaced silicate layers.

Differential thermal curves for halloysites are given in Fig. 71. The hydrated form shows an initial V-shaped endothermic peak resulting from the loss of the interlayer water. This peak is, of course, small or completely absent in the lower-hydration forms of the mineral. The shape of the initial endothermic peak is unlike the one sometimes yielded by poorly crystalline kaolinite at about the same temperature. The peak given by kaolinite is less intense and less abrupt than that of halloysite.

The differential thermal curves above about 200°C are essentially like those for kaolinite. The sharp endothermic reaction due to loss of OH water tends to develop a peak at a slightly lower temperature than that in the case of kaolinite. Grimshaw, Heaton, and Roberts found in their differential thermal analyses that the endothermic peak for halloysite was at 500°C, for poorly crystalline kaolinite at 550° to 562°C, and for well-crystallized kaolinite at 583°C. Kerr, Kulp, and Hamilton state

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45 Kerr, P. F., J. L. Kulp, and P. K. Hamilton, “Differential Thermal Analyses of
that this peak for halloysite is asymmetrical, being more abrupt on the high-temperature side than the similar peak for kaolinite.

For the temperature interval above the dehydration reaction for OH lattice water, the differential thermal curves of some halloysites are like that of well-crystallized kaolinite, suggesting that some structure is retained after dehydration and up to the temperature of the slight endothermic reaction at about 900°C. It is not known whether or not this is a characteristic of all halloysites.

Glass\(^7\) has investigated the phases developing on heating halloysite, and the samples studied by him developed $\gamma$-$\text{Al}_2\text{O}_3$ at the temperature of the exothermic reaction of the differential thermal curve (950°C$\pm$); mullite developed at 1250°C; and cristobalite at 1300°C. Like poorly crystallized kaolinite, and unlike well-crystallized kaolinite, X-ray data for halloysite did not indicate mullite in the temperature region of the exothermic reaction at about 950°C. Richardson\(^6\) found on heating halloysite that $\gamma$-alumina was present from 900°C to 1150°C, cristobalite from 1100°C to 1300°C, and mullite from 1100°C to 1350°C. It would seem from Richardson's data that for halloysite the sharp exothermic reaction at about 950°C must be explained by the formation of $\gamma$-alumina rather than by mullite. However, Johns\(^7\)\(^a\) recent findings suggest that nucleation of mullite is a more likely explanation.

It seems likely that the development of high-temperature phases would be influenced by the presence of traces of various elements in a manner similar to that shown previously for kaolinite.

Hyslop and McMurdo\(^5\) have presented an expansion-contraction curve for halloysite (Figure 84). The curve shows the halloysite to expand slightly up to the dehydration of the mineral at about 500°C. Above this temperature there is a gradual contraction up to about 900°C, followed by a steep contraction up to about 1000°C. From 1000°C to the end of the experiments at 1100°C there is a further small amount of contraction. The difference in the character of the curves for halloysite and kaolinite may reflect differences in the high-temperature phases noted above. When halloysite is fired to temperatures just short of complete vitrification, masses of the mineral crack into small pieces, whereas masses of kaolinite remain intact. The difference in physical character must also reflect a difference in high-temperature phase reactions. Although halloysite is very refractory, it is difficult to use in ceramic products because of this high-temperature characteristic. The tendency of halloysite to crack into pieces at high temperatures makes it difficult to determine its vitrification range and fusion point. It seems that the

mineral fuses at a slightly higher temperature than kaolinite and that the fusion point is preceded by a very short vitrification interval.

Rehydration. The interlayer water lost at room temperature is not ordinarily regained; i.e., the reaction is not reversible. Bradley\(^6\) has shown that certain organic molecules, e.g., glycol, will penetrate between the layers of the dehydrated mineral and that, when the glycol is removed by a solvent such as alcohol, mixed with water, water remains between the layers. According to MacEwan\(^61\) and Brindley,\(^62\) this reintroduction of interlayer water is effective only if the original interlayer water has not been completely removed. Brindley suggests that the glycol molecules cannot enter between the layers unless some water is present to keep them partly open.

Grim and Bradley\(^42\) have shown that halloysite, after being heated to 600°C for 1 hr, regains a very small amount of OH lattice water in the course of standing at room temperature for 70 days. A similar result was found for well-crystallized kaolinite, but not for poorly crystalline kaolinite. They interpret this to mean that some structural organization is left in halloysite after the loss of OH lattice water. The similarity in this attribute between halloysite and well-crystallized kaolinite rather than poorly crystalline kaolinite suggests that the difference between the kaolinite and halloysite structures is based on more than the variation in the stacking of adjacent silicate sheets. Bates et al.\(^63\) have emphasized this point in considering the rolled tube-like shape of the halloysite minerals revealed in electron micrographs.

MONTMORILLONITE

Dehydration and Phase Changes on Heating. Dehydration curves after Ross and Hendricks\(^10\) are given in Fig. 68. The curves show considerable water loss at low temperatures (100° to 200°C), and, as has been shown (pages 175–180), the amount of this water, which occurs mostly as interlayer water between the silicate sheets, is contingent upon the nature of the adsorbed ions and the pretreatment of the sample, e.g., amount of drying, relative humidity, etc. The dehydration curves are S-shaped,

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Dehydration 221

usually showing no distinct break between the temperature of loss of the last interlayer water and the beginning of loss of OH lattice water. Ross and Hendricks have arbitrarily taken the temperature of 300°C as the break point, and this is probably the best single value that can be named. The loss of the interlayer water is accompanied by a reduction in the c dimension to 9.4 to 10 Å, with the exact value depending on the size of the interlamellar ions.

The curves of various montmorillonites show wide variation of temperature for the loss of OH lattice water. For normal montmorillonites, i.e., those with moderate to low substitutions of iron and magnesium for aluminum, rapid loss of OH water begins at about 500°C, and the dehydration is practically complete at 800°C. For nontronites the rapid loss of hydroxyl water begins at about 400°C, and the dehydration is substantially complete at 800°C. Hectorite is unusual, in that the rapid loss does not begin until about 700°C and the loss is still not complete at 930°C. In hectorite the hydroxyls are partially replaced by fluorines, which are possibly more tightly held within the lattice structure than the hydroxyls.

The loss of (OH) water in montmorillonites, unlike that in kaolinite and halloysite, does not begin or end abruptly, except in the case of hectorite. Another point of difference from kaolinite and halloysite, as Caldwell and Marshall⁶⁴ and Kelley et al.⁹ have shown, is the small variation in the dehydration characteristics of montmorillonites with particle size. This is to be expected, since a reduction in particle size of the montmorillonites is essentially a reduction of aggregates and not of primary components; i.e., it is a separation of flakes along basal planes of easy separation rather than a cross breaking of flakes.

The dehydration curves of some of the montmorillonites show flexures in the temperature interval of the loss of OH water; the significance of these will be discussed when the differential curves are considered.

Differential thermal curves for a series of montmorillonites are given in Fig. 72. At low temperatures they show variable endothermic peaks due primarily to the loss of interlayer water. The size and character of these peaks are contingent upon the nature of the adsorbed cation and on the pretreatment of the sample (see pages 178–179).

Most normal montmorillonites with relatively small amounts of iron and magnesium replacing aluminum show an endothermic reaction due to loss of OH lattice water, beginning rather gradually at about 450°C to 500°C, ending at about 750°C, and with a peak temperature of about 700°C. Large replacement of aluminum by iron causes a reduction in the

temperature of the reaction, and for nontronite the peak temperature is 550° to 600°C. Some montmorillonites which have a moderately high magnesium content, e.g., the sample from Otay, California, also show a lowering of the dehydration temperature. On the other hand, the magnesium-rich hectorite dehydrates at a higher temperature than the aluminous montmorillonites.

Some montmorillonites of relatively low iron and magnesium contents show unusually low temperatures for the hydroxyl-loss endothermic reaction, and some samples are known (e.g., montmorillonite from Palmer, Arkansas) that show a dual endothermic peak for hydroxyl water loss. In some cases the dual peak can be explained tentatively by a mixing of montmorillonites, e.g., high-iron and aluminous varieties. In some other examples the possibility of small amounts of kaolinite or halloysite as impurities cannot be eliminated. There are, however, some samples for which there is no satisfactory explanation. Kerr et al.⁶⁹ have reasoned that the explanation may reside in the geometry of the replacement and population of the octahedral positions in the structure. According to these authors, variation in the position of the cations in the octahedral packing and hence variation in the nearness to hydroxyl ions should affect the strength of the bonding of the OH and hence the energy necessary for its release.

Thilo and Schunemann⁶⁶ and Grim and Bradley⁶⁶ have shown that the general layer type of structure illustrated by montmorillonite and the micas is able to survive the elimination of OH water with only moderate readjustments. According to Bradley and Grim,⁶⁷ the removal of hydroxyl water is correlative with increases of 0.1 to 0.3 Å in c-axis periodicity and involves the expulsion of about one-sixth of the oxygens of the octahedrally coordinated portion of the structure. This correlation is apparently confined to the heptahyllite types of montmorillonites. An idealized rearrangement of the octahedral layer which adequately accounts for the meager data observable is illustrated in Fig. 85. It represents merely the lifting of the adjacent oxygen layer out of the packed position, with the immediate consequences that the vertical height is increased and the intensity of the 4.5 Å diffraction line is augmented. A diagram of a typical dehydration specimen is compared with its normal dry state in Fig. 85. Diffraction data for the rearranged material, after Bradley and Grim, are given in Table 28. The idealized

FIG. 85. Probable rearrangement in heptaphyllite-type clay minerals upon loss of hydroxyl water. The diffraction diagrams illustrate the Tatatilla montmorillonite after heating to 550°C (upper) and 725°C (lower). The schematic sketches represent the arrangement within an octahedral layer before and after dehydroxylation, after Bradley and Grim. 67

Scheme shown in Fig. 85 involves shared pairs of octahedral coordination faces for a heptaphyllite and is probably unstable. Applications of the same scheme to an octaphyllite type would demand sharing of three such pairs of faces, which is presumably impossible. No rearranged anhydrite was observed for hectorite and talc, which were the only two certain octaphyllite structures studied by Bradley and Grim. 87

The structure of many montmorillonites persists to temperatures of the order of 800° to 900°C, and Grim and Bradley 66 have correlated the destruction of the lattice with the endothermic reaction frequently shown at about this temperature interval. This correlation probably applies only to heptaphyllite montmorillonites, for, as has just been shown, an anhydrite structure should not persist in the octaphyllite members. Some montmorillonites which have been considered to be heptaphyllites, e.g., some nontronites, do not produce this high-temperature endothermic peak, and therefore it appears that the anhydrite structure may not persist in all heptaphyllites.
#### Table 28. Diffraction Data for Montmorillonite (Tatatilla, Mexico) Ignited to 725°C

(From Bradley and Grim)

<table>
<thead>
<tr>
<th>Indices as orthohexagonal</th>
<th>d, Å</th>
<th>Observed relative intensities</th>
<th>Calculated relative intensities for idealized Scheme of Fig. 85</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>9.7</td>
<td>m</td>
<td>2</td>
</tr>
<tr>
<td>002</td>
<td>4.85</td>
<td>m</td>
<td>2</td>
</tr>
<tr>
<td>110, 020</td>
<td>4.48</td>
<td>s</td>
<td>18</td>
</tr>
<tr>
<td>003</td>
<td>3.22</td>
<td>s</td>
<td>10</td>
</tr>
<tr>
<td>200, 130</td>
<td>2.59</td>
<td>m</td>
<td>4</td>
</tr>
<tr>
<td>220, 040</td>
<td>2.23</td>
<td>Diffuse m</td>
<td>2</td>
</tr>
<tr>
<td>005</td>
<td>1.93</td>
<td>w</td>
<td>1</td>
</tr>
<tr>
<td>240, 150</td>
<td>1.72</td>
<td>w</td>
<td>2</td>
</tr>
<tr>
<td>330, 060</td>
<td>1.67</td>
<td>Diffuse m</td>
<td>2</td>
</tr>
<tr>
<td>400, 260</td>
<td>1.51</td>
<td>m</td>
<td>2</td>
</tr>
<tr>
<td>420, 350</td>
<td>1.25</td>
<td>w</td>
<td>3</td>
</tr>
</tbody>
</table>

\[ss = \text{very strong; } s = \text{strong; } m = \text{moderate; } w = \text{weak.}\]

Page has suggested another explanation for the third endothermic peak of the montmorillonites. According to him, it is due to the loss of OH water which is bonded with magnesiums in octahedral coordination, rather than to lattice destruction. It has not been established that there is a correlation between the magnesium content and the presence or size of this peak. McConnell has recently attributed this high-temperature endothermic reaction to the loss of hydroxyls which are in the silica layer in tetrahedral configuration. McConnell attempts to correlate the peak with the amount of water lost at high temperatures, but the data are not completely convincing. An amount of water of the order of 0.5 to 1 per cent does persist beyond the temperature of the major loss of hydroxyl water at 500°C to 700°C. The amount of water to be lost at high temperatures is small in comparison with the size of the endothermic peak, and furthermore the loss of these hydroxyls does not seem to take place abruptly, as would be required for the development of a peak of the character frequently shown on the thermal curves.

Following the third endothermic reaction, the differential thermal

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Dehydration curves show a wide variety of thermal reactions, indicating that there is considerable variation in the phases formed when various montmorillonites are heated to elevated temperatures (Fig. 72). Data given in Table 29 from Bradley and Grim67 show that this is the case.

**Table 29. High-temperature phases developed on firing montmorillonites**

(From Bradley and Grim67)

<table>
<thead>
<tr>
<th>Sample location</th>
<th>900°C</th>
<th>1000°C</th>
<th>1100°C</th>
<th>1200°C</th>
<th>1300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Otay, California</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Tantilla, Vera</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cruz, Mexico</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Upton, Wyoming</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cheto, Arizona</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Palmer, Arkansas</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sierra de Guadalupe, Mexico</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Harris County, Texas</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Pontotoc, Mississippi</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Fairview, Utah</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Wagon Wheel Gap, Colorado</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Nashville, Arkansas</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Parenthetic numbers signify (1) important, (2) moderate, (3) minor.

Considerably more experimentation is necessary before all the general factors controlling the formation of high-temperature phases for montmorillonites are well known and before a complete correlation of thermal reactions and specific phase formation can be made. However, Bradley
and Grim have arrived at some general conclusions, based on a careful study of many samples, and the following discussion is taken from their work.

The high-temperature portions of the thermal curves of montmorillonites tend to differentiate into two separate types: those which present an S-shaped feature, and those which exhibit a distinct shoulder directly above the third endothermic reaction. Clays yielding the S-shaped curves contain spinel following the first exothermic reaction; it is proportional in amount to the magnitude of the thermal effect. In the second group the first prominent new phase appears to be quartz. The new phase is thus seen to develop in the one case from the octahedral region in the clay and in the other case from the tetrahedral region.

From the point of view of the composition of the mineral, montmorillonite seems to develop quartz if there is substantially no substitution in the tetrahedral sheet, and spinel if there is substantial substitution of Al in tetrahedral positions. The regularity in the composition of the tetrahedral scheme appears to endow it with ability to maintain its unity under conditions which disorganize substituted layers. Furthermore the montmorillonites developing the second type of curve, with the delayed exothermic reaction, are relatively low in iron. In these low-iron montmorillonites, enstatite, mullite, or anorthite develops at about 1000°C, in addition to the β-quartz, probably depending on the amount of magnesium present and possibly also on the amount of exchangeable Ca++.

Clays of either type, which have undergone either of the foregoing syntheses, may show an additional, fairly prominent reaction near 1200°C which seems to be due to either mullite or cordierite with about equal frequency. Bradley and Grim point out that the first high-temperature phases appear to be largely determined by the structural attributes of the montmorillonite itself. The initial phases are not the ones which necessarily would be expected from phase-diagram considerations and bulk chemical composition but are due primarily to "inheritance" from the original structure. The later phases developed at higher temperatures are dependent primarily on bulk composition, and here "inheritance" is of little importance. Thus in the case of the development of mullite or cordierite, the controlling factor is probably the amount of magnesium present.

The spinel-forming specimens all develop more or less cristobalite around 1000° or 1100°C without going through the quartz intermediate stage. No separate features appear in the differential thermal curves to indicate any energy effect associated with the growth of the cristobalite. Since this is true also of opal fired alone, it is assumed that any exchange involved is not picked up by the thermal method. Cristobalite is actually effectively somewhat less dense than the condensed-layer con-
Dehydration

figuration derived from the articulation of the silica layers (see page 228) and might even require an energy input under the conditions of the analyses.

The spinel tends to disappear at temperatures above about 1200°C in all samples studied except the nontronite sample.

Bradley and Grim67 have considered the structural changes involved in the development of high-temperature phases when montmorillonites are heated, and the following statements are also from their work.

As the spinel phases first appear, X-ray-diffraction lines are notably diffuse, and probably the phase does not have any particular composition. Rather, it is merely an irregularly constituted assemblage of small cations, some octahedrally coordinated and others tetrahedrally coordinated, with only the oxygen packing actually approaching crystalline regularity. The spinels grow rapidly to a clearly crystalline powder affording a clean diffraction diagram. No noticeable difference in relative intensities is observed between the diffuse and the sharp patterns, although cube-edge parameters may change somewhat (with changing composition), and no erratic appearance of new lines has been observed.

The cryptocrystalline quartz produced on firing many montmorillonites at about 1000°C exhibits many vagaries with respect to its apparent relation to high-low inversion. Synthesized quartz, when observed by Bradley and Grim at room temperature, was found in some cases as the α, in others as the β modification, and in one case apparently intermediate. Both the α and β forms make the normal slow transition to cristobalite at more elevated temperatures. Bradley and Grim67 suggest that the failure to invert is caused by the trapping of occasional extraneous ions in the channels of the structure.

The synthesized quartz develops suddenly with a correlative sharp exothermic effect, and the crystallites are subject to moderate grain growth in soaking periods of a few hours before eventually transforming into cristobalite. The original concept of the layer silicates was drawn from observations of the dimensional compatibility of brucite and the cristobalite-tridymite type of tetrahedral layer. One might postulate that a quick crystallization of silica would lead to one of these forms, but that does not seem to be the case. Bradley and Grim67 picture the synthesis of the quartz as illustrated in Fig. 86, which shows two sets of linked tetrahedrons, representing adjacent montmorillonite surfaces, in which oxygens are partitioned into two kinds. Suitable articulation of these pairs actually does simulate the quartz arrangement of height equivalent to one complete unit cell, and the new grouping effects a localized gain in density of the order of about 10 per cent. This postulation of the articulation of montmorillonite surfaces into the quartz arrangement is a consequence of extended clean clay-mineral surfaces.
FIG. 86. The articulation of tetrahedrally arranged montmorillonite surfaces to form quartz, after Bradley and Grim. (a) A montmorillonite surface; (b) two distorted arrangements of a; (c) a superposition of the two levels b.

To articulate two such surfaces into a segment of the cristobalite structure would require the introduction of additional oxygen between surfaces to complete the coordination of any silicons which might provide valence bonds between layers.

The fine-grained cristobalite resulting from syntheses in heterogeneous matrices is noticeably variable and of uncertain inversion character. Such material gradually becomes typical cristobalite upon ignition to sufficiently high temperatures, apparently without any sudden energy effects.

The MgSiO$_3$ formed in the firing of some montmorillonites is comparable with the “mesoenstatite” of Thilo and Rogge. This material is probably to be looked upon as a rudimentary nucleation rather than as a normal crystallization. The structural relations of the layer silicates and of the pyroxenes are such that projections onto the respective orthohexagonal axes are approximate equivalents. In the imperfectly developed diffraction diagrams of the fired montmorillonites, the lines which appear are only those which relate to the pseudohexagonal nature. In fact they constitute an identification of MgSiO$_3$ only in the sense that they correspond to equivalent lines which appear in better and better crystallized materials of higher magnesium content for gradations up to and including the typical enstatite crystallization obtainable on firing tremolite asbestos.

Bradley and Grim have discussed the development of forsterite from chrysolite and clinochlore. They conclude that the transition from the old to the new phase requires no chaotic disintegration followed by the

Dehydration

reconstitution of a new assemblage, but simply the freedom of a few Mg ions to migrate to the nearest equivalent interstices. In other words the oxygen packing remains substantially the same, and the transformation is a matter of the shift of a few magnesium ions. They conclude further that the development of mullite from pyrophyllite, which is probably similar to its development from montmorillonite, is carried forward to a considerable extent along the same lines as the development of the forsterite.

Steger\textsuperscript{71} has investigated the expansion-contraction of montmorillonite. The specimen examined by him showed a very slight gradual expansion from 200° to about 700°C. Between 700° and 800°C there was a rapid expansion possibly to be correlated with the development of the anhydride form. This expansion was immediately followed by a large contraction up to about 950°C, when the sample again expanded (Fig. 87).

Rieke and Mauve\textsuperscript{74} have shown (Table 27) that the specific gravity of a sample of montmorillonite decreased on heating from 600° to 800°C, followed by a slight increase when it was heated to 950°C. There was a further slight decrease on firing to 1000°C, the maximum temperature of the experiments.

As would be expected from the large variations in the chemical composition of the montmorillonites, the fusion point of montmorillonite minerals exhibit wide variations. Iron-rich members of the group may fuse below 1000°C, whereas iron-poor members may not fuse until about 1200° to 1300°C. The presence of alkalies and alkaline earths renders montmorillonites nonrefractory. The vitrification range of montmorillonite minerals is frequently not large.

Rehydration. Hofmann and Endell\textsuperscript{72} have shown that the property of montmorillonite to regain interlayer water and expand is lost for Li


montmorillonite after heating to 105° to 125°C, for H or Ca montmorillonite after heating to 300° to 390°C, and for Na montmorillonite after heating to 390° to 490°C. Hofmann and Endell carried their rehydration tests over short periods of time, and somewhat different results might be found for longer intervals of rehydration. Grim and Bradley have shown that Na montmorillonite, after being heated for 1 hr at 600°C, very slowly picked up interlayer water, so that a small amount is shown at the end of 268 days. Samples heated to 800°C showed no pickup of interlayer water after the same length of time. The same authors present data for a Ca montmorillonite showing that it also regained interlayer water after heating to 600°C and that the rehydration was slightly slower than for the Na montmorillonite.

According to Grim and Bradley, samples heated to 600°C for 1 hr regained about one-fourth of the original OH lattice water in 268 days. As shown in Fig. 88, the endothermic reaction corresponding to the removal of this rehydration water yields a double peak, suggesting that the regained water is of two kinds or forms in the lattice. Some of the rehydration water is removed at about the same temperature as the original hydroxyl water, and the remainder at a temperature about 150°C lower. Both kinds or forms of water are regained at about the same rate. The rehydration of the OH lattice water does not afford any clear-cut X-ray-diffraction interference, but in the light of the anhydrous configuration illustrated (Fig. 85), it seems reasonable to assume that only a small part is recombined into the original configuration, with an additional significant amount attaining some other bonding of lower energy.

Experience in drying bentonite commercially has shown that, as a practical matter, regaining of interlayer water is difficult if the last trace of interlayer water is removed. So long as some water remains between the layers, swelling is generally relatively easy.

**Fig. 88.** Differential thermal curves of sodium montmorillonite (bentonite), Clay Spur, Wyoming, after Grim and Bradley. (A) Not heated; (b) heated, 500°C for 1 hr, curve run after standing 13 days; (C) heated, 600°C for 1 hr, curve run after standing 11 days; (D) heated, 600°C for 1 hr, curve run after standing 68 days; (E) heated, 600°C for 1 hr, curve run after standing 146 days; (F) heated, 600°C for 1 hr, curve run after standing 268 days; (G) heated, 800°C for 1 hr, curve run after standing 76 days; (H) heated, 800°C for 1 hr, curve run after standing 268 days.
Dehydration and Phase Changes on Heating. A dehydration curve published by Nutting\(^6\) (Fig. 66) shows a large water loss below about 100°C, and a gradual loss from this temperature to about 850°C, where dehydration is substantially complete. The curve shows flexures indicating relatively more rapid dehydration in the vicinity of 400°C and above 700°C. Walker\(^7\) has also published dehydration curves for vermiculite. His data show the water to be lost mostly in three steps: below 100°C, from 250° to about 400°C, and from 600° to 850°C. According to Walker, the water lost in each of these steps expressed as percentage of total water content of the mineral is about 48, 25, and 27 per cent, respectively.

Barshad\(^4\) and Walker\(^7\) have published differential thermal curves for the mineral (Fig. 75). Natural vermiculites show a large, dual, initial endothermic reaction with a peak at about 150° to 200°C, immediately followed by a smaller peak at about 250° to 275°C. This reaction results from the loss of interlayer water.

Walker\(^7\) explains the character of the initial endothermic peaks as follows: The interlayer water in natural vermiculites consists of a hydration shell around the Mg ions made up of six water molecules and also includes “unbound” water in the space between the hydrated Mg\(^{++}\). The initial endothermic peak corresponds to the loss of the unbound water, which is driven off on heating to about 100°C. Accompanying the loss of the unbound water is the collapse of the c dimension to 11.8 Å, which provides room for only a single molecular layer of water between the silicate sheets. The collapse of the structure causes the hydration envelope of the Mg\(^{++}\) to be spread out flat, so that two water molecules become unbound and the Mg\(^{++}\) is surrounded by only four water molecules. The two water molecules becoming unbound in the collapse of the structure are also lost as part of the initial endothermic reaction. The second low-temperature endothermic reaction corresponds to the loss of the remaining four water molecules around the Mg\(^{++}\).

As shown in Fig. 75, the part of the differential curves corresponding to the loss of interlayer water varies with the exchangeable cation carried by the vermiculite. This variation is to be expected, since Barshad\(^4\) has shown that, when Ca\(^{++}\) and Mg\(^{++}\) are the exchangeable ions, there is a double layer of water; when Ba\(^{+}\), Li\(^{+}\), and Na\(^{+}\) are the exchangeable ions,

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there is a single layer of water; and when NH₄⁺, K⁺, Rb⁺, and Cs⁺ are the exchangeable ions, the mineral has no interlayer water. The sizes and complexities of the initial peaks for vermiculite with any of these ions vary in accordance with the hydration characteristics of the particular ion. Thus K vermiculite shows only a very slight low-temperature endothermic reaction, and Na vermiculite shows only a single initial endothermic peak.

It appears from the data given by Nutting,6 Barshad,14 and Walker 73 that the OH lattice water from the silicate part of the structure is lost gradually from about 500° to 850°C and hence does not tend to cause a sharp corresponding thermal reaction. The endothermic reaction between 700 and 800°C is probably due to the destruction of the silicate structure, accompanied by the loss of the last hydroxyl water. The endothermic peak at 600°C for the sample from Pennsylvania (Fig. 75) is probably due to some chlorite in mixed layers with the vermiculite.

According to Barshad,74 the initial stages of dehydration are attended by a contraction of the lattice, with the development of diffraction characteristics like those of biotite. When vermiculite is heated abruptly to about 300°C, the mineral exfoliates, with the production of a material of low bulk density of considerable economic importance. The exfoliation does not take place on heating to about 150°C, from which fact it may be concluded that all interlayer water must be driven off for it to occur.

The high-temperature phases formed on the ignition of vermiculite have not been studied in detail. Walker 73 has shown that enstatite is formed, corresponding to the sharp exothermic reaction at about 800°C in samples studied by him. The high-temperature phases could be expected to show considerable variation, depending on lattice substitutions and exchangeable ions, and probably would develop the general composition and high-temperature phase relations shown by montmorillonites (see pages 225–227). Indeed, in the high-temperature parts of the thermal curves shown by Barshad for vermiculite prepared with various exchangeable cations (Fig. 75), the variations must mean a considerable variety in high-temperature phases.

No information is available concerning the expansion-contraction of vermiculite as it is heated to elevated temperatures. Also there are no data on specific-gravity changes with temperature. The temperature of fusion of the mineral and its vitrification range would be similar to those of montmorillonite.

Rehydration. Walker 73 has shown that the unbound water driven off at about 100°C is regained almost instantly on cooling to room temperature, with an expansion of the lattice to its original dimensions. Barshad 74 has shown that, after all the interlayer water is driven off at
Dehydration

temperatures up to 550°C, the mineral will still rehydrate rapidly and regain its original lattice dimensions and dehydration characteristics.

The ability to rehydrate disappears gradually above 550°C, and according to Walker it is completely lost at about 700°C. Apparently the loss of the rehydration ability accompanies the loss of hydroxyl water. Since the silicate unit is octaphyllitic, a loss of structure would probably accompany the loss of hydroxyls, and the ability to rehydrate after heating to the higher temperatures would not be expected.

ILLITE

**Dehydration and Phase Changes on Heating.** As currently defined, the illite group includes clay minerals having either the muscovite type or the biotite type of structure, and it is necessary to consider the dehydration properties of muscovite and biotite, as well as of the clay-mineral micas. Dehydration curves for muscovite, biotite, and phlogopite are given in Fig. 89, after Roy. The dehydration curve shows that muscovite has a slow, relatively gradual loss of water up to about 800°C without any restricted interval of large water loss. Phlogopite shows virtually the same dehydration characteristics as muscovite. Biotite loses water gradually up to about 400°C; it shows very little loss between about 400° and 850°C and considerable loss between 850° and 1000°C. Walker has also presented a dehydration curve for biotite, and, unlike Roy’s curve (Fig. 89), it shows an almost uniform rate of water loss up to

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about 850°C, where the dehydration is essentially complete. Kelley, Jenny, and Brown present dehydration curves for muscovite which show an interval of relatively rapid dehydration between about 450° and 850°C. The variation in dehydration data obtained by various investigators for the micas undoubtedly results to a considerable extent from the factor of time. Very great differences in water loss are obtained by heating at a given temperature for varying intervals of time.

Roy has investigated the length of time required for dehydration of muscovite to be completed at various temperatures, and his results are given in Fig. 90. His data show that about 10 hr is required for complete dehydration at 300°C, i.e., for removal of all the water which can possibly be removed at this temperature under ordinary pressure. At 450° and 650°C some water was still being lost at the end of 100 hr, and at 650°C the loss of water in 1 hr is only 20 per cent of the total lost in 100 hr. Obviously, tremendously variable dehydration results can be obtained for muscovite micas unless the time factor is carefully considered. The same conclusion probably holds also for the biotite micas.

Dehydration curves for illites published by Grim, Bray, and Bradley (Fig. 69) show a considerable water loss below 100°C, a gradual loss from 100°C to about 350°C, a relatively abrupt, large loss from 350° to about 600°C, and a gradual loss above 600°C. These illites have a muscovite type of crystallization. A sample of weathered biotite which probably is somewhat representative of an illite with biotite attributes is shown by Walker to have a small loss of water below 100°C, a gradual, very slight loss from 100° to about 300°C, a rather sharp but gradual loss from 300° to 600°C, and a slow, gradual loss above 600°C. Thus, the dehydration properties of the illites with muscovite and biotite attributes for which data are available are about the same. The illites differ from muscovite and biotite by having a water loss below 100°C and a more abrupt loss of much of the OH lattice water between about 300° and 600°C. The low-temperature water loss is to be expected, since the clay-mineral micas

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![Dehydration curves for muscovite, after Roy, showing relation of water loss to time of heating.](image)
Dehydration
differ from the well-crystallized micas in having some interlayer water, which is a consequence of fewer interlayer cations, less bond between layers, less uniform orientation of successive layers, smaller particle size, and/or a difference in composition within the silicate layer itself. The difference in loss of hydroxyl water cannot be so completely explained but is probably largely the result of the difference in particle size, as shown in the following discussion of differential thermal curves.

Differential thermal curves (Fig. 73), after Grim and Bradley, for coarse-grained muscovite (10 to 20 microns) show only a single dehydration reaction, beginning at about 800°C with a peak at about 900°C. In the rapid heating of the differential thermal procedure there would be little loss of hydroxyls below about 800°C, and then, in accordance with Roy's data, an abrupt loss of the OH water should occur. Grim and Bradley show that a decrease in the particle size of the muscovite is accompanied by a reduction in the temperature of the beginning of the endothermic dehydration reaction and by an increase in the temperature interval during which it takes place. Differential thermal analyses of biotite yield a curve without any pronounced deflections up to 1000°C, indicating an absence of any abrupt dehydration in this temperature range under the conditions of the analyses (heating rate, 10°C/min).

Differential thermal curves for illite presented by Grim and Bradley show an initial endothermic reaction corresponding to the loss of interlayer water, a second endothermic reaction beginning at about 450° to 500°C with a peak at about 550° to 650°C, a third, slight endothermic reaction between about 850° and 950°C, and frequently an exothermic reaction between about 900° and 1000°C (Fig. 73). The size and temperature interval of the second endothermic peak, which corresponds to the loss of OH lattice water, vary in different samples, and the final part of the curve also shows considerable variation. Information is not yet available on the precise variation of thermal characteristics of illites with differences in their structural and composition attributes. Grim and Bradley (Fig. 73G) have shown one octaphyllitic illite that yields a differential thermal curve like those of heptaphyllitic illites. On the other hand, another sample of glauconite showed a relatively smaller initial endothermic reaction and a relatively higher temperature for the reaction accompanying the loss of hydroxyl water than the heptaphyllitic illites. Mackenzie, Walker, and Hart have recently described an illite showing a double endothermic reaction in the hydroxyl dehydration

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interval, with peaks at 550° to 600°C and 713°C, and for which there is as yet no satisfactory explanation.

According to Roy, muscovite shows no marked structural change on heating to 940°C, and the loss of the structure takes place between 940° and 980°C. The expulsion of at least most of the OH lattice water is accompanied by a slight expansion of the lattice in the c dimension and not by complete destruction of the lattice. On heating, phlogopite exhibits the same characteristics as muscovite, except that its structure is lost at a temperature about 50°C lower. The biotite structure, according to Roy, persists to about 1100°C, and the biotite structure, therefore, is also not lost simultaneously with the expulsion of the OH lattice water. This is surprising in view of the reasoning of Bradley and Grim that octaphyllite anhydrite-mica structures are unlikely (see page 223).

Grim and Bradley have shown that the loss of OH water in the illite studied by them is not accompanied by a loss of structure. It is accompanied by a slight structural change of the kind described for montmorillonite (see page 223). According to these investigators, the structure of these illites is not destroyed until at least 850°C, and Grim and Bradley would correlate its destruction with the third endothermic reaction in the differential thermal curves. The illites studied by them had the muscovite type of crystallization. Maegdefrau and Hofmann have also reported the continuation of an illite-like structure beyond the loss of OH water, and, in at least one of their samples, it is retained to 1000°C.

Roy reports that muscovite on firing at 1000°C develops \( \gamma-Al_2O_3 \) and/or spinel (the X-ray data were too poor for a positive determination); at 1200°C the presence of \( \gamma-Al_2O_3 \) is definitely established, and \( \alpha-Al_2O_3 \) appears; and above 1400°C corundum (\( \alpha-Al_2O_3 \)) and glass are the only phases present. Zwetsch has reported that muscovite ignites at 1050°C to \( \gamma-Al_2O_3 \), \( \alpha-Al_2O_3 \), and leucite, and finally at 1300°C the crystalline phases are leucite and \( \alpha-Al_2O_3 \). On firing phlogopite, according to Roy, spinel is formed at 1000°C, and this persists as the only crystalline phase to 1550°C. On firing biotite to about 1100°C, the phases developing are a high-iron magnetic spinel, leucite, and mullite; at about 1300°C the phases are the high-iron spinel and leucite; and at 1500°C only olivine and glass are to be found. In a biotite studied by Grim and Bradley, leucite, \( \gamma-Fe_2O_3 \), and a spinel were identified after firing to 1200°C.

On heating several illites, Grim and Bradley found spinel appearing in all of them at about 850°C, and the spinel increased in amount and particle size up to about 1200°C. These investigators suggested that the

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octahedral sheet of the illite lattice, carrying the alumina, magnesia, and
iron, goes into the formation of the spinel, and that the alkalies and the
silica from the tetrahedral layers yield an amorphous glass. They found
that at 1300°C the spinel had dissolved in the glass, and that mullite
became apparent at 1100°C and persisted to at least 1400°C. The
amounts of spinel and of mullite appeared to be complementary, and the
specimens richer in spinel were subject to fusion at a somewhat lower
temperature. These investigators found no clear evidence of a quartz
phase developing from their illites at elevated temperatures.

It is reasonable to expect that there would be considerable variation in
the high-temperature phases developed from illites of different structural
and composition attributes, and indeed the variations in the high-tem­
perature portions of the differential thermal curves show that this must
be true. Considerably more study of ignited illites is necessary before
general conclusions can be reached regarding high-temperature phase
transformations in these minerals.

Hyslop and McMurdo52 have published expansion-contraction curves
for two illite samples (Fig. 84). Both samples show considerable expan­
sion (1.1 and 0.8 per cent, respectively) up to 800°C. Above 800°C one
of the samples showed an abrupt contraction, which was continuous up
to the limit of the experiments at 1100°C. The other sample showed
slight contraction between 800° and 950°C, followed by a secondary
expansion from 950° to 1000°C. The secondary expansion could well be
explained by a reaction producing gas from an impurity in the sample and
probably is not a characteristic of the mineral.

The fusion point of the illites varies between wide limits. Some
glauconites fuse below 1000°C, whereas iron-poor varieties relatively
low in alkalies do not fuse until temperatures of the order of 1300°C.
In general, illites with the higher fusion point have a moderately long
vitrification range (200°C).

Rehydration. Grim and Bradley42 have studied the rehydration prop­
erties of three illites. In one of them (Fig. 91), after heating to 600°C
there was a rapid pickup of adsorbed water and hydroxyl lattice water,
so that a considerable part (25 per cent) of both types of water was
regained within a few hours. Additional amounts of adsorbed and
hydroxyl water were regained slowly for a period of many months. The
loss of rehydration hydroxyl water on heating again began at a lower
temperature (400°C) than that of the original water (475°). After
heating to 800°C there was also a gradual regaining of adsorbed water and
OH lattice water. The data suggest that, on heating to either 600° or
800°C, there was an initial, relatively rapid rehydration followed by a
very slow and gradual rehydration. A second sample of illite showed
nearly the same rehydration characteristics as those just described, except
that the rehydration was slower and there was no lowering of the temperature required to remove the water regained on rehydration. The third sample studied by Grim and Bradley contained some chlorite mixed with the illite. After heating to 600°C, this sample showed a slow gradual pickup of adsorbed water, and after 217 days a larger amount was adsorbed than had been present in the original sample. Also in this sample, some hydroxyl lattice water was regained in material heated to 800°C. Roughly the same amount of hydroxyl water was taken up by samples heated to both 500°C and 800°C. The total amount of OH lattice water taken up by each of the illites in about 9 months was close to one-third of the original amount. The nature of the probable pairing of the layers in the illites investigated is such that data similar to that obtained for montmorillonites cannot be obtained (see page 223). However, it seems likely that the structural changes are much the same for both minerals.

Roy75 succeeded in re-forming muscovite and phlogopite from material decomposed at 1050°C by heating the latter to 400° to 650°C for at least 12 hr under pressures varying between 1,000 and 10,000 psi. No success was attained in a similar treatment of decomposed biotite.

CHLORITE

Dehydration and Phase Changes on Heating. Nutting6 has presented dehydration curves for several chlorites (Fig. 66). All of Nutting’s curves for the chlorite minerals show very little water loss prior to about 500°C and a sharp loss of a good deal of water between about 500° and 550°C. The curves above about 600°C show considerable variation; some of them show a gradual continuous loss of weight from about 600° to 850°C, where dehydration is essentially complete, whereas others show a relatively slight loss between 600° and about 750° to 800°C, and then a relatively abrupt loss from 800° to essentially complete dehydration at 850° to 900°C.

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**Fig. 91.** Differential thermal curves of illite, Fithian, Illinois from Grim and Bradley: (A) not heated; (B) heated, 600°C for 3 hr, curve run after standing 2 hr; (C) heated, 600°C for 1 hr, curve run after standing 1 days; (D) heated, 600°C for 1 hr, curve run after standing 70 days; (E) heated, 800°C for 1 hr, curve run after standing 13 days; (F) heated, 800°C for 1 hr, curve run after standing 70 days; (G) heated 800°C for 1 hr, curve run after standing 147 days; (H) heated, 800°C for 1 hr, curve run after standing 275 days.
Orcel, and Renaud, Barshad, and the writer have obtained differential thermal curves for a large number of chlorite samples (Fig. 75). The samples that have been studied show little or no low-temperature endothermic reaction, indicating an absence of interlayer or adsorbed water. Further work may well reveal chlorites yielding such a reaction, as it seems likely that very fine grained chlorites with some interlayer water would occur in some clay materials. All the samples exhibited a distinct, sharp endothermic reaction between 500° and about 700°C. Most of them showed a second endothermic reaction at about 800°C, and this peak was frequently followed immediately by a sharp exothermic peak. Orcel concluded from his work that the hydroxyl water of the chlorites is driven off in two stages, and when a second endothermic peak is not shown, the two stages of dehydration occur within such a narrow temperature interval as to be unresolved by differential analyses. Unpublished work by the writer and studies by Barshad show that extremely sensitive differential analyses of a series of chlorites (Fig. 75) do tend to resolve the endothermic reaction into two parts. Nutting's dehydration curves show definitely that the chlorites he investigated lost their OH water in two stages, but that the second stage may immediately follow the first stage without an interval during which no water is lost, and further that the second stage may take place gradually. Differential curves of chlorites in which the second-stage loss of water was very gradual would be expected to show an overlap of thermal reactions or even the complete absence of a second endothermic reaction.

All the available dehydration and differential thermal data are for well-crystallized chlorites, and the variations that would be found in clay-mineral chlorites are a matter of surmise. Reasoning from analogies with illites as compared to muscovite and biotite, it appears likely that clay-mineral chlorites would show the same thermal reaction as the well-crystallized chlorites, but perhaps at somewhat lower temperatures. The smaller particle size of the chlorite clay minerals and possibly some defects of orientation of layers would permit the loss of some of the OH water of the brucite sheet at a relatively lower temperature. Also, the clay-mineral chlorites could well have some interlayer water, providing a small initial endothermic reaction as in many illites.

Brindley and Ali have investigated the changes taking place in some

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chlorites (penninite, clinochlore, and sheridanite) after heating to successively higher temperatures. According to these investigators, in the temperature range from 400° to 700°C, the intensities of the (001) reflections progressively change; in particular, the (001) reflection becomes several times more intense, and the (002) and (003) become several times weaker. Also the lattice constants change, $c_0$ showing a small contraction and $a_0$ and $b_0$ showing small expansions. These changes are attributed to the gradual breakdown of the brucite layer, while the mica layer remains unaffected. The dehydration of the brucite layer corresponds to the first endothermic reaction of the differential thermal curves. At 700°C about two-thirds of the hydroxyls of the brucite layer have been removed, and Fourier syntheses of (001) intensities show that the magnesium atoms move away from their original position in a plane midway between the mica sheets to positions directly adjacent to the mica-unit surface. This change precedes the dehydration of the mica-layer portion of the chlorite structures. In some chlorites the loss of water by the mica layer is abrupt, whereas in others it is gradual. In either case it is accompanied by the total destruction of the chlorite structure, which in turn is immediately followed by the crystallization of olivine. The endothermic reaction frequently shown at 750° to 800°C is correlated with the dehydration of the mica layer and the loss of its structure. The exothermic reaction at about 800° to 900°C is correlated with the development of the olivine.

Brindley and Ali\textsuperscript{83} have shown that the newly formed olivine phase has a high degree of preferential orientation relative to the structure of the original chlorite, and they have considered in detail the probable shifts in the atomic lattice accompanying the formation of the olivine. They have shown that the temperature of lattice destruction and the temperature of the formation of olivine vary for different chlorites. They have also shown that other phases in addition to olivine form when various chlorites are heated, and that the temperature of formation of the additional phases is also variable. Thus for penninite, olivine first appears at about 800°C, for clinochlore at 850°C, and for sheridanite at 950°C. According to these workers, penninite at 950°C shows olivine and spinel, and at 1180°C olivine, spinel, and enstatite; clinochlore at 850°C shows olivine and spinel; and sheridanite at 1100°C shows olivine, spinel, and enstatite. Brindley and Ali\textsuperscript{83} also present differential thermal curves for these same chlorites carried to high temperatures, and they are unable to correlate the thermal reactions satisfactorily in each case with the phase developed as shown by X-ray-diffraction analysis.

The explanation for the apparent lack of correlation between the high-temperature phases revealed by X-ray analysis and the reactions shown by differential thermal curves for chlorites and for some other clay
minerals is probably as follows: In some cases the new phase may develop slowly and/or involve only a very slight structural shift, so that it would not be accompanied by an intense or sudden energy change, and consequently no thermal reaction would be expected on the differential thermal curve. In other cases, the reaction may begin abruptly by a somewhat crude nucleation of the new phase, which would involve a structural change of considerable magnitude and a definite thermal reaction but would not yield discernible diffraction evidence of the new phase. Further heating or more time would be required to develop the new phase to the point where distinct diffraction effects become obvious. In the writer's experience, the thermal reaction for a new phase frequently precedes its distinct appearance in X-ray reflections, and the X-ray reflections further precede its appearance in optical measurements.

No data are available for the expansion-contraction properties of chlorite on heating or for the changes in specific gravity of the mineral on firing. Also no precise data are available for the fusion temperature and vitrification range of these minerals. It appears likely that they would be closely similar to the biotite type of mica in fusion and vitrification characteristics.

Rehydration. No experimental data could be found on the possible rehydration of the chlorite minerals. Reasoning from structural analogies with the micas, it is likely that the chlorite clay minerals would show a slow, perhaps relatively slight pickup of hydroxyl water, at least in the mica-layer part of the structure, after heating to temperatures of the order of 700°C.

**SEPIOLITE-ATTAPULGITE-PALYGORSKITE**

**Dehydration and Phase Changes on Heating.** The dehydration and high-temperature characteristics of only a few samples of these minerals have been studied, and there is no assurance that the results obtained have wide application to the group as a whole.

A dehydration curve for a sepiolite given by Nutting\(^6\) (Fig. 66) shows a large water loss below about 100°C and a gradual continuous loss above that temperature to complete dehydration at about 800°C. There is a relatively slight increase in water loss between about 200°C and 400°C and above 675°C. Migeon\(^12\) has presented (Fig. 70) a continuous, i.e., not equilibrium, weight-loss curve for sepiolite which is generally similar to Nutting's curve in that it shows a large loss below 100°C and a gradual loss above that temperature, with flexures indicating relatively rapid loss at about 275° to 325°C, 550° to 600°C, and slightly above 800°C.

A differential thermal curve for a sepiolite is given in Fig. 76. It shows a large initial endothermic peak beginning below 100°C, followed by a
series of slight endothermic peaks between about 200° and about 700°C. The exact temperature of these peaks is known to vary from sample to sample. Between 700° and 800°C there is generally a fairly sharp endothermic reaction, followed immediately by a sharp exothermic reaction. Caillere\textsuperscript{84} has published a series of differential thermal curves for many sepiolites, and they show the same general characteristics and variations noted above.

Some variation is to be expected in the dehydration characteristics of the sepiolites because of probable variations of composition. Also, in a mineral such as sepiolite in which the dehydration is gradual rather than abrupt, the corresponding thermal reactions would be slight, with the consequence that small variations in experimental techniques would be expected to give somewhat different results.

According to Migeon\textsuperscript{12} and Longchambon\textsuperscript{85} the water driven off below about 350°C is both hygroscopic and zeolitic water. The hygroscopic water is considered to be surface-adsorbed water and the zeolitic water to be present in the structural channels. The zeolitic water would be lost at the higher temperatures, and many differential thermal curves of sepiolites show a double endothermic reaction below about 350°C, the lower-temperature peak corresponding to the loss of hygroscopic water and the higher-temperature peak to zeolitic water. There is no change in the structure of the mineral on heating to 350°C. Above this temperature, the loss of water is accompanied by slight change in the lateral dimensions of the fibers. The \(a\) dimension, according to Migeon and Longchambon, is increased, and the \(b\) dimension is decreased. There is no change in the length along the fiber. These investigators designate this modification of the mineral as sepiolite II. The modified form of sepiolite persists to about 700°C, when it passes into an amorphous phase, according to Caillere.\textsuperscript{84} Apparently the OH water is retained initially in the modified phase, sepiolite II. As firing proceeds, it is lost gradually and later abruptly at the time of the loss of structure. The high-temperature endothermic reaction at 700° to 800°C corresponds to this final dehydration and the accompanying loss of structure.

The exothermic reaction just above 800°C is probably due to the development of a magnesium silicate phase. At 1000°C Longchambon\textsuperscript{85} records the presence of enstatite and at 1300°C a mixture of enstatite and cristobalite.

Longchambon\textsuperscript{85} has shown, in a series of dilation curves for sepiolite,

\textsuperscript{84}Caillere, S., 
\textsuperscript{85}Longchambon, H.,

that there are two intervals of contraction perpendicular to the fiber axis, one interval of about 1 per cent at about 350°C, and another of about 2 per cent taking place abruptly at about 800°C. Parallel to the fiber axis, there is a slow gradual contraction of about 0.5 per cent up to 800°C. The contraction during this temperature interval becomes more prominent as the temperature increases. At 800°C, a further contraction, exceeding 2 per cent in the direction parallel to the fiber axis, takes place suddenly.

Nutting has presented a dehydration curve for a palygorskite (Fig. 66), showing a sharp water loss below 100°C, abrupt water losses at 150°C to 200°C and 375°C to 425°C, and a gradual loss above 425°C, with complete dehydration at about 700°C. A continuous weight-loss curve (Fig. 70), given by Longchambon, shows similar results.

Differential curves for a palygorskite and an attapulgite (Figs. 76A and C) show an initial endothermic reaction below about 200°C and additional endothermic reactions at about 225°C to 350°C and 400°C to 525°C, corresponding approximately to the intervals of abrupt water losses shown by the dehydration curves. There is no definite-higher-temperature endothermic peak, and apparently the small water loss above about 550°C causes no thermal reaction adequate for recording.

Caillere and Henin have presented a series of differential thermal curves for palygorskites, and they in general have similar characteristics (Fig. 76D), except for larger initial endothermic reactions. The various palygorskites that have been analyzed show additional variations in detail, particularly in the high-temperature part of the curves, and this is to be expected because of the probable differences in composition, with resulting variations in high-temperature phases.

Bradley has stated that the water molecules in the channel-like interstices of the structure are lost below 100°C, a temperature which would correspond to the initial endothermic reaction. The water coordinated about the magnesium ions is lost at a slightly higher temperature, and this dehydration is probably correlated with the second endothermic reaction. The loss of the hydroxyl water from the silicate unit is probably correlated with the third endothermic reaction. Apparently most of the hydroxyl water is lost at about 400°C, with the remainder being lost slowly between 450°C and about 700°C.

The palygorskites-attapulgites differ in dehydration from the sepiolites in the loss of the hydroxyl water more abruptly and generally at a lower temperature. Also in at least some sepiolites, there is little or no indica-
tion of so-called zeolitic water, which in attapulgite is that coordinated with the magnesiuns.

According to Longchambon,⁸⁸,⁸⁹ the loss of water up to about 400°C is not accompanied by any structural changes. At about 400°C, there is a rapid contraction of the crystal lattice normal to the length of the fiber. The modified structure persists to about 775°C, when the structure is destroyed and further shrinkage takes place.

According to Caillere and Henin,⁹⁰ a comparison of the results of Longchambon and Bradley indicates that above 400°C the \((hk0)\) reflections are replaced by halos. This is explained by dislocations in the octahedral units of the amphibole chains, which lead to a closing of the cavities or channels with the subsequent disappearance of the water-adsorbing property. No satisfactory structural explanation has been offered for the contraction of the lattice normal to the fiber axis described by Longchambon.

Caillere and Henin⁹⁰ state that the high-temperature phases of some attapulgites-palygorskites are probably enstatite, sillimanite, and cristobalite. The high-temperature parts of the differential thermal curves show large variations, which indicate that there is significant difference in the high-temperature phases formed when these minerals are heated. This is expected, by analogy with the montmorillonite minerals, because of probable large variations in their chemical composition and possibly also in their structure. The precise nature of these high-temperature phases and their relation to composition and structure remain for future research.

According to Grim,⁹¹ attapulgite fuses at approximately the same temperature as montmorillonite. Data are not available for the fusion point of other members of this group, but probably they would be similar to attapulgite.

**Rehydration.** Very little data are available regarding the rehydration of the sepiolite-attapulgite-palygorskite minerals. According to Migeon,²² the water lost below 350°C by sepiolite is easily regained, whereas water lost at higher temperatures is not taken up again. Attapulgite-palygorskite minerals probably have about the same rehydration characteristics as sepiolite.

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⁸⁹ Longchambon, H., Recueil des communications du congrès technique de l'industrie de céramique, pp. 75–141 (1938).
CLAY-MINERAL MIXTURES

Many clay materials are made up of mixtures of several different clay minerals. The mixtures may be of two types: a combination of discrete particles of the separate minerals or an interstratification of layers of the separate minerals in which the thickness of the layers is of the order of one or a few unit layers.

In mixtures of discrete particles the dehydration characteristics tend to reflect those of the individual components. Numerous investigators have published differential thermal curves of prepared mixtures of various clay minerals. As shown in Fig. 92, such mixtures may show the thermal effects of the separate clay minerals with intensities proportionate to their relative abundance.

Fig. 92. Differential thermal curves of discrete mixtures of kaolinite and montmorillonite, from Spiel et al.27

Dehydration

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Grim\textsuperscript{37} has published a large series of differential thermal curves of clay-mineral mixtures prepared in different ways. He has shown that the thermal characteristics depend on the intimacy of mixing and on the nature of the clay minerals themselves. In mixtures prepared by combining dry powders without subsequent wetting, the dehydration characteristics of the individual components are maintained in proportions roughly equal to their relative abundance. If the mixing is done by stirring together wet suspensions of the separate minerals, and particularly if the mixture is allowed to dry and then rewetted and remixed several times, the dehydration characteristics of the individual components may be modified significantly. As shown in Fig. 93, the modifications may be such as to mask completely the presence of relatively minor components. Amounts of the order of 25 per cent could easily be hidden by such modifications of dehydration characteristics.

In such mixtures of discrete particles the modification of dehydration properties takes place more readily and to a greater degree as the crystallinity decreases. Thus, the effect is more pronounced for poorly crystalline kaolinite than for the well-crystallized mineral.

In general, it seems that, as the intimacy of mixing increases, the temperature for the loss of hydroxyl water is reduced and the loss of this water is more gradual, so that its thermal effect is spread out over a wider temperature interval.

With regard to interlayer mixtures, the published curves show that in some cases the individual components are registered in the differential thermal data and that in other cases they are not. Grim and Rowland\textsuperscript{33} have shown that a series of samples listed as beidellite provided differential thermal curves indicating that they are mixtures. Grim and Bradley\textsuperscript{77} have shown (Fig. 74) that the so-called sarospatite and bravaisite from the type localities are mixtures of mica and montmorillonite and that both components are indicated by the thermal curves.
same investigators point out that other samples composed of mixtures of illite and montmorillonite provide thermal data suggestive of a single mineral (Fig. 74) and also that mixtures of illite and chlorite may give no definite indication of more than one component.

In unpublished work by the author and his colleagues, it was found that some bentonites from Texas composed of mixtures of kaolinite and a low-iron montmorillonite in nearly equal amounts, yielded a single endothermic peak at about 600°C for the loss of hydroxyl water. In contrast to this finding, some of the kaolins from the Georgia area contain 15 to 20 per cent of montmorillonite, and differential thermal curves reveal distinct thermal reactions for both the kaolinite and the montmorillonite.

The factors determining whether or not the individual components are revealed by dehydration data are not completely known. The tendency for a separate reaction decreases as the relative abundance of the component decreases. Also a further factor probably is the nature of the interlayering; e.g., a component present in layers of nearly unit-cell thickness would not be revealed, whereas if the same mineral were present in the same amount but concentrated in layers several unit cells thick, its presence might be shown. Variations in composition may be a further influencing factor. Thus, in mixtures of illites and montmorillonites, a montmorillonite of one composition may be more readily concealed than one with a different composition.

Differential thermal data are used widely for clay-mineral identification, and in some cases quantitative estimates have been made solely on such data. The foregoing discussion illustrates the fact that such identifications must be made with caution. Differential thermal data are extremely valuable for clay-mineral identifications, but they cannot be used blindly, basing identifications solely on data derived from a few pure clay minerals. Frequently, trustworthy identifications can be made only on the basis of several types of analytical data, e.g., differential thermal plus X-ray diffraction plus chemical data.

Substantially no specific information is available on the high-temperature phases formed in clay-mineral mixtures. It seems likely that the initial high-temperature phases of interlayer mixtures, in some cases at least, would be considerably different from those of the individual components. This surmise is based on variations shown in the high-temperature portion of the thermal curves for such mixtures.

ADDITIONAL REFERENCES

Clay Mineralogy


Dehydration


CHAPTER 10

Clay-mineral–Organic Reactions

INTRODUCTION

Investigations of clay materials in many different fields for many years have produced evidence of some kind of a reaction between the fundamental components of clay and organic material. For example, early literature\(^1\) on decolorizing oil with clays refers to the adsorption of some components of the oil during the process and to changes in the nature of the oil as a consequence of decolorization.

Students of soils in the field of agriculture have presented evidence for some sort of inorganic-organic combination in many soils. For example, Demolin and Barbier\(^2\) showed a definite fixation of humic acid and protein by clay, and Mattson\(^3\) demonstrated a reduction in base-exchange capacity by complexing clay with protein. Sedletsky\(^4\) investigated the matter in considerable detail and concluded that many soils contain clay-mineral–organic complexes.

Further evidence for such reactions is provided by the color reactions produced when certain clays and organic compounds are mixed (see pages 274–276). The development of color or a change in color requires some kind of reaction between the clay and the organic compound added. The fact that montmorillonite and halloysite experience changes in their optical properties when immersed in certain oils (see pages 286–288) also indicates a reaction between these clay minerals and some organic compounds.

Prior to the determination of the exact nature of the fundamental constituents of clays and soils, there could be no precise concept of the reaction between the components of clay and organic compounds and of the nature of clay-organic complexes. The finding that clay materials are composed of small crystalline particles and the determination of the structure of the particles provided a new basis for studying clay-organic

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\(^4\) Sedletsky, I. D., \textit{“X-ray Study of Soils,”} Moscow (1939).
Clay-Mineral–Organic Reactions

reactions, and since the early 1930s a large amount of work has been done on this problem, and the character of clay-mineral–organic reactions has now been fairly well established. Thus, in 1934, Smith reacted organic bases and their salts with montmorillonites and presented evidence that the reaction was one of ion exchange. Gieseking and Jenny in 1936 showed that methylene blue replaced sorbed cations in certain clays, and later Gieseking and his colleagues showed definitely that organic ions enter into cation-exchange reactions with the clay minerals, particularly with montmorillonite.

Hofmann and his colleagues in 1934 showed that the c-axis dimension of montmorillonite varied following treatment with alcohol, acetone, and ether. In 1939 Ensminger and Gieseking showed definitely that organic ions could be sorbed on the basal plane surfaces of montmorillonite.

The early work of Hofmann et al. in 1934, and that of Myers and Sharov in 1937, suggested that organic compounds with polar active groups could be adsorbed by the clay minerals. Bradley in 1945, and MacEwan at about the same time quite independently, showed definitely that the nonionic organic molecules of polar character could be adsorbed by the clay minerals. These investigators also considered the nature of the bond between the nonionic organic molecules and the clay minerals.

REACTIONS WITH MONTMORILLONITE AND HALLOYSITE

The reactions of montmorillonite and halloysite with organic compounds have been studied more thoroughly than those of other clay minerals, and they illustrate well the nature of the reactions and their effect on certain properties of the clay minerals themselves; hence they will be discussed first and in considerable detail.

Ionic Reactions. Many common organic cations contain basic amino groups, and it is the reaction between these compounds and the clay minerals that has been studied in most detail. These cations are ammonium ions in which one or more of the hydrogens have been substituted by organic groups.

Because of its low cation-exchange capacity, such reactions with halloysite are relatively slight and unimportant. The organic ions are held around the edges of the particles by the same bonding mechanism as that operating for montmorillonite.

The data in Fig. 94, after Ensminger and Gieseking,9 show that the adsorption of gelatin may have a very marked effect on the cation-exchange capacity of montmorillonite and a montmorillonitic soil. The gelatin-clay complexes were prepared by mixing alkaline suspensions of gelatin and clay together and then acidifying to pH 2.6 with acetic acid. These authors showed that the protein did not reduce the cation-exchange capacity in an alkaline medium. As the hydrogen-ion concentration is increased, however, the cation-exchange capacity decreases. They conclude, from the fact that an increase in hydrogen-ion concentration increases the basic properties of the protein, that it is adsorbed as cations.

The data in Table 30, after Hendricks,17 show that the cation-exchange capacities determined with relatively small organic molecules are nearly the same as that found by displacement of the hydrogen ion with the barium ion. Hendricks showed also that extremely weak bases like the o- and m-nitroanilines do not form salts with montmorillonite, and that

\[ \text{Hendricks, S. B., Base-Exchange of the Clay Mineral Montmorillonite for Organic Cations and Its Dependence upon Adsorption Due to van der Waals Forces, J. Phys. Chem., 45, 65–81 (1941).} \]
large molecules like the alkaloids brucine (strychnos group) and codeine (morphine group) neutralize less of the hydrogen on the clay, even though they are stronger bases than aniline and benzidine. Thus codeine, in concentrations of 4 meq to 0.5 meq of acid clay in 25 cc of water, neutralized 0.63 meq of hydrogen per gram of clay, and brucine similarly neutralized 0.65 meq of hydrogen per gram of montmorillonite. The difference, namely, about 0.30 meq per gram, between these amounts and the exchange capacity of the montmorillonite (see Table 30) represents the amount of hydrogen so covered by the large alkaloid molecules as to be unavailable for neutralizing other molecules (cover-up effect). Organic ions larger than the area per exchange position, \( i.e., \) about 80 \( \AA^2 \), would be required to produce the cover-up effect. Hendricks has shown that both groups of an organic diamine are effective in neutralizing an acid clay.

\[ \text{Table 30. Cation-exchange Capacity of a Montmorillonite Determined with Certain Organic Cations} \]

<table>
<thead>
<tr>
<th>Base</th>
<th>Cation-exchange capacity, meq/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzidine</td>
<td>91</td>
</tr>
<tr>
<td>p-Aminodimethylaniline</td>
<td>90</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>86</td>
</tr>
<tr>
<td>a-Napthylamine</td>
<td>85</td>
</tr>
<tr>
<td>2,7-Diaminofluorene</td>
<td>95</td>
</tr>
<tr>
<td>Piperidine</td>
<td>90</td>
</tr>
<tr>
<td>Barium</td>
<td>90–94</td>
</tr>
</tbody>
</table>

Hendricks\(^{17}\) has indicated that the organic ions are held by Van der Waals forces in addition to the coulombic force. In general, the larger ions are more strongly adsorbed because of the greater Van der Waals forces, and larger organic ions are difficult or impossible to replace with smaller ions. Grim, Allaway, and Cuthbert\(^{18}\) have shown that small ions are adsorbed only up to the cation-exchange capacity, whereas larger ions may be adsorbed in excess, and that these excess molecules are not dissociated and probably are adsorbed by Van der Waals forces. Bradley and Grim\(^{19}\) believe that the coulombic forces are supplemented by C—H· · ·O bonds (see pages 259–261) between the organic molecule and the clay-mineral surface.

The adsorption of the organic ions on the basal plane surface of montmorillonites is shown conclusively by the shift in the c-axis spacing of the montmorillonite units accompanying the adsorption (Fig. 95). Hendricks\(^{17}\) has indicated that the organic ions are held by Van der Waals forces in addition to the coulombic force. In general, the larger ions are more strongly adsorbed because of the greater Van der Waals forces, and larger organic ions are difficult or impossible to replace with smaller ions. Grim, Allaway, and Cuthbert\(^{18}\) have shown that small ions are adsorbed only up to the cation-exchange capacity, whereas larger ions may be adsorbed in excess, and that these excess molecules are not dissociated and probably are adsorbed by Van der Waals forces. Bradley and Grim\(^{19}\) believe that the coulombic forces are supplemented by C—H· · ·O bonds (see pages 259–261) between the organic molecule and the clay-mineral surface.


Hendricks, Bradley and Grim, and Jordan have shown that for some organics more than one molecular layer may be adsorbed on the basal surfaces of the montmorillonite planes. Jordan has determined the c-axis spacing of montmorillonite from Wyoming bentonite treated with aliphatic amines of increasing chain lengths. Calculating the total internal surface area per cation-exchange position as 165 Å², the c-axis spacings are plotted in Fig. 95 as a function of amine chain length. The stepwise separation of the flakes in increments of 4 Å, which is about the Van der Waals thickness of a methyl group, indicates that the chains lie flat along the clay flake surfaces with the planes of the zigzag carbon chains parallel to the plane of the mineral. On this basis the areas covered by the amine chains have been computed from atomic dimensions and included in Fig. 95. When the organic chains occupy no more than half of the available area per exchange position, the organic molecules on the top surface of one layer fit into the gaps between those on the bottom surface of the layer directly above it, so that the resulting separation of the two layers is 4 Å, or the thickness of one hydrocarbon chain. When the chains occupy more than 50 per cent of the surface area per exchange position, adjacent laminae are unable to approach more closely than 8 Å, which is the thickness of two hydrocarbon chains.

The water-adsorbing properties of montmorillonite are gradually reduced as the basal surfaces of the mineral are coated with the organic

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Clay–Mineral–Organic Reactions

Fig. 96. Schematic drawing showing position of organic cations between montmorillonite layers, after Hendricks.
ions. In general, the larger the organic ion, the greater the reduction in the water-adsorbing capacity. Figure 97 shows differential curves for untreated montmorillonite from Wyoming bentonite and for butyl-dodecyl- and octadecylamine complexes of the same clay after exposure to an atmosphere of 75 per cent relative humidity for 4 days. These curves show a progressive decrease in the size of the low-temperature endothermic peak; this decrease results from the loss of adsorbed water with an increase in the size of the aliphatic chain. Gieseking, Hendricks, and Grim, Allaway, and Cuthbert have presented data on the relation of water adsorption to amine adsorption which indicate the same conclusion.

Jordan has shown that the viscosity of aqueous bentonite suspensions

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Fig. 97. Differential thermal curves of amine-treated and untreated montmorillonite, from Jordan.21

varies with the amount of treating amine, and that the maximum affect is obtained in the region of complete cation exchange. As shown in Fig. 98, maximum flocculation with maximum viscosity is reached in an octadecylamine-montmorillonite when the amount of the added amine is nearly equal to the cation-exchange capacity.

![Graph showing the effect of octadecylamine acetate on the viscosity of montmorillonite](image)

Fig. 98. Effect of octadecylamine acetate on the viscosity of montmorillonite (Wyoming bentonite), after Jordan. Concentration of suspension, 1.9 per cent.

**Adsorption of Polar Molecules.** Debye has shown that many non-ionic and organic molecules are dipoles as a result of the lack of symmetry of electron distribution within individual molecules. Such molecules act as if they carried both centers of positive charges and centers of negative charges. Since the clay-mineral structures are also polar, when they are in contact with liquids, solutions, or suspensions containing other polar substances, the negative centers on the clay minerals attract the positive centers on polar substances in surrounding liquids, and positive centers on clay minerals attract negative centers on surrounding polar particles. The foregoing notion of dipole character is valuable as a general concept. However, it should be borne in mind that more than one polar group can enter many molecules, and some quite stable associations occur with molecules which have no dipoles.

The water molecule is polar, and it is by far the most important polar compound sorbed by the clay minerals. Bradley in 1945 showed that glycols, polyglycols, and polyglycol ethers were adsorbed on the basal plane surfaces of montmorillonite, displacing water from these surfaces.

About contemporaneously and quite independently, MacEwan showed that a large variety of polar organic molecules can be adsorbed on the basal surfaces of both montmorillonite and halloysite (Table 31). The c-axis spacing of both minerals varies with the organic molecule adsorbed. The inorganic cations present on the surfaces of the clay min-

<table>
<thead>
<tr>
<th>Complex-forming substances</th>
<th>Montmorillonite</th>
<th>Halloysite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Meth. of formation</td>
<td>Δ obs.</td>
</tr>
<tr>
<td><strong>Normal monohydric alcohols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>a</td>
<td>7.4</td>
</tr>
<tr>
<td>Ethanol</td>
<td>a</td>
<td>7.2</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>b</td>
<td>4.5</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>b</td>
<td>4.6</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>b</td>
<td>4.6</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>b</td>
<td>4.1</td>
</tr>
<tr>
<td>1-Heptanol</td>
<td>b</td>
<td>4.1</td>
</tr>
<tr>
<td>1-Octacosnene</td>
<td>K</td>
<td>4.1d</td>
</tr>
<tr>
<td>Other monohydric alcohols</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Octanol</td>
<td>b</td>
<td>4.1d</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>a</td>
<td>7.6</td>
</tr>
<tr>
<td>1,3-Butanediol</td>
<td>a</td>
<td>8.6</td>
</tr>
<tr>
<td>Alcohol ethers and others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>a, b</td>
<td>5.6</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>a</td>
<td>4.2</td>
</tr>
<tr>
<td>Butyl cellulose</td>
<td>a</td>
<td>5.4</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>a</td>
<td>4.6d</td>
</tr>
<tr>
<td>Trethylene glycol</td>
<td>a</td>
<td>5.6</td>
</tr>
<tr>
<td><strong>Hydrocarbons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane</td>
<td>b</td>
<td>1-2d</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>b</td>
<td>0.6d</td>
</tr>
<tr>
<td>Benzene</td>
<td>b</td>
<td>4.6d</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>b</td>
<td>3.6d</td>
</tr>
<tr>
<td>Tetrahydrohypthalene</td>
<td>b</td>
<td>4.6d</td>
</tr>
<tr>
<td>Decahydrohypthalene</td>
<td>b</td>
<td>0.6d</td>
</tr>
<tr>
<td><strong>Other compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroethanol</td>
<td>b</td>
<td>8.1</td>
</tr>
<tr>
<td>Ethanediamine</td>
<td>b</td>
<td>4.3</td>
</tr>
<tr>
<td>1,2-Propanediol</td>
<td>a, b</td>
<td>8.2</td>
</tr>
<tr>
<td>Diethyllamine</td>
<td>a</td>
<td>10.2</td>
</tr>
<tr>
<td>Acetone</td>
<td>a, b</td>
<td>10.4</td>
</tr>
<tr>
<td>Acetonaldehyde</td>
<td>a</td>
<td>10.4</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>b</td>
<td>10.4</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>b</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Δ = "clear space" between mineral sheets measured from the surface of the O or OH layers, in kX

a = treated with large excess of cold liquid
b = boiled down to half volume with excess of liquid
c = dehydrated at 100°C over P₂O₅ in vacuum, then covered with liquid
e = covered with excess of liquid, and heated to 100°C for 1 to 2 hr
f, g, h, i = like a, starting from complex with ethanediamine (f), methyl cellulose (g), methanol (h), or chloroethanol (i)
K = treated with the molten alcohol at about 200°C
d = diffuse or double line.
eral are not necessarily displaced by the adsorption of the organic molecules.

On the basis of one-dimensional Fourier syntheses of diffraction data, Bradley concluded that the polar molecules are held to the clay surface through a C-H-·-O (clay-mineral surface) bond. MacEwan has come to the same conclusion regarding the nature of the bond. In general, the sorption energy for the organic dipolar molecules is greater than for water molecules, for montmorillonite dehydrated at 400° to 500°C will not rehydrate in water but will take up glycol and expand. The organic dipolar molecules are oriented between the basal surfaces of the clay minerals in positions as flat as possible.

Bradley showed that some organic dipoles were adsorbed in multiple molecular layers by montmorillonite. MacEwan has confirmed this finding for montmorillonite and has indicated that a single molecular layer is the general result for all organic polar molecules with halloysite. In the case of montmorillonite, three molecular layers is the greatest number that has been observed.

MacEwan explains the multiple-layer adsorption by montmorillonite as compared to the single-layer adsorption by halloysite as follows: Each of the surfaces of the montmorillonite sheets is formed by a layer of oxygen ions, and thus they behave rather like sheets with a uniform diffuse negative charge. Each sheet of montmorillonite will tend to collect a layer of dipoles on both its surfaces, so that between such sheets there will be two layers. In the case of nonpolar molecules or groups, only the Van der Waals force of attraction between them and the montmorillonite sheets need be considered. Since this force is nondirectional, the question of orientation does not arise and only a single molecular layer could be held in common by two neighboring montmorillonite sheets. Thus markedly polar molecules would form a two-layer structure, and less polar molecules a one-layer structure. Very strongly polar liquids may form even more than two layers (e.g., acetonitrile and nitromethane). According to MacEwan, the number of layers in montmorillonites in contact with excess of the liquid appears to increase with the function $\mu/[P]$ where $\mu$ is the molecular dipole moment and [P] is molecular size (parachor). Some polar groups appear to be necessary for adsorption, for saturated hydrocarbons do not form complexes (see Table 31). Presumably, therefore, as the hydrocarbon chain of a monohydric alcohol is made longer and longer, the adsorption would gradually dimin-


ish. The necessity of polar groups for adsorption is no doubt bound up with the fact that the montmorillonite sheets are charged and are held together by positive ions between the sheets. The energy of formation of a purely Van der Waals adsorption complex is presumably insufficient to cause the breakup of the charged-sheet–ion–charged-sheet complex. But if a few polar groups are present, these will tend to congregate about the charged spots on the sheets and about the positive ions. The result will be an effective increase of the radius of the ions and a consequent diminution in electrical stress. The resulting structure may be more stable than the dehydrated montmorillonite structure, in which the base cations occur between the structural sheets.

With halloysite only highly polar molecules are adsorbed between the unit layers. In this mineral the adjacent sheets of successive layers carry positive and negative charges, respectively, and there is no tendency for two layers of polar molecules to form. Figure 99, after MacEwan, shows schematically the process of complex formation.

On the basis of observed distances between successive clay-mineral sheets in the complexes from c-axis measurements and computed values based on Van der Waals dimensions (Table 31), MacEwan concluded that each layer of dipoles occupies its full “clearance space” in the c-axis direction, i.e., the space necessary to allow its molecules to move freely over a plane parallel to the surface of the structural sheets. This suggests that the adsorbed layers are in the state of a two-dimensional liquid, firmly adhering to the clay surface but able to move over it in a random manner. This conclusion is supported by the extremely labile nature of the complexes, which is such that one complex is changed to another by washing with excess of another miscible liquid, and by the absence of a simple integral number of molecules per unit cell, which would be expected for a crystalline arrangement of the adsorbed molecules on the clay surface.

MacEwan has indicated that, when glycol complexes are made in the presence of water, less glycol is needed to form the complex. He stated
that regardless of the water present the c-axis spacing is the same, and concluded that the glycol molecules must set the pattern into which the water molecules fit. Mackenzie\textsuperscript{25} has found that the c-axis spacing of a montmorillonite–ethylene glycol complex can be maintained by adding water if the glycol content is low. The additional water is proportional to the glycol deficiency in the molecular ratio of about 1:6. Recently Glaeser\textsuperscript{26} has shown that this conclusion does not hold for all complexes. For example, in the case of acetone-montmorillonite complexes, when the complex is formed in the absence of water, the distance between the montmorillonite layers is 3.7 to 3.9 \textgreek{\AA}; at 5 per cent relative humidity, 8.0 to 8.2 \textgreek{\AA}; and at 100 per cent relative humidity, 12.5 to 15.1 \textgreek{\AA}. Apparently a water-acetone complex develops between the montmorillonite layers. The data given in Table 31, therefore, may be subject to variations in some cases depending on the water present during the preparation of the complexes. Glaeser\textsuperscript{27} has shown also that the character of the adsorbed cation is only of slight importance in the formation of dipole complexes if they are formed in the absence of water or at low relative humidities. However, if they are formed at high relative humidities, the thickness of the adsorbed layer may vary greatly according to the cation present. Thus for acetone-montmorillonite complexes formed at 100 per cent relative humidity, the distance between the units is about 12.5 \textgreek{\AA}, if Na\textsuperscript{+} is the adsorbed ion, and 15.1 \textgreek{\AA}, if it is Ca\textsuperscript{++}. The explanation probably resides in the hydration tendencies of the cation.

**Comparison of Ionic and Polar Complexes.** Figures 95, 100, and 101, from Jordan,\textsuperscript{20} Bradley,\textsuperscript{12} and MacEwan,\textsuperscript{23} after MacEwan,\textsuperscript{24} show the variation in the c-axis spacing of montmorillonite with the number of carbon atoms in the chain, in complexes with the straight-chain amines, alcohols, glycols, and nitriles. In each case the spacing always corresponds to the presence of a whole number of molecular sheets between the montmorillonite layers. The spacing

alters in a homologous series in jumps of one sheet at a time. The figures illustrate the difference between ionic and polar types of complexes. In the ionic type the spacing increases with increasing number of carbon atoms, whereas in the polar type the spacing decreases with increasing number of carbon atoms. The explanation is that, in the case of the ionic type, enough organic molecules must be present to neutralize the charge on the montmorillonite, and if the molecules are large, this will require more than two layers. In polar adsorption the number of layers is determined by the energy of adsorption, which decreases as the nonpolar part of the molecule becomes larger.

**REATIONS WITH CLAY MINERALS OTHER THAN MONTMORILLONITE AND HALLOYSITE**

**Kaolinite.** Grim, Allaway, and Cuthbert have shown that kaolinite enters into ion-exchange reactions with organic ions and that the watersorption properties are reduced by the replacement of inorganic cations with organic cations. Because of the low cation-exchange capacity of these minerals, the quantity of organic cations sorbed is small. Bradley has pointed out that the adsorption of polar molecules would take place...
on the surfaces of kaolinite. The organic molecules do not penetrate between the unit layers of kaolinite as they do in halloysite and montmorillonite and, therefore, would be retained only around the edges and exterior surfaces of the particles.

**Illite.** It has been shown\(^{18}\) that illite enters ion-exchange reactions with organic cations and that the water-sorption properties are reduced after reaction with such ions. The quantity of organic ions sorbed is somewhat greater than for kaolinite because of the higher cation-exchange capacity. The sorption of polar molecules undoubtedly takes place in a manner similar to that previously described for kaolinite.

**Chlorite.** No data are available on the reaction of organic molecules with the chloritic clay minerals, but it seems certain that they would react similarly to illite and kaolinite. Because of the increase in ion-exchange capacity and surface area with decreasing particle size, the sorption of both ionic and polar organic molecules would increase greatly with decreasing particle size for chlorite as well as for kaolinite and illite.

**Vermiculite.** Bradley\(^{14}\) pointed out that the ideal structure of vermiculite suggests that the interlayer water could be displaced by organic molecules. Walker\(^{28}\) has shown that complexes are formed with organic ions and that the amount of displacement of the vermiculite basal reflection depends on the concentration as well as the nature of the organic ion. Barshad\(^{29}\) has shown that Mg, Ca, Ba, H, Li, and Na vermiculite take up a single layer of glycol molecules, with a c-axis spacing of 14.3 Å, when immersed in hot anhydrous glycol. Under similar conditions montmorillonite takes up two molecular layers of glycol, with a c-axis spacing of 17.7 Å. Also under similar conditions NH\(_4\), K, Rb, and Cs vermiculite remain contracted, taking up no glycol molecules between unit layers. Walker\(^{28}\) has shown that ethylene glycol, methane, cyclohexanol, acetone, and acetonitrile show limited penetration of Mg vermiculite, or none at all, but that penetration is easy if Li vermiculites are used. Probably because of the generally larger size of the vermiculite flakes and the higher perfection of stacking orientation, penetration of organic molecules is more difficult in vermiculites than in montmorillonites.

Walker\(^{28}\) has emphasized that the c-axis spacing of glycol-vermiculite (14.28 Å) is very close to that of natural magnesium-saturated vermiculite (14.36 Å), and therefore the penetration of the glycol molecule is difficult to observe. Walker also points out that in the montmorillonite complex the glycol molecule orients itself with a height of 3.9 Å, whereas in vermiculite the space available is 5 Å; hence it is concluded that in

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vermiculite the organic molecules either (1) attach themselves to the clay-
mineral surfaces by a weaker bonding force than that in a montmorillonite
complex or (2) orient themselves differently with respect to the adjacent
silicate surfaces. In vermiculite, single layers of glycol are interleaved
with the aluminosilicate layers, whereas in montmorillonite there are
multilayers. Walker states that vermiculite exerts a catalytic effect on
the decomposition of glycerol. Vermiculite boiled a few minutes in
glycerol acquires a black metallic coating on interlamellar as well as
boundary surfaces. The basal spacing of such a vermiculite complex is
14.06 Å.

**Atapulgite.** The fibrous clay minerals belonging to the sepiolite-
atapulgite-palygorskite group should adsorb organic ions and polar mol-
ecules around their edges like kaolinite, illite, and chlorite. Bradley pointed out that the dimensions of the cross section of the channels in
atapulgite are about 3.7 by 6.0 Å, which is the approximate cross-
sectional dimension for single strings of ethylene glycol molecules. The
presence of organic molecules in the channels would be difficult to detect
by X-ray diffraction, because only minor intensity variations in the
reflections would be expected. However, careful determinations of the
change in the optical properties of atapulgite on treatment with glycol
suggest that a few of the organic molecules have penetrated the channels.
Nederbragt has presented evidence, based on the preferential adsorption
of some paraffins, indicating that some aliphatic chains are adsorbed in
the open channels or in the gutters around the edges of particles and per-
haps also in the interior channels.

**RESISTANCE OF ADSORBED ORGANIC MOLECULES TO BIOLOGICAL
DECOMPOSITION**

The work of several investigators suggests that the resistance of some
organic materials to biological decomposition may be increased when they
are adsorbed by the clay minerals. Thus, Waksman reached this con-
clusion because it is easier to build up the humus content in a clay-rich
soil than in a clay-poor soil. Mattson believed that adsorbed proteins
might be more resistant to microbial decomposition than free proteins.
Ensminger and Gieseking and Erickson have investigated the matter

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30 Nederbragt, G. W., and J. J. deJong, The Separation of Long-Chain and Compact
31 Waksman, S. A., "Humus: Origin, Chemical Composition and Importance in
32 Ensminger, L. E., and J. E. Gieseking, Resistance of Clay-Adsorbed Proteins to
33 Erickson, A. E., Ph.D. thesis, University of Illinois (1948). Reference from J. E.
of the decay of adsorbed organics and have shown that the decay characteristics are often quite different in free as compared to clay-mineral-adsorbed organic material. Ensminger and Gieseking observed that protein-montmorillonite complexes prepared by ion exchange in which relatively large amounts of protein were adsorbed as cations, showed only a slight tendency to putrefy. These same authors showed that the adsorption of albumin and hemoglobin by ion exchange in montmorillonite interfered with the enzymatic hydrolysis of these proteins in both acid pepsin suspensions and alkaline pancreatin suspensions. In kaolinite complexes there was no significant effect on the hydrolysis of albumin and hemoglobin. Apparently sorption between basal units, as in the case of montmorillonite, rather than around particle edges, as in kaolinite, is necessary to retard chemical change. Ensminger and Gieseking\(^3\) conclude that the hydrolysis is reduced because the protein molecules, when adsorbed by the clay, are oriented in such a way that the active groups are inaccessible to the enzyme. Another possible explanation is that the enzyme is partly adsorbed and thereby rendered partly inactive.

Erickson\(^3\) has shown that the stability of amine-montmorillonite complexes, or their tendency to decomposition, depends on the enzyme and on the amine used in the complex. Actually in some cases, e.g., in tyrosine-montmorillonite complexes, after an initial lag in oxidation, the clay seems to catalyze the enzymatic reaction.

**ORGANOPHILIC CLAY-MINERAL COMPLEXES**

Hauser\(^3\) appears to have discovered that certain organic compounds of montmorillonite have the property of swelling and dispersing in organic liquids. Jordan\(^2\) has investigated this matter in great detail and the following statements are based on his work.

The gel volume of a series of normal primary aliphatic amine-montmorillonite complexes plotted as a function of the number of carbon atoms are given in Fig. 102. The gel volumes were determined in nitrobenzene, benzene, and isoamyl alcohol. The data show that the organophilic properties are negligible until an amine with a chain of 10 carbon atoms is reached, and that 12 carbons are required for maximum swelling. An amine with a 12-carbon chain covers slightly more than half of the available basal surface of the montmorillonite units per exchange position, and initiates the interlayer distance of about 8 Å, which is the thickness of two molecular layers, (Fig. 95). Apparently this condition is necessary for maximum swelling.

The swelling behavior of dodecylamine complexes in a wide variety of liquids is given in Table 32. These data suggest that swelling is low in

liquids of a nonpolar nature, such as the aliphatic and aromatic hydrocarbons, and that generally the gel volume increases with the dielectric constant of the liquid, although the correlation is not perfect. It appears that the most effective liquids are those which combine highly polar with

![Graph showing effect of amine chain length on swelling of organic-ammonium-montmorillonite in organic liquids, after Jordan.](image)

**Fig. 102.** Effect of amine chain length on swelling of organic-ammonium-montmorillonite in organic liquids, after Jordan. ²⁰

highly organophilic characteristics, good examples being nitrobenzene and benzonitrile. It is thought that, in the case of an incompletely clad amine-montmorillonite complex, adsorption of a highly polar organic liquid on the uncoated portion of the clay surface would greatly enhance solvation of the micelle in the remainder of the liquid.

Jordan found that, for complexes prepared with single-chain primary amines of less than sufficient size to coat the montmorillonite particles
Clay-Mineral–Organic Reactions

TABLE 32. Gel Volumes of 2-g Samples of Dodecylammonium-Bentonite in Various Liquids
(After Jordan23)

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Gel volume, ml</th>
<th>Liquid</th>
<th>Gel volume, ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (untreated bentonite)</td>
<td>31</td>
<td>Butyl Carbitol</td>
<td>12.5</td>
</tr>
<tr>
<td>Water (dodecylammonium-bentonite)</td>
<td>2.0</td>
<td>n-Butyl phthalate</td>
<td>12.5</td>
</tr>
<tr>
<td>Petroleum oil, Gulfpride SAE 10</td>
<td>2.5</td>
<td>Isophorone</td>
<td>12.5</td>
</tr>
<tr>
<td>Petroleum oil, Gulfpride SAE 40</td>
<td>2.5</td>
<td>Benzyl alcohol</td>
<td>13.0</td>
</tr>
<tr>
<td>Dow Corning Fluid 200</td>
<td>2.5</td>
<td>Bromoform</td>
<td>13.0</td>
</tr>
<tr>
<td>Petroleum ether</td>
<td>3.0</td>
<td>Ethyl acetate</td>
<td>13.0</td>
</tr>
<tr>
<td>Piperidine</td>
<td>3.0</td>
<td>Tricresyl phosphate</td>
<td>13.0</td>
</tr>
<tr>
<td>Naphtha</td>
<td>3.5</td>
<td>Acetone</td>
<td>13.5</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>4.0</td>
<td>Ethanol (96%)</td>
<td>13.5</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>4.0</td>
<td>Nitroethane</td>
<td>13.5</td>
</tr>
<tr>
<td>Dibutylamine</td>
<td>4.0</td>
<td>Acetonitrile</td>
<td>14.0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>4.5</td>
<td>Isoamyl acetate</td>
<td>14.0</td>
</tr>
<tr>
<td>Tributylamine</td>
<td>4.5</td>
<td>Castor oil</td>
<td>14.0</td>
</tr>
<tr>
<td>Amyl nitrate</td>
<td>6.0</td>
<td>Linseed oil</td>
<td>14.0</td>
</tr>
<tr>
<td>α-Butylene bromide</td>
<td>6.0</td>
<td>Oleic acid</td>
<td>14.5</td>
</tr>
<tr>
<td>Eucalyptol</td>
<td>6.5</td>
<td>n-Butylaldehyde</td>
<td>15.0</td>
</tr>
<tr>
<td>Styrene</td>
<td>6.5</td>
<td>Cyclohexanone</td>
<td>15.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>6.5</td>
<td>Dodecylamine</td>
<td>15.5</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>7.0</td>
<td>Ethyl bromide</td>
<td>15.5</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>7.0</td>
<td>n-Butyl tartrate</td>
<td>16.5</td>
</tr>
<tr>
<td>Cymene</td>
<td>7.5</td>
<td>n-Heptaldehyde</td>
<td>18.0</td>
</tr>
<tr>
<td>Aniline</td>
<td>8.0</td>
<td>Methyl iodide</td>
<td>18.0</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>8.0</td>
<td>γ-Picoline</td>
<td>18.0</td>
</tr>
<tr>
<td>Ethylene dichloride</td>
<td>8.0</td>
<td>Acetophenone</td>
<td>19.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>9.0</td>
<td>Tetraethyl orthosilicate</td>
<td>19.0</td>
</tr>
<tr>
<td>Paraldehyde</td>
<td>9.0</td>
<td>Coconut oil</td>
<td>20.0</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>10.0</td>
<td>Dodecyl alcohol</td>
<td>20.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>10.0</td>
<td>Methyl ethyl ketone</td>
<td>20.0</td>
</tr>
<tr>
<td>o-Cresol</td>
<td>10.0</td>
<td>Diethyl ketone</td>
<td>21.0</td>
</tr>
<tr>
<td>Ethyl malonate</td>
<td>10.0</td>
<td>Hexadienial</td>
<td>21.0</td>
</tr>
<tr>
<td>Formamide</td>
<td>10.0</td>
<td>Pyridine</td>
<td>28.0</td>
</tr>
<tr>
<td>Furfuryl alcohol</td>
<td>10.0</td>
<td>Benzaldehyde</td>
<td>31.0</td>
</tr>
<tr>
<td>Toluidine</td>
<td>10.0</td>
<td>Benzyl chloride</td>
<td>33.0</td>
</tr>
<tr>
<td>Phenol</td>
<td>10.5</td>
<td>Crotonaldehyde</td>
<td>34.0</td>
</tr>
<tr>
<td>Butyl stearate</td>
<td>11.0</td>
<td>Ethyl ether</td>
<td>35.0</td>
</tr>
<tr>
<td>2-Nitropropane</td>
<td>11.0</td>
<td>Furfural</td>
<td>35.0</td>
</tr>
<tr>
<td>Acetic acid, glacial</td>
<td>12.0</td>
<td>Benzonitrile</td>
<td>50.0</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>12.0</td>
<td>Nitrobenzene</td>
<td>88.0</td>
</tr>
<tr>
<td>1-Nitropropane</td>
<td>12.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

completely with a layer of hydrocarbon chains, swelling can be developed in nonpolar hydrocarbons if a second organic liquid that is highly polar, e.g., an alcohol, ester, ketone, or aldehyde, is added to the system. Figure 103 shows the great influence of small additions of alcohols on the swelling characteristics of octadecylammonium-montmorillonite in toluene.
It is postulated that the highly polar additive is adsorbed on the uncoated surface of the montmorillonite, thereby rendering the individual flakes entirely organophilic and compatible with the hydrocarbon portion of the solvating liquid. In Fig. 104, data are presented for toluene-ester systems with octadecylammonium-montmorillonite; these data indicate that the acid portion of the ester is more important than the alcohol portion. For example, ethyl formate is more effective than methyl acetate; methyl, ethyl, and butyl acetate are approximately equal in effect; and butyl stearate is practically without influence.

![Swelling of octadecylammonium-montmorillonite in toluene-ester mixtures, after Jordan.](image)

Jordan has shown that montmorillonite complexes with quaternary ammonium salts having two long aliphatic chains are organophilic in single-hydrocarbon liquid systems. Dispersion in toluene takes place much more readily and completely with the double-chain complexes than with the single-chain complexes, probably because the completely coated particles are more compatible with the hydrocarbon. In the case of double-chain complexes, there is a tendency for an initially greater separation of the montmorillonite units than in single-chain complexes.

Jordan concludes that the swelling process involves two factors for an incompletely clad clay complex: (1) high adsorption energy of liquid for uncoated clay, and (2) high solvation energy of liquid for the organic coating. Both conditions are fulfilled by a single liquid like nitrobenzene or by a binary liquid system of the toluene-alcohol type. Adsorption of polar molecules by the clay must tend to separate the plates, thereby rendering the micelle more organophilic and the organic coating more accessible. The dialkyl quaternary complexes are solvated by toluene alone because of the complete coating of organic matter and the initially
higher separation of the plates. Data for this conclusion are given in Fig. 105, which shows gel volumes for several organic-ammonium-montmorillonite complexes in several primary aliphatic alcohols. In agreement with this conclusion, octylammonium-montmorillonite solvates most in the most polar alcohol, while dimethyllaurylcetylammonium montmorillonite solvates least in methanol and to a progressively greater extent in the less polar members of the series.

![Figure 105](image-url)

**Fig. 105.** Effect of chain length on swelling of organic-ammonium-montmorillonite in alcohol, after Jordan.20

**STRUCTURAL IMPLICATIONS OF MONTMORILLONITE-ORGANIC COMPLEXES**

Studies of the reactions between montmorillonite and organic molecules have led some investigators to certain conclusions regarding the atomic structure of the mineral. Thus, Berger concluded that methylation takes place when dry hydrogen montmorillonite is treated with diazomethane, and that this requires the presence of acidic hydroxyls on the exterior of the montmorillonite structure. Berger further concluded from quantitative determinations of the methylation that the Hofmann struc-

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ture would not provide an adequate number of such hydroxyls. Since the Edelman-Hofmann structure (see page 61) postulates an abundance of such hydroxyls, the methylation was believed to be evidence for this structure. Edelman has pointed out that the capacity for methylation of montmorillonite determined by Berger requires the inversion of only about one-third of the number of silica tetrahedrons (see page 62) originally postulated as inverted by Edelman and Favejee.

Gieseking has expressed the opinion that the reaction of acetyl chloride with air-dried montmorillonite, producing a lyophobic material which no longer swells in water, affords evidence for the occurrence of OH groups on the basal surfaces of montmorillonite.

Deuel et al. have studied the esterification of hydrogen montmorillonite by 1,2-epoxides and the reaction of sodium montmorillonite and mustard gas, with the production of hydrophobic clay esters of largely reduced cation-exchange capacities. The clay esters produced in the reactions can be saponified. These investigators also found that hydrogen clays can be transformed by reaction with SOCl₂ into clay chlorides, which in turn will react with alcohols to form esters. Deuel et al. conclude that these reactions require the presence of a sufficiently large number of surface hydroxyls to provide evidence for the Edelman-Favejee structure.

Numerous investigators have pointed out that the Edelman-Favejee structure is not supported by diffraction data for montmorillonite. For example, the value of $d(001)$ in completely dried alkali and alkaline-earth montmorillonites is less than 10 Å, which is too low for the inverted silica tetrahedron structure of Edelman and Favejee. Projecting silica tetrahedrons from the basal planes of the mineral would require a $d(001)$ value of at least 11 Å in the dried condition.

The problem of the structural implications of montmorillonite-organic reactions cannot now be resolved, but in the face of the X-ray-diffraction data, it seems that some explanations other than the Edelman-Favejee structure must be found for the reactions described by Berger, Gieseking, and Deuel. An alternative explanation, which cannot yet be evaluated adequately, is the structure suggested by McConnell (see page 63),

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which would provide some hydroxyls in the basal montmorillonite surfaces without projecting silica tetrahedrons.

**ANALYTICAL TECHNIQUES BASED ON CLAY-MINERAL-ORGANIC REACTIONS**

The reactions of clay minerals and organic molecules have been used as the basis for analytical techniques for the identification of the clay minerals, for the determination of certain properties of the clay minerals themselves, and for the determination of the geometry and properties of the organic molecules.

**X-ray Techniques.** The montmorillonite minerals commonly give diffuse reflections and a nonintegral series of basal reflections. Bradley and MacEwan have pointed out that organic-montmorillonite complexes tend to have a high degree of regularity in the $c$ spacing, giving an integral series of very sharp reflections. Thus, the identification of montmorillonite by X-ray diffraction is greatly simplified by preliminary treatment with certain organic reagents. It is desirable to use an organic liquid of low volatility which is readily miscible with water, so that the natural hydrated montmorillonite may readily be changed into an organic complex. Glycerol and ethylene glycol are used extensively. The hydration state of the natural mineral does not alter appreciably the position or intensity of the reflections given by the organic-montmorillonite complex. It is common practice to add enough glycerol to air-dried material to make it visibly moist. Any montmorillonite present will give rise to a periodicity along $c$ of about 17.7 Å, with a series of higher orders, most of which will be adequately separated from reflections given by the other clay minerals. By the use of the organic treatment technique, relatively small amounts (5 per cent) of montmorillonite can be identified. Prior to the development of this technique, such small amounts of montmorillonite would not have been detected.

Glycerol treatment of halloysite (4H$_2$O) causes a shift in the basal reflections to 11 Å, and first, third, and fifth orders from this spacing are apparent. A similar shift takes place for the dehydrated form of this mineral if the dehydration is not essentially complete. Thus, air-dried samples will show the shift, whereas samples dried at 75°C for about 12 h or at higher temperatures for shorter intervals do not form the complex and exhibit no shift.

Glycerol forms complexes with vermiculite with a spacing of 14 Å, which is so close to the spacing of the fully hydrated natural mineral that it has little diagnostic value.

The glycol or glycerol treatment technique is of tremendous value in resolving very intimate interlayer mixtures of some of the clay minerals.
For example, the reflections from a mixture of montmorillonite and illite are likely to be diffused and complex because of the variable c spacing of the former mineral. Treatment with glycol or glycerol develops a uniform spacing of the montmorillonite and thereby sharpens the reflections so that they can be interpreted more readily. Use of the organic treatment technique has shown that many materials described as single species are actually interlayer mixtures. Thus, the type bravisite and many materials described as beidellite were found to be mixtures of illite and montmorillonite (see page 36). For a detailed discussion of the glycol-glycerol diffraction technique the works of MacEwan and Bradley should be consulted.

**Differential Thermal Techniques.** When clay-mineral–organic complexes are heated, the organic material is oxidized, and an exothermic reaction takes place. Allaway, working with piperidine-montmorillonite complexes, showed that the detailed features of the exothermic reactions varied with the composition of the montmorillonite. Triethanolamine, monoethanolamine, and n-butylamine complexes gave results similar to those for piperidine complexes. Allaway found that the exothermic reaction was always multiple and that a peak at 700°C suggested a high-magnesium montmorillonite, a peak between 450° and 500°C suggested an iron-rich montmorillonite, and a peak at about 600°C suggested a member of the montmorillonite group containing some aluminum in tetrahedral coordination. Similar variations in the exothermic reactions were found for several illites, but they were of relatively lower intensity than for the montmorillonites. Piperidine treatment had little effect on the differential thermal curves of kaolinites.

Allaway concluded that the piperidine held by the montmorillonite breaks down on firing with a loss of hydrogen, leaving a coating of carbon on the external surfaces and between the unit layers of the clay mineral. The carbon is burned off rather slowly as long as the clay-mineral structure remains intact, but when the structure breaks down, the carbon is quite rapidly oxidized. The use of organic cations is essentially a technique for magnifying the thermal effects of the breakdown of such structures as can be coated with carbon, with strong exothermic reactions replacing weaker endothermic reactions. Certain lattice changes which appear in the ordinary differential thermal procedure to be slow gradual breakdown of the clay are resolved into two separate peaks of thermal activity by the use of the piperidine treatment. Thus, the treatment procedure may resolve mixtures or permit the identification of certain mineral components which would not be revealed by the usual method of thermal study.

Optical Methods. The adsorption of organic molecules between the basal plane surfaces of montmorillonite and to a lesser extent of halloysite causes a slight but definitely determinable change in their indices of refraction (see pages 286–288). Therefore, when these clay minerals are mounted in certain liquids for optical determinations, the indices of refraction can be seen to change as the liquid is adsorbed by the clay mineral. This characteristic can be used as a diagnostic criterion for the identification of montmorillonite and halloysite. No specific data are available for vermiculite, but its indices of refraction should also change, since it possesses the property of interlamellar adsorption of organic molecules.

Cation-exchange Capacity. Robertson and Ward\textsuperscript{42} have recently described a rapid method for estimating the cation-exchange capacity of clay materials based on the adsorption of methylene blue. The change in color of a standard methylene blue solution produced by the adsorption of the clay material permits a determination of the amount of the organic molecule adsorbed, from which the cation-exchange capacity can be calculated. For most clays the results are in good agreement with those obtained by other procedures.

Surface-area Determination. Dyal and Hendricks\textsuperscript{43} have pointed out that the total surface, the external surface, and, by difference, the internal surface of clays can be determined from adsorption reactions with polar molecules, \textit{e.g.}, ethylene glycol. Total surface can be determined by the retention of ethylene glycol in an evacuated system. After the clay has been heated to about 100°C for halloysite and 600°C for montmorillonite, the organic molecule does not penetrate between the unit layers, and values for retention on external surfaces alone are obtained. The difference between total retention and external retention expresses the amount of interlayer surface, and from this value the amount of halloysite or montmorillonite can be estimated.

Geometry and Properties of Organic Molecules. The study of clay-mineral–organic reactions and the resulting complexes provides an approach to the investigation of the shape and certain bonding characteristics of the adsorbed organic molecules themselves. Thus the space required for the organic molecules between the montmorillonite layers, as revealed by determination of \textit{d}(001) spacings, provides information on the thickness, areal dimensions, and in some cases the bond distribution in the organic molecules. This subject is aside from the field of this volume, and for information concerning it, the works of Hendricks,\textsuperscript{27} MacEwan,\textsuperscript{28} and Bradley\textsuperscript{13} should be consulted.

STAINING TESTS FOR CLAY MINERALS

According to Faust, who has investigated the history of staining techniques in general and has summarized much of the early work, Behrens in 1871 appears to have first applied staining methods to mineralogy. Staining techniques were used for biological material beginning about 1838. An extensive literature has grown up regarding the use of staining methods, and many persons have attempted to apply them to clays.

The adsorption of various organic substances by natural and chemically altered or heat-treated clays can produce color changes in the clay. Frequently such changes vary, depending on the identity of the clay mineral and its composition. The color changes, therefore, provide a possible basis for identifying the clay-mineral components of clay materials. A staining test has the advantage of being rapid and simple to perform, even in the field.

In general, the reaction and resulting color change are slight or absent for clay minerals of low adsorptive capacity, such as kaolinite, but typically are pronounced for highly adsorptive clay minerals, such as montmorillonites. Two mechanisms have been proposed to explain the color reactions obtained with clay minerals and various reagents: (1) an acid-base reaction in which the natural or acid-treated clay reacts as an acid, and (2) an oxidation-reduction phenomenon in which certain ions, mainly ferric iron contained in the clay-mineral lattice, cause an oxidation of the reagent. Substances probably causing color changes by the acid-base reaction include triphenylmethane, azine, and azo dyes. Substances probably changing the color of clays by the oxidation-reduction reaction include benzidine and other aromatic amines.

The general applicability of staining tests for the identification of the clay minerals is restricted, because the development of characteristic color reactions can be inhibited, augmented, or masked by several common ingredients of clay materials other than the clay minerals. Manganese dioxide may cause the oxidation-reduction reaction with benzidine, even in the absence of adsorptive clays, and ferrous iron and other reducing agents may prevent the color-forming reaction from taking place. In techniques that require the preparation of hydrogen clays for the staining reaction, the acid treatment may destroy the structure of the clay minerals. Thus iron- and magnesium-rich montmorillonites, and consequently some nontronites and hectorite, might not appear to react with the staining solutions like other members of the montmorillonite group.


Table 33. Characteristic Staining of Clay Minerals
(After Mielenz et al. 46)

<table>
<thead>
<tr>
<th>Clay mineral</th>
<th>Untreated clay</th>
<th>Acid-treated clay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzidine</td>
<td>Safranine Y</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>No reaction</td>
<td>Red-purple red.*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strong to weak pleochroism.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>From reddish purple parallel to cleavage to yellowish red perpendicular to cleavage.</td>
</tr>
<tr>
<td>Dickite</td>
<td>No reaction</td>
<td>Crystals not stained.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Very weak pleochroism from reddish purple or purple parallel to cleavage to reddish yellow perpendicular to cleavage.</td>
</tr>
<tr>
<td>Nacrite</td>
<td>No reaction</td>
<td>Crystals not stained.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Weak pleochroism from reddish purple parallel to cleavage to yellowish red perpendicular to cleavage.</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Purple-blue</td>
<td>Purple-blue</td>
</tr>
<tr>
<td>Nontronite</td>
<td>Blue-green</td>
<td>Red-purple red*</td>
</tr>
<tr>
<td>Hectorite</td>
<td>Purple-blue</td>
<td>Red-purple red*</td>
</tr>
<tr>
<td>Illite</td>
<td>No reaction</td>
<td>Red-purple red*</td>
</tr>
<tr>
<td>Attapulgite</td>
<td>No reaction</td>
<td>Red-purple red*</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>No reaction</td>
<td>Not stained</td>
</tr>
</tbody>
</table>

* Dye absorbed without change in color. Samples of nontronite included in these tests did not change the color of the dyes in these tests, but specimens of nontronite reacting in a manner similar to montmorillonite have been examined.

Also, the strong original color of a sample particularly rich in iron might tend to mask the color change which would result from the adsorption of the staining reagent.

Because of the above factors caution must be used in applying any staining test indiscriminately to clay materials. Under restricted conditions, when the samples to be studied are relatively pure clay-mineral...
materials, or where the range of composition is restricted and known in
general terms, staining techniques may be entirely satisfactory. For
example, some of the sedimentary kaolins in the Georgia area contain
montmorillonite in addition to kaolinite. There are no other constitu­
ents of these kaolins that might cause a color reaction, and a staining
test quickly shows the presence of montmorillonite.

A very large number of reagents have been suggested and tried for
clay-mineral staining tests. In recent years the tendency has been to
use several reagents separately in a test, so that the deficiencies of one can
be compensated by the value of another for a given material. Such a
test has been described by Mielenz, King, and Schieltz and appears to
give quite satisfactory results. In this procedure a pulverized portion of
the natural clay is treated with benzidine, and portions of the clay, after

treatment with strong hydrochloric acid and washing to remove the
excess chloride, are treated separately with a saturated solution of safran­
ine Y in nitrobenzene and with a saturated solution of malachite green
in nitrobenzene. In addition to the visual determination of the color
developed, the samples are examined with the petrographic microscope
to determine the development of any pleochroic colors and other changes
in optical characteristics. The results of the use of these reagents are
summarized in Table 33 taken from the work of Mielenz, King, and
Schieltz. Even with such an elaborate staining technique, caution
must be used; anomalous results are sometimes obtained because various
nonclay substances may cause or inhibit staining reactions; and some
clays fail to react in a characteristic manner for as yet inexplicable
reasons.

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CHAPTER 11

Optical Properties

The optical properties of the clay minerals as reported in the literature are summarized in Table 34. In general it is necessary to give a range of optical values instead of a single value, because of inherent variations in the clay minerals themselves and because of difficulties in measuring precisely the optical properties of the extremely small clay-mineral particles. Also, it is usually possible to determine only some of the optical characteristics.

Inherent variations in the clay minerals which cause changes in optical properties are replacements within the lattice. Also, variations in the amount of any interlayer water in the expanding-lattice minerals are reflected by changes in optical properties. In addition, the clay minerals from time to time may exhibit strain or warping within the lattice or deviations from perfection of crystallinity, which would cause some alteration in optical characteristics. The variation due to strain or imperfections in crystallinity is likely to be small. Further, the optical values of some clay minerals are different in different liquids which may be used as index liquids to measure them (see pages 286–288).

KAOLINITE

As shown in Table 34, there is a measurable and diagnostic difference in the optical properties of kaolinite, dickite, and nacrite. The optical characteristics of anauxite are substantially the same as those of kaolinite.

Because of the absence of replacements within the kaolinite lattice and the low adsorptive properties of the mineral, kaolinite exhibits narrowly restricted optical values. Kaolinite frequently occurs in particles of sufficient size to permit fairly complete and precise optical measurements. As the degree of crystallinity decreases, the poorly crystallized variety has slightly decreasing indices of refraction and birefringence.

The data in Fig. 106, after Mehmel, show that the mean index of refraction of kaolinite increases slightly on heating up to the point of loss of OH lattice water slightly above 400°C. Accompanying this dehydra-

### Table 34. Optical Properties of the Clay Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$\alpha$</th>
<th>$\gamma$</th>
<th>$\gamma - \alpha$</th>
<th>Sign</th>
<th>$2V$</th>
<th>Dispersion</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>1.553–1.563</td>
<td>1.560–1.570</td>
<td>0.006–0.007</td>
<td>$-$</td>
<td>$24^\circ$–$50^\circ$</td>
<td>$p &gt; v$ weak</td>
<td>Optic plane and $Z \perp$ to (010); $X \perp$ (001) = $3^\circ \pm$</td>
</tr>
<tr>
<td>Dickite</td>
<td>1.560–1.562</td>
<td>1.566–1.571</td>
<td>0.006–0.009</td>
<td>$+$</td>
<td>52°–80°</td>
<td>$p &lt; v$ weak</td>
<td>$Z = b; X \perp C = +15–20^\circ$</td>
</tr>
<tr>
<td>Naclerite</td>
<td>1.557–1.560</td>
<td>1.563–1.566</td>
<td>0.006</td>
<td>$-$</td>
<td>40°</td>
<td>$p &gt; v$</td>
<td>$Z = b; X \perp (001)$ 10–12°</td>
</tr>
<tr>
<td>Allophane</td>
<td>$n = 1.468–1.512$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X about $\perp (001)$</td>
</tr>
<tr>
<td>Halloysite 4H$_2$O</td>
<td>Mean value: 1.526–1.532</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pleochroic; yellow–brown–green</td>
</tr>
<tr>
<td>Halloysite 2H$_2$O</td>
<td>Mean value: 1.548–1.556</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>1.480–1.500</td>
<td>1.515–1.630</td>
<td>0.025–0.040</td>
<td>$-$</td>
<td>0–$30^\circ \pm$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hectorite</td>
<td>1.485</td>
<td>1.516</td>
<td>0.031</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td>Pleochroic; yellow green</td>
</tr>
<tr>
<td>Saponite</td>
<td>1.480–1.490</td>
<td>1.510–1.525</td>
<td>0.030–0.035</td>
<td>$-$</td>
<td>Moderate</td>
<td></td>
<td>Pleochroic; green–brown–yellow</td>
</tr>
<tr>
<td>Nontronite</td>
<td>1.565–1.600</td>
<td>1.600–1.640</td>
<td>0.035–0.040</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td>Pleochroic; green brown</td>
</tr>
<tr>
<td>Volchonskite</td>
<td>1.551</td>
<td>1.585</td>
<td>0.034</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td>X about $\perp (001)$; pleochroic; green brown</td>
</tr>
<tr>
<td>Saxeconite</td>
<td>1.550–1.575</td>
<td>1.592–1.615</td>
<td>0.035–0.042</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>1.545–1.563</td>
<td>1.57–1.67</td>
<td>0.022–0.055</td>
<td>$-$</td>
<td>$0–20^\circ \pm$</td>
<td>$p &gt; v$</td>
<td>X about $\perp (001)$; some pleochroic Pleochroic; yellow green</td>
</tr>
<tr>
<td>Glauconite</td>
<td>1.545–1.63</td>
<td>1.57–1.66</td>
<td>0.023–0.040</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td>Pleochroic; green–brown–yellow</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>1.59–1.62</td>
<td>1.64–1.67</td>
<td>0.045–0.055</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td>Pleochroic; green brown</td>
</tr>
<tr>
<td>Chlorite</td>
<td>1.57–1.64</td>
<td>1.575–1.645</td>
<td>0.003–0.007</td>
<td>$\pm$</td>
<td>Small</td>
<td></td>
<td>X about $\perp (001)$; pleochroic; green brown</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>1.525–1.56</td>
<td>1.545–1.585</td>
<td>0.020–0.030</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sepiolite</td>
<td>1.490–1.520</td>
<td>1.505–1.530</td>
<td>0.009–0.015</td>
<td>$-$</td>
<td>0–$60^\circ$</td>
<td></td>
<td>Z $\parallel$ elongation</td>
</tr>
<tr>
<td>Attopulcate</td>
<td>1.510–1.520</td>
<td>1.540–1.555</td>
<td>0.025–0.032</td>
<td>$-$</td>
<td>Small</td>
<td></td>
<td>Z $\parallel$ elongation</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>Mean value: 1.50–1.555</td>
<td>0.025–0.035</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
tion reaction, there is a sharp reduction in the mean index from about 1.575 to about 1.525 and probably also a complete loss of birefringence.

HALLOYSITE

Usually only the mean indices of refraction can be determined for the halloysite minerals because of their low degree of crystallinity. As shown
in Fig. 107, the transition from the $4H_2O$ to $2H_2O$ form is accompanied, according to Mehmel\textsuperscript{1} and Correns and Mehmel,\textsuperscript{2} by an increase in index from about 1.532 to almost 1.550. Alexander and colleagues\textsuperscript{3} have computed the theoretical value of the $4H_2O$ form at 1.490, assuming the structure for the mineral suggested by Hendricks\textsuperscript{4} and using the molecular refractivity of kaolinite and water. No indices nearly as low as 1.490 appear to have been reported for the $4H_2O$ form, which may be taken as lack of support for this structural concept of the mineral.

On heating to temperatures above 100°C, halloysite shows a slight gradual increase in index of refraction, until the OH water is driven off at

---


The dehydration of the mineral is accompanied by a sharp reduction in the index of refraction from about 1.560 to 1.535, as shown in Fig. 106.

**MONTMORILLONITE**

The montmorillonite clay minerals show large variations in optical properties as a consequence of substitutions within the lattice. The data in Fig. 108, after Ross and Hendricks, show that an increase in the Fe$_2$O$_3$ content from 0 to 32 per cent is accompanied by an increase in the index from about 1.545 to 1.645 and by an increase in the birefringence from about 0.025 to 0.045. Mehmel has shown that the indices increase as the content of magnesium increases. In the samples of montmorillonite studied by him, the mean index increased from about 1.530 to 1.548 as the MgO content increased from about 2 to 6 per cent.

As shown in Fig. 107, the mean index of refraction increases in the range from about 1.49 to 1.55 as the thickness of the interlayer water decreases. The identities of the exchangeable cations affect the indices indirectly under certain conditions of humidity because of their control of the thickness of the interlayer water. Thus air-dried Na montmorillonite tends to have interlayer water one molecular layer thick, whereas Ca montmorillonite under the same conditions tends to have interlayer water two molecular layers thick. Under such conditions the Ca montmorillonite will have the lower indices. There is no positive evidence that the exchangeable cations themselves directly influence the optical properties, but the data by Marshall on birefringence in an electrical field (see page 290) suggest that such an influence does exist.

Mehmel, as shown in Fig. 106, and Grim and Bradley have independently shown that the mean index of refraction of a montmorillonite rel-

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Relatively low in iron increases from about 1.54 to about 1.570 when all the
interlayer water is eliminated on heating to 250° to 300°C. At higher
temperatures there is no appreciable change in indices until about 450° to
500°C, when the OH lattice water is lost, accompanied by a sharp drop
in mean index to about 1.52. This drop in index is accompanied by a

![Graph showing refractive indices and birefringence of nontronite and saponite.](image)

**Fig. 109.** Effect of heating on the refractive indices and birefringence of nontronite
and saponite, after Caldwell and Marshall.

reduction in birefringence. Caldwell and Marshall present data for sap-
onite (Fig. 109) showing somewhat the same effect of heating, except that
the decrease in indices accompanying the loss of OH water is more grad-
ual. These investigators show also that at higher temperatures, above
that at which the hydroxyl water is lost, there is an increase in indices and
birefringence. A sample of nontronite investigated by Caldwell and
Marshall showed (Fig. 109) a gradual increase in indices on heating to
about 850°C, with only a slight flattening of the curve accompanying loss
of OH water. These authors also show that the birefringence of non-
tronite increases as the mineral is dehydrated, up to about 700°C. At
temperatures above 700°C, the birefringence decreases moderately.

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*Caldwell, O. G., and C. E. Marshall, A Study of Some Physical and Chemical
Univ. Missouri Research Bull. 354 (1942).*
ILLITE

The exact variations of the optical properties of the illites accompanying substitutions within the lattice are not known, but they are probably of the same order of magnitude as those for the montmorillonite minerals. The illites with the muscovite type of structure have somewhat lower indices of refraction and lower birefringence than muscovite itself, and the same relation apparently holds for the illites with the biotite type of structure. Thus, in the case of illite with the muscovite structure, the $\gamma$ value is frequently of the order of 1.570 to 1.580, as compared to 1.595 for muscovite itself. For biotite-type illite the $\gamma$ value is frequently 1.62 to 1.63, as compared to 1.64 to 1.66 for biotite. This difference must result, at least in part, from the lesser population of interlayer cations and from the presence of some water molecules between the silicate layers of the illites. It probably also is somewhat dependent on the crystallinity of the clay minerals, i.e., on defects in the stacking of the silicate layers and on some variations in the population of the silicate units.

Grim and Bradley $^7$ have shown (Fig. 110) that on heating there is frequently a slight increase in indices at very low temperatures (200°C); e.g., the $\gamma$ value increases from about 1.575 to 1.585. Above about 200°C there is little change until about 400°C, when there is a drop in indices accompanying the loss of OH water. At this temperature the $\gamma$ index decreases from about 1.585 to 1.560. At still higher temperatures, there is a further decrease in the $\gamma$ index, and the birefringence also decreases.

CHLORITE

There is substantially no information available in the literature on the optical properties of the chlorite clay minerals. Unpublished data...
obtained by the author indicate that the chlorite clay minerals have somewhat lower indices of refraction than the well-crystallized chlorite minerals, and that the difference is of about the same order of magnitude as that for the illites as compared to muscovite and biotite. There are no experimental data on the changes in optical properties on heating the chlorite clay minerals, but it is probable, by analogy with the illite minerals, that they would show an increase in indices accompanying any loss of adsorbed water and a decrease in indices at higher temperatures, accompanying the loss of hydroxyl water.

VERMICULITE

There are no precise data available on the optical properties of the vermiculite clay minerals. However, they probably have substantially the same optical characteristics as those of coarse grain vermiculite. Because of the structural similarity of vermiculite and montmorillonite, it would be expected that the optical properties of vermiculite would vary with the degree of hydration and with substitutions within the lattice in a similar manner to that discussed for the montmorillonite clay minerals. Also, it would be expected that heating vermiculite would cause changes in optical characteristics similar to those found for the montmorillonites.

SEPIOLITE-ATTAPULGITE-PALYGORSKITE

The optical properties of only a few specimens of these clay minerals have been measured, so that the possible variations are not definitely known. It appears probable that the $\gamma$ index varies from about 1.50 to 1.555 and that the birefringence varies from about 0.01 to 0.035. According to Von Englehardt, the indices increase in the palygorskites as the magnesium content increases. The similarity between the indices and birefringence of some of these clay minerals and those of the montmorillonites is noteworthy and has led sometimes to their erroneous identification as montmorillonites.

Caillere has stated that the indices of sepiolite increase from a mean value of 1.49 to 1.54 when the mineral is dehydrated above about 465°C. At still higher temperatures the mean index increases further to about 1.61 on calcination.

Caldwell and Marshall showed that attapulgite behaves differently.
from the other clay minerals on heating (Fig. 111). It shows an increase in indices up to about 100°C, the \( \gamma \) value increasing from 1.52 to 1.55; there follows a decrease to about 200°C, \( \gamma \) decreasing to 1.53. Above 200°C there is a slight gradual increase up to about 850°C, with \( \gamma \) attaining a value of about 1.56.

![Graph](image)

**Fig. 111.** Effect of heating on the refractive indices and birefringence of attapulgite, after Caldwell and Marshall.

**INFLUENCE OF IMMERSION MEDIA ON OPTICAL PROPERTIES**

Larsen and Wherry\(^{11}\) in 1917 found that the indices of refraction of a clay material from Beidell, Colorado, now known to contain a montmorillonite mineral, increased gradually when the material was immersed in a mixture of cinnamon oil and oil of clove. This appears to be the first mention in the literature of variations in the optical properties of the clay minerals resulting from the media in which they are immersed. Correns and Mehmel\(^{8}\) showed that the indices of montmorillonite and halloysite (4H\(_2\)O) varied in different liquids. In general, the indices of the mineral increased with time over a period of about 2 hr, and it is now known that much longer time, perhaps several days, would be necessary for equilibrium to be reached. In the case of montmorillonite, changes in optical values were noted for both air-dried samples and material dried at 105°C. Correns and Mehmel believed that the effect was due to the penetration of the organic molecules between the silicate layers and thought that no effect would be produced by organic molecules too big for such penetration.

Van Baren\(^{12}\) investigated the influence of a variety of organic liquids on the indices of refraction of kaolinite, halloysite (2H\(_2\)O), and montmorillonite (Table 35). He found no changes in the indices of kaolinite or halloysite (2H\(_2\)O) but significant increases for montmorillonite for some immersion liquids. It is probable that under somewhat different conditions and perhaps with different liquids, halloysite material with only

---


Optical Properties

TABLE 35. INDEX OF REFRACTION IN RELATION TO IMMERSION LIQUID
(After Van Baren\textsuperscript{12})

<table>
<thead>
<tr>
<th>Liquid and index of liquid</th>
<th>Kaolinite</th>
<th>Halloysite</th>
<th>Nontronite</th>
<th>Montmorillonite (HCl treated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean index of mineral</td>
<td>1.57</td>
<td>1.575</td>
<td>1.565</td>
<td>1.50</td>
</tr>
<tr>
<td>Chlorobenzene, 1.524</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Ethylenebromide and chlorobenzene, 1.535</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Benzylicloride, 15.41</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Benzyllamine, 1.546</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>o-Nitrotoluene, 1.547</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Nitrobenzene, 1.552</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Monobromobenzene, 1.560</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Xyldine, 1.560</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>o-Anisol, 1.562</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>o-Toluidine, 1.572</td>
<td>=</td>
<td>+</td>
<td>x</td>
<td>+</td>
</tr>
<tr>
<td>Anisidine, 1.576</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>x</td>
</tr>
<tr>
<td>Aniline, 1.585</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Bromoform, 1.596</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iodobenzene and bromobenzene, 1.605</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iodobenzene and bromobenzene, 1.616</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chinolone, 1.624</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>x</td>
</tr>
<tr>
<td>α-Tetrahydro-ar-naphthylamine, 1.631</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>?</td>
</tr>
</tbody>
</table>

+ = index of mineral higher than liquid  
− = index of mineral lower than liquid  
= = index of mineral and liquid the same  
x = index of mineral increased but not to a value higher than liquid

slightly more than 2H\textsubscript{2}O would show some variation in optical properties. Van Baren concluded that organic molecules with NH\textsubscript{2} radicals are most likely to cause significant variations in optical characteristics and that the time necessary for the liquid to obtain its maximum influence increased as the size of the organic molecule increased. He showed further that the indices of a montmorillonite, when immersed in a liquid of higher index than the highest index of the mineral, sometimes increase to even higher values than that of the liquid itself. That is, the indices of the mineral may not only increase to equal that of the liquid but may become higher than that of the liquid. Thus a montmorillonite with a mean index of 1.50 increased to a value above that of benzylamine (1.546) when immersed in this liquid.

Vendel\textsuperscript{13} has recently studied in detail the characteristics which are


likely to be found in liquids causing a variation in indices of the clay minerals. According to him, a liquid should have the following properties to permit a determination of the true optical values of the clay minerals:

1. The liquid must not chemically attack the clay mineral.
2. It must not be soluble in water, and water must not be soluble in it; otherwise a change in hydration state might develop with an attendant change in optical values.
3. It must not enter into any ion-exchange reaction with the clay.
4. It must not permit the dissociation of any of the adsorbed ions of the clay.
5. It must be nonpolar.
6. Its index must be approximately that of the mineral.
7. If a mixture is used, the components must be completely miscible and must have nearly the same boiling point.
8. The liquids should be well-defined compounds.

Montmorillonite, halloysite, and possibly vermiculite to a limited extent (see Chap. 10) have the property of adsorbing certain organic molecules on their basal plane surfaces. The types of organic molecules adsorbed are also those which influence the optical properties. The variation in optical properties is, therefore, undoubtedly largely a consequence of this adsorption. The optical properties of these minerals could also be altered by certain liquids as a consequence of an effect on the extent of interlayer hydration water. Illite, kaolinite, and chlorite minerals would be expected to show no variation with different immersion liquids, because of their very low adsorptive power for organic molecules and because of their lack of interlayer water. For the same reasons the attapulgite-sepiolite minerals also should show no effect from immersion liquids except in the rare cases when an organic molecule is of the correct size and shape to enter the channels of their structure.

This attribute of the clay minerals requires that the index liquids used in their study must be carefully chosen, and, in general, when values are published, the liquids in which they were determined should be recorded. Obviously, the influence of immersion liquids on certain clay minerals and not on others can be of diagnostic value in the identification of the clay minerals.

**ORIENTED-AGGREGATE TECHNIQUE**

When the flake-shaped clay-mineral particles settle from a deflocculated clay-water-suspension on a horizontal surface, they tend to come to rest with one flake on top of another so that their basal plane surfaces are substantially parallel. Frequently successive flakes assume positions in which there is a considerable degree of parallelism of the \( a \) and \( b \) crystallographic axes. In other words, an aggregate orientation closely approxi-
imating crystal growth may take place in the accumulation of such mate­
rial under the foregoing conditions.

Grim in 1934 described a technique taking advantage of the above
phenomenon for the preparation of oriented aggregates for the determi­
ation of the optical properties of the clay minerals. In this technique, a
clay-water suspension is allowed to stand until some of the clay mineral
has accumulated on a flat surface, either the bottom of a vessel or a glass
plate hung in a horizontal position in the suspension. The flat surface
with the accumulated clay is then removed from the suspension and dried.
Aggregate particles are sliced or cut from the dried film of clay for mount­
ing in index-of-refraction liquids.

The $\alpha$ and $\gamma$ indices and the birefringence of such aggregates can usually
be determined with considerable accuracy. Frequently the aggregates
yield reasonably good interference figures, from which the sign of the
mineral and the order of magnitude of $2V$ can be determined. Measure­
ment of the latter value implies considerable orientation parallel to the
$a$ and $b$ crystallographic axes.

Without the use of oriented aggregates, it is often possible to determine
only a mean index of refraction from the more or less randomly oriented
clay-mineral particles in the crude clay. The birefringence and other
optical values frequently cannot be even approximated in the crude clay.

INTERLAYER MIXTURES

It has been pointed out (see pages 79–80) that clay materials may be
composed of several clay minerals mixed primarily by interstratification
on substantially unit-cell dimensions. Such materials may be composed
of aggregates made up of alternations of one or a few unit layers of the
component clay minerals. Also in some clay materials the clay-mineral
units are interlayered with ferric hydroxide units.

Optical data from such intimate interlayered mixtures can easily be
mistaken for that of a single mineral. Thus, Grim and Rowland showed
that a sample from Namiquipa, Mexico, previously described as beidellite
on the basis of optical values, was actually a mixture of halloysite and
limonite. X-ray and differential thermal data left no doubt regarding
this interpretation, whereas the optical values were suggestive of a single
clay mineral of the montmorillonite type.

An example such as that above emphasizes the fact that clay-mineral
determinations based solely on optical data must be made with great

14 Grim, R. E., The Petrographic Study of Clay Minerals—A Laboratory Note, J.
caution to avoid gross errors. Frequently the character of the interference figure reveals whether a clay-mineral aggregate is made up of a single mineral or a mixture. If the interference figure is not good and the isogyres are not reasonably complete, there is probably more than one mineral present. Homogeneity and parallelism in the a and b directions are required for fairly complete figures of the layered clay minerals.

**ORIENTATION IN AN ELECTRICAL FIELD**

Marshall has studied in considerable detail the tendency of clay-mineral particles to orient themselves in an electrical field, and the following statements are taken largely from his publications.

Freundlich, Kruyt, and their coworkers showed that extremely non-equidimensional particles, such as needle-shaped particles, are oriented in a water suspension in an electrical field relative to the electrical lines of force. Procopiu showed that the prime cause of orientation in suspensions of various minerals was the electrical anisotropy of the particles themselves, rather than hydrodynamic effects. Thus, irrespective of the shape of the particles or the hydrodynamic conditions of flow, a turning moment operates when an electric field is applied, until the direction of greatest dielectric constant becomes parallel to the lines of force.

Marshall has measured the birefringence developed in suspensions of various clays when subjected to an electrical field, and some typical results for fractions of a soil listed as beidellite, containing a large proportion of montmorillonite, are given in Table 36. It can be seen from the data in Table 36 that the electrical birefringence is affected by the exchangeable cation. No such variation was found for kaolinite, which is evidence, as Marshall pointed out, for the exterior position of the exchange cations in kaolinite and their internal position in montmorillonite.

Marshall found that dilute suspensions of lithium and sodium montmorillonites sometimes gave a negative instead of a positive birefringence. Recently Muller and Norton have found that, at low frequencies, negative values exist for montmorillonite suspensions and, for high fre-

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Optical Properties

Optical properties of a sediment, the values are positive. The lower the concentration of the clay, the lower the range of frequencies for which negative values were observed. These authors conclude that the negative values are due to the presence of long-range interparticle forces, the positive ones being normal for an orientation like that of the Kerr effect (see Marshall).

Whiteside and Marshall have shown that, at 4,000 volts/cm with 60-cycle a-c current, the saturation values for Na and K clays can be obtained, and, for the Putnam material (beidellite), the Na and K clays are very significantly lower in birefringence than the hydrogen clay. Their data indicate that the optical and electrical ellipsoids are similar in character.

**Table 36. Electrical Birefringence of Putnam (Beidellite) Clay Fractions**

<table>
<thead>
<tr>
<th>Exchange Cations</th>
<th>Birefringence at 800 volts/cm, 60 cycles a-c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500-200 μm</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.023</td>
</tr>
<tr>
<td>Ca⁺⁺</td>
<td>0.026</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.023</td>
</tr>
</tbody>
</table>

**Form Birefringence**

Wiener showed that birefringence ("form birefringence") may arise in a system in which there is a parallel arrangement of plate- or rod-shaped particles when these particles are separated by a medium of different refractive index. There is no form birefringence when the solid and the liquid have the same index of refraction. The birefringence increases as the difference between the indices of the liquid and solid increases. Wiener developed his concepts for isotropic particles, but Ambronn and Frey, who have studied this phenomenon in great detail, have shown that the effect can be superimposed on systems which contain birefringent components. Thus, the inherent birefringence of the clay-mineral particles would augment the form birefringence developed in suspensions.

In the case of the clay minerals, form birefringence would arise primarily because of the penetration of water or an organic liquid between

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the unit layers of the expanding clay minerals. Thus, under the usual conditions for the measurement of optical properties, it might be significant for montmorillonite, vermiculite, and halloysite but probably not for the other clay minerals. Where the ratio of volume of liquid to solid is small, the effect would be small, but when considerable fluid has been adsorbed between layers, it might be significant. Undoubtedly part of the variation of the optical characteristics of montmorillonite and halloysite minerals reported in the literature is due to form birefringence.

Obviously the phenomenon of form birefringence must be kept in mind in any optical study of fine-grained particles in a liquid medium. Unfortunately this has not always been the case.

DISCUSSION OF THE APPLICATION OF OPTICAL METHODS IN CLAY-MINERAL STUDIES

The value of optical methods in studying the clay minerals has been the subject of much discussion. Some students of clays assert that optical methods are worthless for such fine-grained materials, whereas others plead for their universal use and base detailed clay-mineral determinations solely on optical studies. In the writer's opinion, optical methods are very frequently of value, but they must be used with caution, and it must be realized that they are worthless for some types of materials. An optical examination can be made in a very short time, and the chance of obtaining valuable data usually justifies the expenditure of the required time. Also, after some experience has been gained in the study of clay minerals under the microscope, more can be done with them than would be supposed at first. It is usually possible to determine with fair accuracy at least the indices of refraction and the birefringence of clay-mineral samples. The optical properties of the various clay minerals are sufficiently diverse so that an idea of the identity of the clay minerals usually can be gained from such data. As noted previously (page 289), caution must be used because of anomalous results possible from interlayer mixtures.

Certain of the clay minerals frequently have distinctive appearances under the microscope which aid in their identification. Thus, aggregates of the montmorillonite clay minerals often appear as a large single crystal that has been strained. The individual particles of montmorillonite either cannot be seen or else are indistinct and tend to merge into each other. The attapulgite-sepiolite minerals sometimes have a somewhat similar appearance. Aggregates of the other clay minerals have the appearance of being made up of discrete particles, even though the individual particles are less than 1 micron in diameter, and the particles have a high degree of uniform orientation. With a little experience one can
usually recognize relatively pure montmorillonite quite easily under the microscope by its appearance without reference to optical values.

The presence of nonclay minerals, such as quartz, calcite, and feldspar, may cause considerable difficulty if these minerals are present in particles of about the same size as the clay minerals. An abundance of extremely fine quartz or calcite makes optical methods valueless in many cases. Sometimes the presence of such nonclay minerals will produce an unusual appearance or strange optical characteristics which suggest that some such material might be present. However, in many cases, the nonclay material would go undetected by optical methods.

The presence of even relatively small amounts of extremely fine-grained carbonates makes optical study of the clay minerals impossible, because of the high birefringence of these nonclay minerals. Further, it is not possible to remove the carbonates in all cases by dissolving them, because of the susceptibility of some of the clay minerals to acid attack. Certain of the clay minerals (see pages 296-298) are relatively insoluble in acid, but others are quite soluble. Unfortunately many calcareous materials also contain the more soluble clay minerals (see page 359), so that in a study of such material it is necessary to determine the clay-mineral composition by nonoptical methods.

Organic material and ferric iron compounds may mask the optical characteristics of the clay minerals. The organic material can frequently be removed by solvents or by mild oxidants, such as hydrogen peroxide, without altering the clay minerals. Some organic material, particularly that in the older sediments, is not affected by such reagents and can be removed only by vigorous oxidizing agents or by heating to elevated temperatures. Unfortunately, if there is iron present, it may be oxidized in the process, so that it may then conceal the characteristics of the clay minerals.

Sometimes the free iron compounds can be removed by reducing, e.g., by hydrogen sulfide, and then dissolving the ferrous iron. Again caution must be used because of the danger of attack on the clay minerals, particularly those of the montmorillonite and attapulgite-palygorskite groups, by the reducing agents.

Optical methods, of course, are of great value in determining the nonclay minerals present in a clay material. In general, minerals found in particles as small as 5 microns in diameter can be identified. If the mineral has particularly distinctive optical properties, considerably finer particles can be identified. Thus with a little experience carbonates can be spotted in particles at least as small as 1 micron. Quantitative determinations of such nonclay minerals are, however, very difficult for particles smaller than about 5 microns.

The petrographic microscope is, of course, useful in studying the texture
of clays as revealed by thin sections. Examples are the shards which are characteristic of many bentonites and the parallel orientation of the clay minerals in many shales. The textures of clay materials are not included in the objective of this text and will not be considered. The identification of the clay minerals in thin sections is usually difficult and often impossible. Optical methods of identification can be applied best by the use of immersion techniques and prepared, oriented aggregates.

ADDITIONAL REFERENCES


CHAPTER 12

Miscellaneous Properties

SOLUBILITY OF THE CLAY MINERALS

General Statement. The solubility of the clay minerals in acids and alkalies is important fundamentally because it reveals certain attributes of the clay minerals and certain differences between them which are not obvious from other methods of study. From a practical standpoint, solubility characteristics are important in determining the utility of various clay materials as sources of metallic aluminum and for the manufacture of alum. Such data are also of practical value in numerous other ways, e.g., in the bonding of refractories by acid media and in the fixation of certain materials such as phosphates in soils. The solubility characteristics of the clay minerals are important in determining the limitations of acid treatment and electrodialysis as auxiliary tools in the analyses of complex clay materials containing carbonate, and in determining their ion-exchange capacity.

Nutting,¹ who has studied the solubility of the clay minerals in great detail, arrived at the following general conclusions:

The solubility of a number of clays in acids and alkalies of a wide range of concentrations indicates that the solution process is of at least three kinds for every clay, dependent on the concentration of solvent.

At equilibrium, a fraction of the acid or alkali remains free, and a fraction of each clay remains undissolved regardless of the proportions present. Hence the reactions appear to be reversible as indicated by varying equilibrium conditions.

Over a range of low acid concentrations, 0.05 to 0.2 normal, the "solution" is essentially a silicate hydrosol similar in composition to the clay dissolved. At higher concentrations it contains also salts in solution; at lower concentrations excess silica. At acid concentrations of 20 per cent and over, bases but no silica go into solution and no hydrosols are formed.

Over a range of low alkali concentrations, 0.002 to 0.005 normal (0.02 to 0.05 per cent) sodium carbonate, the solution essentially is an alkali silicate hydrosol, only silica being removed from the clay. At concentrations of alkali below the critical range, no carbonate is left in solution.

With montmorillonite clays the critical anion concentration is around 0.1 mole

per liter while the critical cation ($\text{Na}^+$) concentration is around 0.001 mole per liter. Within the critical acid range, the anions may be considered as competing on substantially equal terms with silicic acid for the bases of the clay. Within the critical alkali range, the alkali in solution is competing on equal terms with the bases of the clay for the silica.

In general, above certain minimum concentrations, acids remove alkali metals, alkaline earths, iron, and aluminum from the clay minerals, and alkalies dissolve the silica. The literature contains a large amount of information on acid solubility, because of the general economic importance of the acid-clay reaction, as noted previously, but relatively little data on solubility in alkalies.

**Solubility of Clay Minerals in Acid.** The solubility of the clay minerals in acids varies with the nature of the acid, the acid concentration, the acid-to-clay ratio, the temperature, and the duration of treatment. Also the solubility of the various clay-mineral groups is quite different, and there is great variation in solubility characteristics of members of some individual groups. Thus, in general, a magnesium-rich montmorillonite is much more soluble than one that is rich in aluminum, with an iron-rich member somewhere in between. In the case of the clay minerals showing variations in the degree of crystallinity, such as kaolinite, the solubility increases as the degree of crystallinity decreases. The solubility would, of course, also increase as the particle size decreases. Calcining the clay minerals changes their solubility characteristics and their relative solubility with respect to each other.

Pask and Davies\(^2\) (Table 37) have shown, using 0.5 g of clay dried at 130°C in 30 cc of 20 per cent solution of $\text{H}_2\text{SO}_4$, and boiling for $\frac{1}{2}$ hr, that only 3 per cent of the total alumina is dissolved from kaolinite and only 9 per cent from anauxite. Halloysite is moderately soluble, showing solution of from 50 to 90 per cent of the total alumina under similar conditions. Illite is slightly soluble, with 11 per cent of total alumina going into solution in one sample. Montmorillonite ranges from low to high solubility, showing 33 to 87 per cent of total alumina dissolved. The attapulgite-sepiolite clay minerals would probably have characteristics similar to those of the montmorillonite minerals.

With acid of the same concentration and a similar acid-to-clay ratio, but with digestion under pressure at 155°C, the solubility of all the clay minerals increased (Table 37). All the alumina of halloysite became soluble, and almost all of it was dissolved from the montmorillonites (85 to 93 per cent). Even the ordinarily relatively insoluble kaolinite and illite lost the major part of their alumina, 70 and 87 per cent, respectively, going into solution.

### Table 37. Extraction of Alumina from Various Clay Minerals with Sulfuric Acid

(From Pask and Davies)

<table>
<thead>
<tr>
<th>Clay mineral</th>
<th>Aluminum extracted, per cent total aluminum present</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clay dried at 130°C*</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>3</td>
</tr>
<tr>
<td>Anauxite</td>
<td>9</td>
</tr>
<tr>
<td>Halloysite</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>90</td>
</tr>
<tr>
<td>Illite</td>
<td>78</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>33</td>
</tr>
<tr>
<td>Muscovite</td>
<td>17</td>
</tr>
</tbody>
</table>

* Determinations made after boiling 0.5 g of sample in 35 cc of 20 per cent solution of sulfuric acid for 1 hr.
† Clay dried at 130°C, then digestion of 0.5-g sample in 35 cc of 20 per cent solution of sulfuric acid for one hour.

Under similar conditions of extraction, but after calcining the clay minerals to 800°C, all or substantially all the alumina of the kaolinite, anauxite, and halloysite is soluble, whereas the solubility of the alumina in the illite is increased only moderately, and for the montmorillonites it actually decreases (Table 37). The explanation resides in the fact that the kaolinite and halloysite lattices are probably destroyed or at least considerably disrupted at this temperature, and no new high-temperature phases have yet formed. In the case of illites and montmorillonites the lattice has been changed slightly but not destroyed; hence the solubility of the alumina has been changed, but not so that it can be completely removed. When kaolinite is heated to still higher temperatures (975°C), new crystalline phases develop, and the solubility of the alumina decreases. Similarly, when the other clay minerals are heated to near this temperature (975°C), new high-temperature phases form, which would affect the solubility in acid. In the case of some clay minerals, such as the montmorillonites, the high-temperature phase forming (see page 225) varies considerably with substitutions in the original montmorillonite lattice, and correlative variations in solubility in acid would be expected.

A comparison of the data obtained by Thiebaut with those of Pask

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and Davies\textsuperscript{2} show the great variation in results obtained under different treatment conditions. Using 50 per cent hydrochloric acid, a treating temperature of 80° to 85°C, a treating time of 2 hr, and clay dried at 105° to 108°C, Thiebaut found that the solubility of biotite was 100 per cent, muscovite 5 to 32 per cent, kaolinite 10 per cent, halloysite 6 to 15 per cent, and montmorillonite 62 per cent, based on cation solubility. Using sulfuric acid of similar concentration and the same minerals but evaporating to dryness, Thiebaut found that the solubility of all the above minerals was complete, again based on their cation solubility. The work of Thiebaut\textsuperscript{3} indicates the generality that the clay minerals are more soluble in sulfuric than in hydrochloric acid, and also that for hydrochloric acid, both kaolinite and halloysite are less soluble than the three-layer clay minerals. Biotite occupies an anomalous position in being about equally soluble in both acids.

The solubility of the clay minerals in other acids is not well known. However, investigations of anion exchange indicate that the solubility is likely to be considerable, especially for the acids with an anion having a size and geometry approximating that of the component parts of the clay-mineral lattice. As a consequence, some relatively weak acids may strongly attack certain clay minerals. Murray\textsuperscript{4} has shown, for example, that phosphoric acid attacks the kaolinite lattice under some conditions with greater vigor than sulfuric acid.

Wolf\textsuperscript{5} has presented interesting data showing the effect of concentration of acid on solubility. Using 10 g of Zettlitz kaolinite and cooking for 2 hr, he found that 0.02 N HCl dissolved 3.1 mg of Al\textsubscript{2}O\textsubscript{3} in 100 cc of acid; that in similar amounts of acid 0.5 N HCl dissolved 53.5 mg of Al\textsubscript{2}O\textsubscript{3}; and that 5 N HCl dissolved 124.4 mg of Al\textsubscript{2}O\textsubscript{3}.

**Nature of the Acid Reaction.** In the attack of acid on the montmorillonite clay minerals and probably also on the illite and sepiolite-attapulgite clay minerals, it appears that the alkalies and alkaline earths are removed relatively more rapidly than the aluminum or iron, and that the iron is removed more rapidly than the aluminum. Hofmann and Endell,\textsuperscript{6} Glaeser,\textsuperscript{7} and Mering\textsuperscript{8} have shown that 75 to 85 per cent of the total alumina must be removed from the montmorillonite lattice before it is completely destroyed. Acid attack begins around the edges of the

\textsuperscript{7} Glaeser, R., Effect of Acid Treatment on the Base-Exchange Capacity of Montmorillonite, *Compt. rend.*, 222, 1241–1242 (1946).
Miscellaneous Properties

particles and works inward. In relatively dilute alkaline solutions, the solubility of the silica residue of the structure left around the edges of the particles is increased as a consequence of the attack by acids.

In the case of aluminum it appears that its removal is stepwise; i.e., it moves first from octahedral positions to exchange positions and then to complete solubility. If the sample is dried before all the aluminum is removed, at least some of it appears to move back from exchange positions to octahedral positions.

Brindley and Youell have recently presented data for a chlorite (pen-ninite) indicating that the aluminum in octahedral coordination is more soluble in HCl than the aluminum in tetrahedral coordination. These authors do not suggest that relative solubility can be used as a method for the general determination of octahedral versus tetrahedral aluminum in the clay minerals.

Murray has shown that under similar conditions of treatment the actual sulfate or phosphate compound resulting from treatment with sulfuric and phosphoric acid, respectively, is almost the same for all kaolinites and halloysite, regardless of variations in degree of crystallinity. There were, however, some differences which suggested to him that the structural attributes of the parent clay mineral did exert some influence on the nature of the resulting reaction product.

**Decomposition by Electrodialysis.** Numerous investigators have indicated that electrodialysis of certain of the clay minerals may cause their decomposition. Thus Kelley has shown that, as the cations are replaced by H+, aluminum moves from octahedral positions to exchange positions, and Hofmann and Giese have shown that, in general, unexchangeable cations are lost from within the lattice before all the exchangeable cations are replaced by H+.

The amount of loss of unexchangeable cations during electrodialysis varies with the clay mineral. Magnesium-rich montmorillonite minerals seem to be most susceptible, and Nutting has shown that all the magnesium can be removed from hectorite by electrodialysis with complete breakdown of the structure. Caldwell and Marshall have shown that

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the same results are obtained with saponite. Other montmorillonites are quite susceptible to such alteration, but less so than saponite and hectorite. The iron-rich montmorillonites are more susceptible than those high in aluminum.

Attapulgite-sepiolite, vermiculite, chlorite, and some of the biotite micas are quite susceptible to disintegration by electrodialysis. Roy\textsuperscript{14} has shown that biotite suffers appreciable loss of cations after only a few hours of electrodialysis and that 80 to 90 per cent of all of them are lost at the end of 28 days, without, however, complete destruction of the biotite structure. After a similar length of time, muscovite and phlogopite micas lost only a small amount of their iron and alkalies and substantially no aluminum. It appears that kaolinite is relatively little affected by electrodialysis, and data are not at hand for halloysite.

Electrodialysis has frequently been used to prepare H clays for cation-exchange studies and for use as the starting point for investigations of the physical properties of clays carrying specific exchangeable cations. Because of the likelihood of significant amounts of disintegration of the clay mineral, the procedure must be used with caution. Many of the investigations which have used this procedure are of little value, because the clay minerals were altered, and the cation composition was not what it was thought to be, as a result of very difficultly replaceable aluminum moving from the lattice to exchange positions.

**Cation Liberation by Neutral Salts.** Mukherjee and his colleagues\textsuperscript{15,16} have shown that Al\textsuperscript{3+} and Fe\textsuperscript{3+} may be removed from certain hydrogen clays by repeated treatment with BaCl\textsubscript{2}. They determined the amount of H\textsuperscript{+}, Al\textsuperscript{3+}, and Fe\textsuperscript{3+} in the leachate after leaching the clay minerals with BaCl\textsubscript{2}. The clay minerals had been rendered acid by prior treatment with 0.02 N HCl. After each leaching with BaCl\textsubscript{2}, the clay minerals were rendered acid again before repeated leaching with BaCl\textsubscript{2}. These investigators found that some Al\textsuperscript{3+} and Fe\textsuperscript{3+} continued to come out of the lattice of montmorillonite through at least eight cycles of acid treatment and leaching, whereas for kaolinite there was little effect after the first leaching. The removal of the Al\textsuperscript{3+} and Fe\textsuperscript{3+} from the montmorillonite was accompanied by a reduction in cation-exchange capacity, whereas the capacity of kaolinite was substantially unaffected. The work of Mukherjee shows the extreme sensitivity of some of the clay minerals to chemical treatment.


\textsuperscript{15} Mukherjee, J. N., B. Chatterjee, and B. N. Baeverjee, Liberation of H\textsuperscript{+}, Al\textsuperscript{3+} and Fe\textsuperscript{3+} from Hydrogen Clay by Neutral Salts, *J. Colloid Sci.*, 2, 247–256 (1947).

\textsuperscript{16} Mukherjee, J. N., B. Chatterjee, and A. Roy, Liberation of H\textsuperscript{+}, Al\textsuperscript{3+} and Fe\textsuperscript{3+} from Pure Clay Minerals on Repeated Soil Treatment and Desaturation, *J. Colloid Sci.*, 3, 437–446 (1948).
Rational Analysis. It is frequently desirable, particularly in the industrial use of clays, as in the ceramic industry, to have some rapid, simple method of determining variations in the composition and properties of clays. Before the development of X-ray-diffraction, differential thermal, and improved optical methods about 1930, the only methods available were chemical procedures based on the difference in the resistance of various clay substances to chemical attack. There developed, therefore, so-called “rational methods of analysis” based primarily on the difference in solubility of various clay substances in acids. Such methods were widely used, e.g., in the ceramic industry, for raw-material control.

Most methods of rational analysis were based on the difference in solubility of clay components in hot concentrated hydrochloric and sulfuric acids. The part of a clay soluble in hydrochloric acid was frequently called allophanet, or allophane clay, and the part insoluble in hydrochloric but soluble in sulfuric acid was called kaolint, or kaolin clay. The allophanet often was largely the montmorillonite portion of a clay, together with other components soluble because of extremely fine grain size. The kaolint was likely to include primarily the kaolinite and illite components. Frequently the method was elaborated to obtain some determination or estimation of the potash content as a basis for an evaluation of a possible mica component. Also in some instances a value for silica was obtained to indicate the quartz content. The wide variations in the methods of rational analysis that have been used are summarized by Harkort and Harkort.17

Washington18 and later Correns19 have pointed out the great fallibility of rational analytical procedures because of the tremendous range in solubility of the components of clays as a consequence of particle-size variations. Since about 1930, with the development of other analytical methods, the use of rational analysis has gradually decreased. It should be pointed out, however, that such methods may be quite satisfactory for a specific limited purpose if used with caution and only for a limited range of clays. Thus an industry using only a particular kind of clay can set up an arbitrary set of chemical tests, which would be rapid and simple, to check certain variations in the material supplied to them.

Solubility of Clay Minerals in Alkalies. Except for the investigations of Nutting,1 there has been very little study of the solubility of the clay minerals in alkalies. Nutting has studied particularly the solubility of

montmorillonite and attapulgite in dilute solutions of sodium carbonate. His results for montmorillonite, given in Table 38 and Fig. 112, show that

**Table 38. Silica Dissolved from Montmorillonite (Wyoming Bentonite) by Solutions Containing Sodium Carbonate**

(After Nutting)

<table>
<thead>
<tr>
<th>Per cent Na₂CO₃</th>
<th>0.0</th>
<th>0.005</th>
<th>0.01</th>
<th>0.02</th>
<th>0.05</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ in solution, g/liter*</td>
<td>0.064</td>
<td>0.067</td>
<td>0.132</td>
<td>0.178</td>
<td>0.133</td>
<td>0.260</td>
<td>0.307</td>
<td>0.508</td>
<td>0.700</td>
</tr>
</tbody>
</table>

* After digestion of 48 g of clay in 2-liter solutions for 48 hr at 90°C.

for this clay mineral the amount of silica removed in solution increases as the concentration of sodium carbonate increases to a maximum at about 0.8 per cent sodium carbonate concentration. At higher concentrations, the solubility decreases to a minimum at about 0.05 per cent sodium carbonate and then rises steadily to 0.70 g/liter at 1 per cent sodium carbonate concentration. According to Nutting, only silica is dissolved by the alkali up to a concentration of 0.05 per cent sodium carbonate. He points out that an extremely dilute solution of alkali is very effective in removing silica from montmorillonites and, given enough time, probably could remove all of it.

Additional data for the removal of silica from montmorillonite by sodium carbonate are given in Table 39, together with comparable data for attapulgite. The results for the two clay minerals are much the same, except that the relative amount of silica dissolved is lower for the attapulgite.
Miscellaneous Properties

Table 39. Milligrams of Silica Dissolved from 1 G of Clay in Various Amounts of Water Containing 1 G of Sodium Carbonate
(After Nutting!)

<table>
<thead>
<tr>
<th>Water, liters</th>
<th>Montmorillonite (Wyoming bentonite)</th>
<th>Attapulgite (Quincy, Florida)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>169</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>481</td>
<td>253</td>
</tr>
<tr>
<td>2</td>
<td>215</td>
<td>192</td>
</tr>
<tr>
<td>1</td>
<td>104</td>
<td>79</td>
</tr>
<tr>
<td>0.5</td>
<td>70</td>
<td>87</td>
</tr>
<tr>
<td>0.2</td>
<td>86</td>
<td>50</td>
</tr>
<tr>
<td>0.1</td>
<td>100</td>
<td>59</td>
</tr>
</tbody>
</table>

INFRARED SPECTRA OF THE CLAY MINERALS

General Statement. Atoms which are grouped together in molecules do not remain at rest but are continuously in vibration. Such vibrations produce periodic displacement of atoms with respect to one another, causing a simultaneous change in interatomic distances. The frequencies of the vibrations fall within the range of $10^{13}$ to $10^{14}$ cycles per second, which is of the same order of magnitude as the frequencies of infrared radiations. Vibrations which are accompanied by a change in dipole moment give rise to the absorption of radiations in the infrared region of the electromagnetic spectrum. Several modes of vibration may occur for a particular atomic group, each at a characteristic frequency and normally independent of other modes.

If molecules of a substance whose vibrations are accompanied by a change of dipole moment are irradiated by a succession of monochromatic bands of infrared, those radiated frequencies which correspond to the intramolecular vibrational frequencies may be absorbed wholly or in part. If the per cent of radiation which is absorbed by a substance is plotted against the incident wavelength (or frequency), the ensuing graph may be interpreted in terms of the intramolecular vibration. The graph, therefore, will be characteristic of the material and can be used in its identification. In addition, it should also provide data on the structure and bonding characteristics within the molecule.

Infrared absorption has been used extensively and successfully in the study of organic compounds. Its utility in mineralogy and particularly in clay mineralogy has not been fully explored. For details regarding infrared absorption in general, the text of Barnes et al. should be con-

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sulted, and for the application to clay mineralogy, the pioneer work of Keller and Pickett\textsuperscript{21,22} and Kerr and collaborators (see Adler \textit{et al.}\textsuperscript{23}) should be referred to. The statements herein are taken largely from these publications.

The range of infrared used in absorption studies in general is 4,000 to 400 cm\textsuperscript{-1} in frequency and 2.5 to 25 microns in wavelength. In the case of clay mineral investigations, wavelengths of 2 to 15 microns are used, since the characteristic spectra occur in this range. Wavelength is conventionally expressed in terms of microns and frequency in terms of wave numbers or reciprocal centimeters. The relationship is shown by

$$1 \mu = 10^{-4} \text{ cm}$$

Infrared absorption by powdered material cannot be measured satisfactorily unless scattering and reflection of the radiation from the tiny particles is reduced to a low value. It has been shown that the use of particles smaller than the minimum wavelength of radiation used, about 2 microns, reduces these factors to a very low level and generally improves results. Early work was done by mounting the clay in an oil medium (Nujol), which caused difficulty by adding its own spectrum to that of the clay. Currently techniques are available for mounting the clay without any additive.

\textbf{Data for Clay Minerals.} Kerr and collaborators (see Adler \textit{et al.}\textsuperscript{23}) present infrared absorption spectra obtained by different investigators in different laboratories on the same series of clay-mineral samples. The curves obtained by different investigators for the same clay-mineral samples have the same general characteristics but show considerable variation in detail. Further investigation is required to show which of these minor features of the curves are significant and which are spurious and due to factors of technique. In Figs. 113 to 116 and Table 40 infrared absorption data for a variety of type clay minerals are given. These data are taken from the work of Hunt, one of the contributors to the Report of the American Petroleum Institute,\textsuperscript{23} and they illustrate the general characteristics of the absorption spectra for the various clay minerals.

Buswell and Dudenbostel\textsuperscript{24} have shown that the adsorption at 2.75


Miscellaneous Properties

Fig. 113. Infrared absorption curves for kaolinites and halloysites, after Hunt (see Adler et al.23).

microns is due to unbonded OH, and that bonded OH caused absorption at 2.7 to 3.2 microns and at 6.15 and 7.55 microns. The absorption at about 6.1 microns shown by some of the clay minerals is believed due to adsorbed water, and the absorption at about 9 microns is believed due to the Si-O linkage. The octahedral alumina sheet is probably responsible for the absorption at about 10 microns. The causes of many of the absorption bands shown by the clay minerals are not yet understood.
<table>
<thead>
<tr>
<th>Clay mineral</th>
<th>Number of samples</th>
<th>2 μ</th>
<th>3 μ</th>
<th>4 μ</th>
<th>5 μ</th>
<th>6 μ</th>
<th>7 μ</th>
<th>8 μ</th>
<th>9 μ</th>
<th>10 μ</th>
<th>11 μ</th>
<th>12 μ</th>
<th>13 μ</th>
<th>14 μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>9</td>
<td>2.73 m</td>
<td>6.0 wa</td>
<td>7.55 ws</td>
<td>8.93 s</td>
<td>9.65 s</td>
<td>10.68 s</td>
<td>12.50 m</td>
<td>13.3 ws</td>
<td>14.5 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,663</td>
<td>1,665</td>
<td>1,325</td>
<td>1,120</td>
<td>1,036</td>
<td>936</td>
<td>800</td>
<td>750</td>
<td>690</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dickite</td>
<td>2</td>
<td>2.73 m</td>
<td>6.1 w</td>
<td>7.55 ws</td>
<td>8.15 m</td>
<td>9.1 s</td>
<td>10.68 s</td>
<td>12.55 m</td>
<td>13.3 ws</td>
<td>14.5 w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,663</td>
<td>1,640</td>
<td>1,325</td>
<td>1,227</td>
<td>1,100</td>
<td>936</td>
<td>797</td>
<td>750</td>
<td>690</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.83 m</td>
<td>8.93 s</td>
<td>9.65 s</td>
<td>10.95 s</td>
<td>1,120</td>
<td>1,036</td>
<td>913</td>
<td>800</td>
<td>750</td>
<td>685</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,534</td>
<td>1,120</td>
<td>1,036</td>
<td>913</td>
<td>9.95 s</td>
<td>1,005</td>
<td>875</td>
<td>784</td>
<td>8,489</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halloysite</td>
<td>3</td>
<td>2.73 m</td>
<td>5.9 w c</td>
<td>6.0 w</td>
<td>7.0 w</td>
<td>8.90 s</td>
<td>9.65 s</td>
<td>10.95 s</td>
<td>12.5 w</td>
<td>13.3 w</td>
<td>14.6 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,663</td>
<td>1,695</td>
<td>1,665</td>
<td>1,430</td>
<td>1,124</td>
<td>1,036</td>
<td>913</td>
<td>800</td>
<td>750</td>
<td>685</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.7 to 3.1 m c</td>
<td>6.1 w</td>
<td>7.55 w c</td>
<td>9.9 s</td>
<td>1,040</td>
<td>1,010</td>
<td>875</td>
<td>784</td>
<td>8,489</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>9</td>
<td>2.8 to 3.2 m</td>
<td>6.15 w c</td>
<td>7.55 w c</td>
<td>8.95 m</td>
<td>9.6 s</td>
<td>10.95 m</td>
<td>11.4 m c</td>
<td>12.75 w</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,670</td>
<td>1,626</td>
<td>1,325</td>
<td>1,117</td>
<td>1,040</td>
<td>913</td>
<td>875</td>
<td>784</td>
<td>8,489</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Positions of Band Centers*
<table>
<thead>
<tr>
<th>Mineral</th>
<th>2.8 to 3.1m</th>
<th>3.570 3.225</th>
<th>6.0m 7.0m 8.95m 9.7m 10.95m 12.05m 13.3m 14.4m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>1.665</td>
<td>1.117</td>
<td>1.080 9.13 830 750 695</td>
</tr>
<tr>
<td>Nontronite</td>
<td>1.640</td>
<td>1.325</td>
<td>1.110 9.13 816 750</td>
</tr>
<tr>
<td>Attapulgite</td>
<td>1.665</td>
<td>1.325</td>
<td>1.190 1.030 985 910</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>1.205</td>
<td>1.073</td>
<td>948 868 815 760 695</td>
</tr>
<tr>
<td></td>
<td>1.165</td>
<td>1.053</td>
<td>913 835 800</td>
</tr>
<tr>
<td></td>
<td>8.90s 9.9s</td>
<td>12.80m</td>
<td>781</td>
</tr>
</tbody>
</table>

* Wave numbers (in cm⁻¹) are given below the corresponding wavelength values in microns (μ).

Notes:
- * Only in two out of nine kaolinites
- * In one out of two dickites
- * In one out of three halloysites
- * In six out of nine montmorillonites
- * In four out of nine montmorillonites

The relative intensities of the absorption bands are indicated by the letters s, m, and w as follows: s = less than 25 per cent transmission with a film density of 0.6 mg/cm²; m = between 25 and 75 per cent transmission with a film density of 0.6 mg/cm²; w = more than 75 per cent transmission with a film density of 0.6 mg/cm².
Fig. 114. Infrared absorption curves for dickite, pyrophyllite, nontronite, and hectorite, after Hunt (see Adler et al.36).

For example, the causes of variations in the spectra within the montmorillonite group cannot yet be related to variations of composition or structure.

SURFACE AREA

Many methods have been tried to determine the surface area of clay materials. The most trustworthy results have been obtained with the
Fig. 115. Infrared absorption curves for montmorillonite, after Hunt (see Adler et al.25).

method developed by Brunauer, Emmett, and Teller,25,26 which depends on the adsorption of simple molecules, such as nitrogen, at temperatures in the neighborhood of their boiling point. A comprehensive discussion

of the basic theory of physical adsorption and surface-area measurement has been presented by Brunauer.27 Emmett, Brunauer, and Love28 and

Makower, Shaw, and Alexander\textsuperscript{29} first applied the method to soils and clay materials.

Obviously, specific surface is not a characteristic of any particular clay mineral, since it varies with particle-size distribution, particle shape, and the presence of cracks and pores in the sample. The data given in Table 41, taken from Nelson and Hendricks,\textsuperscript{30} are intended to give comparative

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Mineral & Heat treatment, °C & Loss in weight, % & Specific surface, m\textsuperscript{2}/g \\
\hline
Kaolinite, -0.3 micron & 30 & \ldots & 15.5 \\
 & 200 & 0.2 & 15.3 \\
 & 500 & 12.7 & 18.1 \\
 & 700 & 14.3 & 16.5 \\
 & 900 & 14.6 & 1.5 \\
Illite, -0.3 micron & 30 & \ldots & 97.1 \\
 & 200 & 0.4 & 92.2 \\
 & 500 & 5.8 & 91.6 \\
 & 700 & 7.7 & 80.4 \\
Montmorillonite & 30 & \ldots & 15.5 \\
Halloysite & 30 & \ldots & 43.2 \\
\hline
\end{tabular}
\caption{Specific Surface Area of Some Clay Minerals}
\label{table:specific_surface}
\end{table}

Heated at temperature given until no further weight loss.

values of the order of magnitude of the surface area of some clay minerals. The low surface-area value obtained for montmorillonite is interesting in view of the fine grain and the expanding-lattice characteristics of the mineral. The low value for montmorillonite means that the major part of the potential surface of the mineral could not be reached by the nitrogen or other gases used in the determinations. The theoretical surface of montmorillonite on dispersion to nearly unit-cell dimensions is $8 \times 10^6$ cm$^2$/g.

The values in Table 41 show that only a small amount of surface is lost when kaolinite and illite are dehydrated.

Recently Hendricks and Dyal\textsuperscript{31} have used the adsorption of ethylene glycol for surface determinations. The organic is adsorbed on both

external surfaces and inner surfaces accessible only by swelling. A combination of the Brunauer, Emmett, and Teller method with that of Hendricks and Dyal provides values for both external and swelling surfaces.

**DENSITY**

Determinations of the density of the clay minerals must be made on aggregates of fine particles. The measurement is inherently difficult, because of the likelihood of incomplete penetration of the liquid used into the interstices of the aggregate mass and because of the possibility of a chemical or physical change during the measurements as a consequence of adsorption of the liquid or an exchange reaction between the liquid and the clay mineral. It is particularly difficult to measure the density of the clay minerals in their natural state with their adsorbed water, which, in some of the clay minerals, such as montmorillonites and halloysite (4H₂O), is an integral part of their structure. For these clay minerals the density of the dehydrated material can be determined, but it does not represent the mineral as it occurs naturally.

In the case of the clay minerals which are subject to isomorphous substitution within the lattice, e.g., montmorillonite, illite, etc., the density varies from one specimen to another. For such clay minerals, there is a range of characteristic density values rather than a single value.

**Kaolinite.** According to Gruner, the theoretical density of kaolinite computed from the structure is 2.609. Values given in the literature vary from 2.60 to 2.68, with 2.63 frequently quoted in mineralogical textbooks. Because of the low adsorptive capacities of kaolinite and the general absence of isomorphous substitutions, the value for this mineral is a fairly definite and easily determined quantity.

**Halloysite.** Values of 2.55 and 2.56 are given by Makower and colleagues for completely evacuated material, which was probably close to the 2H₂O form. The hydrated form of the mineral (4H₂O) would have a lower density, and values given in the literature for halloysites in general are as low as 2.0 to 2.2.

**Illite.** Values given by Dana are 2.76 to 3.0 for muscovite and 2.7 to 3.1 for biotite. Illites would be expected to be in this range, but perhaps on the low side because of deficiencies of interlayer ions and slight

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replacement of such ions by hydration. DeWit and Arens\textsuperscript{35} have recently given values of 2.642 to 2.688 for materials with 0.0 per cent adsorbed water. These authors have determined values for the decrease in density of two illites as they pick up adsorbed water in increasing relative humidities (Table 42). A certain amount of such change is to be expected, but a large amount of it would probably indicate the presence of interlayer montmorillonite or vermiculite.

**Montmorillonite.** Makower and coworkers\textsuperscript{29} give a value of 2.53 for a low-iron montmorillonite and 2.74 for one with a somewhat higher iron content (3.6 per cent). DeWit and Arens\textsuperscript{35} give a value of 2.348, and Caldwell and Marshall\textsuperscript{13} give values for nontronite of 2.2 to 2.7 and for saponite of 2.24 to 2.30. These values are for essentially dehydrated

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Relative humidity</th>
<th>Moisture content, oven-dry basis, %</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite (thixotron)</td>
<td>0.00</td>
<td>0.0</td>
<td>2.348</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>11.6</td>
<td>2.199</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>16.6</td>
<td>2.134</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>28.4</td>
<td>2.001</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>46.0</td>
<td>1.772</td>
</tr>
<tr>
<td>Illite (Holland)</td>
<td>0.0</td>
<td>0.0</td>
<td>2.649</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>3.0</td>
<td>2.579</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>4.85</td>
<td>2.504</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>6.9</td>
<td>2.422</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>18.8</td>
<td>2.128</td>
</tr>
<tr>
<td>Illite (Maquoketa shale, Illinois)</td>
<td>0.0</td>
<td>0.0</td>
<td>2.642</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>8.3</td>
<td>2.409</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>12.0</td>
<td>2.310</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>24.8</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>76.0</td>
<td>1.48</td>
</tr>
<tr>
<td>Kaolinite &quot;Brocades&quot;</td>
<td>0.0</td>
<td>0.0</td>
<td>2.667</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>8.3</td>
<td>2.682</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>12.0</td>
<td>2.663</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.4</td>
<td>2.642</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>6.5</td>
<td>2.427</td>
</tr>
</tbody>
</table>

material, and it may be concluded that the density of such montmorillonite ranges from about 2.2 to at least 2.7. Probably 2.7 is too low for the substantially pure, iron-end member of the series.

The data in Table 42 after DeWit and Arens indicate the large change in density of the mineral with the increase in adsorbed water as the measurements were made following treatment at increasing relative humidities.

**Vermiculite.** Precise density data are not available for clay-mineral vermiculite, but the oven-dried material would be expected to have about the density of biotite mica. Because of its hydration properties, natural material would give a lower value than biotite mica, and the density would decrease with increasing adsorbed water, as does that of montmorillonite. The minimum value would be higher for vermiculite than for montmorillonite, since the amount of adsorbed water is restricted in vermiculite.

**Chlorite.** Dana gives values of 2.6 to 2.96 for the chlorite minerals. The clay-mineral chlorites would be expected to give values in this range. Like the illites as compared to muscovite and biotite, they would probably be in the low part of this range. The very low water-adsorptive properties of the mineral would mean that the density of air-dried material would differ little from that of natural material, and there would be little change as determinations were made following treatment at varying relative humidities.

**Attapulgite-Sepiolite-Palygorskite.** Caillere gives a value of 2.08 for sepiolite and 2.29 and 2.36 for two samples of palygorskite. These values indicate the probable range for these minerals, but more data are necessary before their density characteristics are known in any detail.

**ADDITIONAL REFERENCES**

*Solubility of the Clay Minerals*


Miscellaneous Properties


Infrared Absorption Spectra


Surface Area

Emmett, P. H., The Measurement of the Surface Areas of Finely Divided or Porous Solids by Low Temperature Adsorption Isotherms, Advances in Colloid Sci., 1, 1–36 (1941).


Density


CHAPTER 13

Origin and Occurrence of the Clay Minerals

SYNTHESIS OF THE CLAY MINERALS

Introduction. The synthesis of the clay minerals at elevated temperatures and pressures from oxides and hydroxides and from various minerals, particularly the feldspars, in the presence of acids and alkalies has been studied in considerable detail. Some investigation has been made of the synthesis of the clay minerals at ordinary temperatures and pressures, but the amount of such work is inadequate for general conclusions. Consideration is given herein only to synthesis investigations of a sort which throw light on problems of the occurrence and origin of the clay minerals in nature.

The identification of the crystalline phases formed in synthesis experiments is often very difficult because of their very small particle size, their poor crystallinity, and their contamination with large amounts of unreacted or unchanged material. Usually, X-ray diffraction provides the only trustworthy method of identifying the new phases. The identifications made in the years before the development of X-ray-diffraction techniques and before adequate diffraction data were available for the pure clay minerals are, therefore, often open to serious question. Even with the use of diffraction methods, there may be important uncertainties in the identifications reported in the literature. Thus, some of the material reported as kaolinite may actually be halloysite, since in few cases have the identifications been checked by electron micrographs.

Syntheses from Mixtures of Oxides and Hydroxides at Elevated Temperatures and Pressures. Information on this subject is largely the result of the work of Noll,1-4 who has published a series of classic papers on the synthesis of many of the clay minerals.

The reaction products obtained by Noll, for the system Al₂O₃-SiO₂-H₂O

\[ \text{Al}_2\text{O}_3 + \text{SiO}_2 + n\text{H}_2\text{O} \rightarrow \text{phases} \]

at temperatures between 250° and 500°C with varying amounts of alumina and silica, the pressure bomb containing a constant percentage of water, are given in Table 43. Silica gel and alumina gel were used in the experiments; the latter crystallized rapidly to bayerite and boehmite on aging the gel prior to the experimentation. Most of the alumina used was in the form of a mixture of boehmite and bayerite. When the two were used separately, the only observable difference in the results was a difference in the rate of reaction, boehmite reacting more readily. The rate of cooling and the degree of filling of the bomb had little, if any, effect on the nature of the product.

The data in Table 43 indicate that in the absence of silica, boehmite is formed up to 400°C, and at 500°C corundum is formed. According to Roy and Osborne, at very low temperatures gibbsite would form, with a transition to boehmite at about 120°C. Bayerite is a metastable phase formed during the rapid crystallization of alumina hydrate from sodium aluminate solutions. Also, according to these authors, diaspore instead of boehmite would be the monohydrate phase above 280°C under certain conditions of elevated pressure. Roy and Osborne show that γ alumina, a metastable phase, intervenes in the transition of boehmite to corundum (α alumina).

Noll's data show that, with molecular Al₂O₃:SiO₂ ratios of greater than

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**Table 43. Reaction Products in the System Al₂O₃-SiO₂-H₂O**

(After Noll)

<table>
<thead>
<tr>
<th>Temp, °C (Pressure, atm.)</th>
<th>Molecular ratio Al₂O₃:SiO₂ (H₂O constant)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:0</td>
</tr>
<tr>
<td>500° (530–540)</td>
<td>Corundum</td>
</tr>
<tr>
<td>400° (300)</td>
<td>Boehmite</td>
</tr>
<tr>
<td>350° (168) 300° (87) 250° (41)</td>
<td>Kaolinite</td>
</tr>
</tbody>
</table>

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1:2, kaolinite and boehmite are formed up to 400°C, and an unidentifiable phase develops at 500°C. With a ratio of 1:2, only kaolinite is formed up to 350°C; above that temperature kaolinite, pyrophyllite, and boehmite are formed up to 400°C; and at 500°C, kaolinite and boehmite disappear, with pyrophyllite and an unidentifiable phase the only components present. With a ratio of 1:4, kaolinite is the only crystalline phase up to 350°C, and at 400° and 500°C pyrophyllite is the only phase developed. With molecular alumina-to-silica ratios less than 1:4, the results of the synthesis are the same as when the ratio is exactly 1:4, except that amorphous silica is present at all temperatures. In the absence of alumina, no crystalline silica phase is formed under the conditions of Noll’s experiments. Noll points out that the rate of reaction varies greatly with the temperature; e.g., kaolinite formed at 300°C in 1 hr, whereas it took 111 hr at 200°C.

It would seem from the work of Roy and Osborne⁴ that, at very low temperatures and pressures, halloysite (2H2O) may be the resulting phase in the system Al2O3-SiO2-H2O, rather than kaolinite. Up to the present time halloysite (4H2O) does not appear to have been synthesized.

The data in Table 44, after Noll,⁴ show the reactions obtained in the

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Solvent</th>
<th>Composition</th>
<th>0.2:1:4</th>
<th>0.37:1:2</th>
<th>1:1:4</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°C MgO</td>
<td>Alkali solution</td>
<td>Kaolinite (&gt;) Montmorillonite (&lt;)</td>
<td>Montmorillonite</td>
<td>Montmorillonite</td>
<td></td>
</tr>
<tr>
<td>300°C CaO</td>
<td>Alkali solution</td>
<td>Kaolinite (&gt;) Montmorillonite (&lt;)</td>
<td>Montmorillonite</td>
<td>Montmorillonite</td>
<td></td>
</tr>
<tr>
<td>300°C Na2O</td>
<td>Alkali solution</td>
<td>Kaolinite (&gt;) Montmorillonite (&lt;)</td>
<td>Montmorillonite (+ kaolinite)</td>
<td>Montmorillonite</td>
<td></td>
</tr>
<tr>
<td>300°C K2O</td>
<td>Alkali solution</td>
<td>Kaolinite (&gt;) Montmorillonite (&lt;)</td>
<td>Montmorillonite (+ kaolinite)</td>
<td>Mica</td>
<td>K feldspar* + ?</td>
</tr>
<tr>
<td>Acid solution</td>
<td>Kaolinite</td>
<td>Kaolinite</td>
<td>Kaolinite</td>
<td>Kaolinite</td>
<td></td>
</tr>
<tr>
<td>400°C K2O</td>
<td>Alkali solution</td>
<td></td>
<td>Mica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid solution</td>
<td></td>
<td></td>
<td>Pyrophyllite + boehmite and kaolinite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In pure condition at Al2O3:6SiO2.
system \((\text{CaMg})\text{O}-(\text{K}_2\text{Na}_2)\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}\) on heating to 300°C and 400°C for periods of 8 to 24 hr. In each case the bomb was 0.35 per cent filled with water, and the pressure developed was 87 atm at 300°C and 300 atm at 400°C. As the alkalies or alkaline earths are added to a mixture of composition \(\text{Al}_2\text{O}_3:4\text{SiO}_2\), montmorillonite forms in increasing amounts at the expense of kaolinite. A concentration of about 0.2 mole of \((\text{CaMg})\text{O}\) or \((\text{Na}_2\text{K}_2)\text{O}\) per mole of alumina with an \(\text{Al}_2\text{O}_3:\text{SiO}_2\) ratio of 1:4 appears to be the optimum for the formation of montmorillonite. At slightly higher concentrations with \(\text{MgO}\) as the alkaline earth, montmorillonite is still the phase formed. At higher concentrations with \(\text{Na}_2\text{O}\), analcime is formed, and at moderately higher concentrations with \(\text{K}_2\text{O}\), muscovite is formed. The reaction product with \(\text{CaO}\) at higher concentrations could not be determined by Noll.

At very high concentrations of \(\text{K}_2\text{O}\) with the \(\text{Al}_2\text{O}_3:\text{SiO}_2\) ratio equal to 1:4, a potash feldspar was formed. At very high concentrations of \(\text{MgO}\) with the same \(\text{Al}_2\text{O}_3:\text{SiO}_2\) ratio, according to Noll and also Stresse and Hofmann,\(^6\) talc and then serpentine formed plus kaolinite or pyrophyllite instead of montmorillonite. Pyrophyllite rather than montmorillonite is the phase formed if the temperature used is above 400°C.

All the above results are for alkaline systems. Noll shows that for acid systems with \(\text{K}_2\text{O}\), kaolinite rather than the mica is formed. Other data suggest the generality that kaolinite is likely to be the phase formed at 300°C in an acid system containing any of the alkalies or alkaline earths. Gruner\(^7\) confirms the formation of kaolinite at 300°C with \(\text{K}_2\text{O}\) in an acid system, even in the presence of a large excess of potash. However, Gruner shows that at 400°C muscovite will form in an acid system in the presence of potash, and also that kaolinite will be converted to muscovite at this temperature in the presence of an excess of KCl.

Ewell and Insley\(^8\) have reported the formation of nontronite from a mixture of silica gel and ferric oxide heated at 350°C for 6 days at a pressure of 167 atm.

**Syntheses from Mixtures of Crystalline Minerals and Chemical Reagents at Elevated Temperatures and Pressures.** A considerable amount of work has been done on the alteration of ground feldspar subjected to elevated temperatures and pressures in the presence of acids and various other reagents. Unfortunately, little work has been done with minerals other than the feldspars.


According to Gruner, kaolinite, pyrophyllite, muscovite, and boehmite are the phases which may form when microcline and albite are subjected to high temperatures and pressures in the presence of aluminum hydroxide, silica, and potassium chloride under acid conditions. In Gruner's experiments the concentration of the potassium ions and the Al₂O₃:SiO₂ ratio of the system were the factors determining which minerals formed from the feldspars. Kaolinite will form from feldspars and is stable below approximately 350°C, regardless of the potassium-ion concentration provided the ratio of Al:Si is about 1:1. This means that additional easily available aluminum has to be in the system. If the additional aluminum is not present, pyrophyllite formed instead of kaolinite below about 350°C.

In the temperature range from 350° to at least 530°C, pyrophyllite formed from the feldspars if the potassium-ion concentration was low (it must not be much greater than the amount that the acid can remove from the potash feldspars). Under these conditions boehmite formed from any alumina in excess of that required for the pyrophyllite.

If the concentration of potassium and sodium ions was high but no additional alumina was available, the feldspars remained unaltered. No true potassium feldspar was synthesized under the conditions of the experiments. If alumina, silica, and potassium chloride are added to the feldspar, muscovite and pyrophyllite are synthesized without any formation of feldspar.

Muscovite formed readily from feldspar, beginning at about 350° to 525°C, the highest temperature tried, provided that the potassium and aluminum were in sufficient concentration.

Schwarz and Trageser stated that orthoclase and anorthite in the presence of 0.5N HCl gave kaolinite as an alteration product at temperatures below about 400°C, pyrophyllite and boehmite at temperatures of 400° to 550°C, and corundum at about 600°C.

Badger and Ally produced kaolinite when a potash feldspar was heated at 225°C for 24 hr in the presence of 5 per cent hydrofluoric acid. These same authors found no reaction when the same feldspar was heated in the presence of carbonic acid for 156 hr at 60°C and a pressure of 1,800 psi.

The formation of secondary silicate compounds from solid phases like feldspar and aluminum hydroxide in the foregoing type of experiments

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is little understood. Schwarz and Trageser\textsuperscript{10} believe that the hydrolysis of the original mineral is essentially complete and that the new insoluble compounds are reaction products of the hydrolyzed components. Gruner\textsuperscript{9} suggests that the degree of ionization, particularly with respect to SiO\textsubscript{4} groups, must be very small in such systems. Jander and Wuhrer\textsuperscript{12} suggest that there is only partial hydrolysis of the original mineral with the formation of some kind of an amorphous intermediate product. Various investigators have favored a structural transformation of the primary minerals to the secondary ones with only very slight hydrolysis. Schwarz and Trageser\textsuperscript{10} point out that kaolinite can form under similar conditions from a variety of parent minerals (e.g., leucite, in addition to the feldspars), which means that no single original structure is required if the change is largely a structural transformation.

**Syntheses from Mixtures of Oxides and Hydroxides at Ordinary Temperatures and Pressures.** Only a few investigations have been made of the formation of the clay minerals from their constituent oxides at ordinary conditions of temperature and pressure. The resulting data are scant, and in some cases the identifications of the resulting products are not very convincing.

Sedletsky\textsuperscript{13} mixed sodium silicate and sodium aluminate and then leached with \( N \text{MgCl}_2 \) until the pH of the leachate was 5.6. After further washing to remove all the free chloride, the gel was held in a closed vessel at the temperature of the laboratory for 4 years, at the end of which X-ray diffraction showed the presence of a product similar to montmorillonite.

Caillere and Henin\textsuperscript{14} report the synthesis of clay minerals by the electrolysis of a solution of silica or a mixture of solutions of silica and alumina. Platinum was used as the cathode and various anodes of aluminum, iron, nickel, and magnesium were tried. The product depended on the anode used; e.g., with a magnesium anode an antigorite-like mineral was formed, and with aluminum the product seemed to be kaolinite.

Stresse and Hofmann\textsuperscript{6} report that magnesium silicate gels obtained by boiling together solutions of MgCl\textsubscript{2} and hydrated silica developed clay-mineral structures when they were boiled further with potassium hydroxide, calcium hydroxide, or sodium hydroxide. The structures in every case were like those of montmorillonite, except when the concentration


\textsuperscript{11} Sedletsky, I. D., Genesis of Minerals from Soil Colloids of the Montmorillonite Group, Compt. rend. acad. sci. URSS, 17, 375-377 (1937).

\textsuperscript{12} Caillere, S., and S. Henin, Essais de synthèse des minéraux argileux, Verre silicates indus., 13, 63-64 (1948).
of potassium hydroxide became fairly high; then a mica structure developed.

Teichner and Pernoux\textsuperscript{15} have pointed out that some catalysts for the Fischer process frequently are prepared by impregnating kieselguhr with nickel and that in the impregnation of the silica the catalyst develops a montmorillonite-like structure. Unpublished reports\textsuperscript{16} indicate that nearly all the clay minerals have been synthesized with nickel proxying for aluminum. The conditions under which the syntheses were made, however, have not been revealed.

\textbf{Transformations of Clay Minerals at Ordinary Temperatures and Pressures.} Many investigators, including Caillere and Henin,\textsuperscript{17} Volk,\textsuperscript{18} Aleshin,\textsuperscript{19} and Barshad,\textsuperscript{20} have shown that a material substantially like illite is produced from montmorillonite when all the exchange positions are occupied by potassium ions and the material is thoroughly dried at about 110°C. Such material does not again expand, even on treatment with a polar organic liquid, and it has substantially the same X-ray-diffraction characteristics as illite. Similar results are obtained under the same conditions by treating montmorillonite with NH\textsubscript{4}\textsuperscript{+}. Vermiculite reacts with both K\textsuperscript{+} and NH\textsubscript{4}\textsuperscript{+}, as does montmorillonite, and with similar results.

Caillere and Henin\textsuperscript{21} and Barshad have shown also that the treatment of either montmorillonite or vermiculite under certain conditions with a solution containing Mg\textsuperscript{2+}, so that all the exchange positions are occupied by the magnesium ions, produces a product which does not expand and has the X-ray-diffraction characteristics of chlorite. The exact experimental conditions of the treatment process necessary to obtain chlorite rather than montmorillonite with exchangeable Mg\textsuperscript{2+} are not known.

Caillere and Henin\textsuperscript{22} report the formation of kaolinite from montmorillonite in the laboratory. The kaolinite was obtained by treating montmorillonite with 20 per cent CaCl\textsubscript{2}, 0.5 per cent Na\textsubscript{2}AlO\textsubscript{3}, and 10


per cent Al(NO₃)₃ for 3 to 4 days and then precipitating with HCl or NH₄OH.

**General Conclusions from Synthesis Data.** Some general conclusions regarding the environmental conditions favorable for the formation of the clay minerals can be reached from the available data from synthesis experiments. At low temperatures and pressures, acid conditions apparently favor the formation of the kaolinite type of mineral, whereas alkaline conditions favor the formation of montmorillonite, or mica, if potassium is the alkali metal and if it is present in concentration above a certain level. From the work of Noll the minimum concentration of K₂O necessary for the formation of the mica is between 0.2 and 0.37 mole per mole of Al₂O₃. The presence of magnesium particularly favors the formation of montmorillonite.

At temperatures somewhat above about 350°C and with moderate pressures, pyrophyllite forms in place of kaolinite, with any excess Al₂O₃ forming boehmite. At more elevated temperatures and pressures, other alumina phases develop. At more elevated temperatures, the foregoing generalities for results under acidic and alkaline conditions do not always hold. Thus, mica can form under acid conditions, and kaolinite or pyrophyllite can develop in the presence of an excess of K₂O, depending on the temperature, the amount of K₂O, and the Al₂O₃:SiO₂ ratio.

**CLAY MINERALS OF HYDROTHERMAL ORIGIN**

**Introduction.** It has been recognized for a long time that argillaceous alteration products due to hydrothermal action are frequently to be found as an aureole around metalliferous deposits. Such alteration products are also found associated with hot springs and geysers. The size of the alteration envelope varies widely. At Butte, Montana,²³ for example, a width of 10 ft is common in the peripheral area of the ore body, whereas the width may become 100 ft or more in the zone of intermediate mineralization intensity. In fissure veins the alteration lies parallel to the walls of the fissure and is of relatively uniform width, varying according to the size of the vein. If the veins are closely spaced, the alteration halos may merge, as in the central zone at Butte and in porphyry copper deposits.

Bateman²⁴ has pointed out that, with epithermal veins, the alteration zone is likely to be narrow and the changes may be hardly discernible, whereas, with mesothermal veins, the alteration halo is likely to be wide and intense. The alteration products associated with hypothermal deposits are generally not argillaceous, and the secondary products

found with other types of metalliferous ore bodies are likely to contain few or substantially no clay minerals.

Descriptions of hydrothermal alteration products, before the development of modern X-ray, thermal, and optical methods of clay-mineral identification, are of little value because of questionable clay-mineral identifications. For example, a large mass of hydrothermal halloysite at Eureka, Utah, was first described as talc. Unfortunately, even in very recent years, some students of ore deposits have failed to realize the complexities of clay-mineral identification and have published determinations which are questionable because they are based on insufficient analytical data.

The study of the alteration products associated with many ore bodies is complicated by the difficulty of distinguishing between hypogene and supergene products. In many cases, later supergene alteration is superimposed on earlier hypogene alteration, and the same clay mineral may be developed in both processes. Kaolinite, for example, in some instances may be formed as a hypogene product and later by supergene alteration of some other clay minerals.

The probable economic importance of wall-rock alteration has been recognized in recent years, because of the likelihood of significant relationships between kind of alteration and mineralization. As a consequence, the problem has been studied by many investigators, but much of the data have not yet been published, and the topic has not reached the place where many broad generalizations are established.

Types of Clay Minerals in Hydrothermal Deposits. All the various clay minerals, with the possible exception of attapulgite-palygorskite and vermiculite, have been authentically reported in hydrothermal bodies. The various forms of the kaolinite minerals are recorded, including anauxite, dickite, and nacrite, as well as various montmorillonites, including nontronite and the magnesium-rich members. The white mica found in alteration halos is frequently described as sericite and undoubtedly has similarities to illite. The beidellite which is frequently recorded, particularly in the earlier literature, is probably often a mixture of clay minerals. Halloysite and allophane are often reported, and although the identifications are sometimes established, some are based solely on optical measurements and must be questioned. Material appearing to be isotropic and therefore amorphous and called allophane, may be revealed by X-ray diffraction to be largely crystalline but extremely fine grained and an aggregate of randomly oriented particles.

In some instances, hydrothermal clay-mineral bodies are of large size (of the order of 100 ft in diameter) and are composed substantially of a

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Origin and Occurrence of the Clay Minerals

single clay mineral. An example is the Cornish kaolin, whose hydrothermal origin is now well established by the finding of kaolin masses which are overlain by sills and which do not reach the surface. Other examples are the halloysite body at Eureka, Utah, which is composed of a single clay mineral. The so-called bentonite from the Island of Ponza, Italy, may be an example of a huge mass of almost pure montmorillonite formed from the alteration of an eruptive igneous rock.

In many, perhaps most, instances, the alteration product is a mixture of several clay minerals. The association is frequently so intimate that the identification of the individuals is very difficult. Mixed-layer clay mineral specimens are extremely common in hydrothermal deposits.

Mode of Formation and Occurrence. In many hydrothermal clay bodies a zonal arrangement of the clay minerals has been observed. Often there is an inner halo of sericite (the term sericite will be used for the white-mica alteration product, since that name is used in the literature and since the precise relationship to illite is not established), an intermediate zone of kaolinite, and an outer zone of montmorillonite and chlorite, with chlorite being most abundant on the outermost fringe. The boundaries of the zones are gradational. In some other bodies the alteration products appear to be superimposed rather than zonal, as if they had been developed in several fairly distinct stages.

Because of the seeming difference in the occurrence of the argillaceous alteration products, two concepts of their formation have been suggested. On the basis of their classic study of wall-rock alteration at Butte, Montana, Sales and Myer conclude that the alteration is essentially contemporaneous with ore deposition and that different mineralogical zones in the surrounding rock may be regarded as reaction rims, representing diminishing activity of the powerful solution that deposited the ore minerals. The different mineralogical and chemical responses within the wall rock are dependent not on a drastic change in the hydrothermal fluid itself, or on a periodicity in its operation, but on continuously varying conditions of physicochemical environment within the wall rock outward from the vein.

The second concept appears in the writings of Lovering, Kerr, Schwartz, and others who have described wall-rock alteration at numerous deposits which seems to have developed in stages, by differing

28 Schwartz, G. M., Hydrothermal Alteration of the "Porphyry Copper" Deposits, Econ. Geol., 42, 319-352 (1947).
solutions appearing at different periods separated by time intervals of relative inactivity. In some cases the products developed during a given stage show some zoning. Often there appears to be an early stage of the development of chlorite and sericite mica, a second stage of development of halloysite, kaolinite, and montmorillonite, and a late stage of development of sericite. In the second stage, the halloysite and kaolinite are likely to be close to the vein, and Lovering has recognized a zoning in some deposits of dickite-kaolinite-halloysite outward from the vein.

It seems likely that both concepts are applicable at particular deposits. Adequate information is not yet at hand to determine what controls the operation of one or the other process at a given deposit. Also, adequate data are not available for broad generalizations on the nature of the zoning or on the sequence of clay minerals likely to develop in the periodic process.

According to Sales and Meyer, the alteration of the quartz monzonite at Butte, Montana, consists of an outermost fringe in which the hornblende and biotite are changed to chlorite. Progressing toward the vein, montmorillonite becomes the dominant alteration product developing from plagioclase, with the nontronite variety forming from hornblende. A small amount of amorphous material is also formed with the montmorillonite. Progressing further toward the vein, kaolinite is found in increasing abundance with the gradual reduction in the amount of montmorillonite. In the kaolinite subzone there is always some montmorillonite present, and frequently there is a regeneration of the chlorite. In the argillaceous alteration zone, the orthoclase is unaltered except for a faint trace of kaolinization at the innermost edge. The argillaceous zone grades veinward into the sericite zone, which is made up solely of sericite, quartz, and pyrite. In this zone all the remaining silicate minerals are altered.

Sales and Meyer show that the abundance of lime, soda, and silica declines considerably and magnesia moderately, from the unaltered rock toward the vein. They conclude that there is a continual removal of these components during the gradual outward movement of the alteration; i.e., these components are carried outward as they are released by the breakdown of the parent minerals. The result over a period of time is a gradual pushing outward of the front of attack as the total envelope of alteration grows wider while maintaining the identity and positions relative to each other of its component zones. The montmorillonite subzone, for example, prevailed, until the outward migration caused a depletion of alkalies and alkaline earths, when kaolinite became the stable phase.

According to Sales and Meyer, sericitization and argillization are contemporaneous processes. The potash content is nearly constant
throughout the entire alteration halo. The orthoclase feldspars break down only in the sericite zone, and in fact the beginning of the sericite zone coincides with the destruction of the potash feldspar. Orthoclase is broken down only close to the vein as a consequence of the higher temperatures and the greater potency of hydrothermal acid water. With the destruction of the orthoclase near the vein, the potash necessary for the formation of sericite is available. Sericite is not formed at a distance from the vein because of the absence of available potash as a result of the stability of the orthoclase. An alkaline environment, in addition to the presence of potash, is usually required for the formation of white mica, but Gruner has shown that the mica can form in an acid environment at temperatures of the order of 350°C in the presence of an excess of potassium.

Lovering describes wall-rock alteration in the Tintic district of Utah as a periodic development. The first stage is chloritization of the volcanic rocks and dolomitization of the limestones, both involving the addition of magnesium. The second stage, or argillitic stage, witnessed the development of the clay minerals other than chlorite. The clay minerals are better developed in the volcanics than in the limestones, and Lovering was able to detect a zoning within the argillitic zone consisting of dickite-kaolinite-halloysite (2H₂O)-beidellite-halloysite (4H₂O), reading progressively away from the ore deposit. The final stage was extensive sericitization and silicification.

Kerr and colleagues have described the hydrothermal alteration of intrusives at Santa Rita, New Mexico, as occurring in several stages. The initial stage of clay mineral development is chloritization of biotite and hornblende. The next stage is one of “hydromica-argillic alteration,” with the development primarily of hydromica from the biotite and chlorite, and of sericite and kaolinite from the plagioclase feldspars. The final stage is one of sericitization and silicification, in which nearly all the primary silicates are altered. The absence of montmorillonite at Santa Rita is noteworthy.

Peterson and colleagues describe three stages of alteration at Castle Dome, Arizona. The earliest stage is the development of chlorite and sericite with some nonclay minerals. This is followed by an argillitic stage in which montmorillonite and “hydromica” are the important constituents. Kaolinite is also developed in the argillitic stage, but it is of minor abundance. The final phase is one of intense sericitization and silicification.

Schwartz has summarized the data for the alteration associated with a series of porphyry coppers and has shown that there is great variation.

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in the kind and amount of alteration in various ore bodies. In some deposits, notably at Ajo, Arizona, there are substantially no clay-mineral alteration products, whereas, in others, e.g., at Morenci and Miami, Arizona, hypogene clay minerals are extensively developed. He has shown also that the identity and relative abundance of the clay minerals differ widely in different deposits. In most deposits, however, the development of argillie material seems to be followed by a final period of intense sericitization and silicification.

As stated earlier, the available data are not adequate to establish general conclusions, but they do suggest a general tendency toward sericite adjacent to the vein, an outer chloritic zone, and an intermediate zone of kaolinite, halloysite, allophane, and/or montmorillonite. In the intermediate zone, montmorillonite is mostly in the outer part and the kaolinite minerals in the inner part. In some cases the sericitization seems to be later than the argillie development.

Nature of the Hydrothermal Solutions. Information concerning the composition of the hydrothermal solutions is scant, but in many, perhaps most, cases, such waters are thought to be acid to begin with, carrying chlorine, sulfur, carbon dioxide, and/or silica. The composition of the solutions must change as reactions take place with the host rock, and in the case of silicate rocks the solutions would become alkaline as a consequence of such reactions. The alkaline constituents would probably be transported outward by the solutions, and the alkalinity of the solutions would persist only so long as alkali or alkaline earths were being released by the breakdown of the parent rock. As the action of the acid water proceeded, therefore, the acid-alkaline front would move outward as the alkaline earths and alkali were carried outward. As Sales and Meyers have postulated, the later breakdown of a resistant mineral, such as orthoclase, which had persisted through the beginning of the acid encroachment until temperatures or solution concentration became sufficiently high to break it down, can cause a reversal to alkaline conditions.

It is by no means established that hydrothermal solutions are always acid initially. Andreatta,31 for example, has described a sequence of hydrothermal clay minerals developed in the order micaceous clay mineral–montmorillonite–halloysite–kaolinite; this sequence he believes to have formed from warm water originally alkaline and rich in potassium which became neutral and finally acid with progressive cooling.

Relation to Parent Materials. If the hydrothermal alteration is intense, as a result of relatively high temperatures and concentrations, and long continued, so that all the original minerals have been affected, and if there has been considerable transportation of components, such

as alkalies and alkaline earths released by the breakdown of the parent minerals, the alteration products will tend to be the same regardless of the parent rocks, except for carbonate and quartzitic rocks. In the case of limestones, the tendency is toward silicification. In the case of dolomitic rocks, silicification may also be the result, but the reaction between the magnesia and the silica sometimes forms a magnesium-rich clay mineral. The deposit of the montmorillonite mineral hectorite, at Hector, California, has probably had such an origin.

If the hydrothermal alteration is relatively slight, the character of the primary mineral largely determines the alteration product. With very slight alteration, the magnesium-rich minerals such as the hornblendes and biotite tend to change to chlorites. With slight alteration and in the presence of alkalies and alkaline earths, except potassium, the micas, the ferromagnesium minerals, and the plagioclase feldspars are likely to yield montmorillonite. The presence of magnesium particularly favors the formation of montmorillonite. The presence of potash, either from feldspars or primary micas, favors the development of secondary micas. Zsolnay,\(^\text{32}\) for example, has described alteration in adjacent rhyolite and andesite; the former shows illitic secondary products and the latter, alteration to montmorillonite. The literature has many references to montmorillonite types of alteration products in basic igneous rocks, indicating the frequency of montmorillonitic alteration in this type of rock.

Kaolinite may form from any constituents, if the alkalies and alkaline earths are removed approximately as fast as they are liberated from the parent rock or if the environment is acid and the temperature is moderate. When present in the environment, calcium particularly appears to retard the formation of kaolinite.

Sales and Meyer,\(^\text{23}\) Ross and Hendricks,\(^\text{33}\) and others have shown that the clay minerals themselves alter to other clay minerals if the hydrothermal environmental conditions change. Such alterations take place in accord with the generalities just mentioned above.

**Relation to Mineralization.** The impetus for much of the recent study of wall-rock alteration associated with ore bodies has been the hope that correlations of type of alteration with mineralization would provide keys for prospecting. Very little such data have been published, but the meager published data suggest that in some cases, at least, the hopes have been realized.

Lovering\(^\text{26}\) has shown at Tintic, Utah, that ore values are not found when the late stage of sericitization and silicification has not been opera-

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Clay Mineralogy

At Santa Rita, New Mexico, Kerr and colleagues have shown that at least part of the mineralization is contemporaneous with the argillic alteration. These authors also point out that the feldspars in the area of copper mineralization show prominent kaolinite alteration, whereas in the zinc area, montmorillonite is the dominant alteration product. Sales and Meyer have observed a general close association of sulfides and the sericite alteration at Butte, Montana.

Clay Minerals Associated with Hot Springs, Fumaroles, Etc. The action of hot springs, fumaroles, etc., provides an excellent opportunity to study hydrothermal alteration of which clay mineralogists have not yet taken full advantage. Fenner, studying samples from boreholes in the Yellowstone area, found that beidellite was the alteration product at depths greater than about 95 ft when the solutions were alkaline. At shallower depths kaolinite was found, and it was believed to have resulted from descending meteoric acid waters. The acid resulted from the oxidation of sulfides.

SOILS AND WEATHERING

Modern investigations by Kelley, Hendricks, MacEwan, Henin, Marshall, Jackson, and many other students of soils have provided a tremendous amount of information on all phases of clay mineralogy. Each of these investigators and many others have extensive bibliographies dealing with clay mineralogy, so that it is not feasible to attempt to list even the major publications of the most active workers. Soil investigators were the first to apply modern methods of clay-mineral analysis to their problems extensively. In this section, the distribution of clay minerals in various soil types and the environmental conditions leading to the formation of particular clay minerals during weathering processes will be considered.

Factors Controlling Weathering Processes. No arrangement of the factors controlling weathering processes in a general order of importance is possible, since the factors are closely interdependent and since their relative importance is not always the same.

Parent Rock. The composition and texture of the parent rock are important in initial stages of weathering, but their importance decreases as the duration of weathering increases. Under conditions of drastic alteration under humid conditions, as in the development of podsolic and lateritic soils, the influence of parent rock is relatively short-lived, whereas in aridic zonal soils it prevails almost indefinitely. It has been proved that soils containing kaolinite and soils containing montmorillonite can both develop from the same parent rock under different condi-

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tions of climate, topography, and time. Also it has been shown that the same type of soil with a characteristic clay-mineral composition can develop after a relatively long period of time from rocks of widely different composition and texture.

The most important factor of composition in parent rocks is the content of alkalies and alkaline earths. Rocks containing no alkalies, such as kaolin clays, can yield only kaolinite or lateritic weathering products unless ground-water movement brings alkalies and/or alkaline earths to the environment. Igneous rocks, shales, slates, schists, and argillaceous carbonates can yield a variety of weathering products, at least in the initial stages of weathering, because of their content of alkalies and alkaline earths in addition to alumina, silica, etc.

Climate. The temperature and the rainfall, particularly its seasonal distribution, are the significant climatic factors. Decay of the parent minerals is most rapid in warm, humid climates. The direction of the movement of water through the weathering zone and the leaching of soluble salts from the material depend on the amount of rainfall and its seasonal distribution. Thus, in a continuously wet climate the movement of the water is downward, tending to remove downward the components liberated by the decay of the parent minerals. In a continuously dry climate or seasonal one with long dry seasons, the prevailing water movement may be upward, and the decay components would not be removed from the decay zone. The climate determines the amount and kind of vegetation and further the amount and kind of organic alteration products yielded by the decay of the organic material. Thus in a humid cool climate an abundance of organic material decays slowly to produce an abundance of active organic acids and other compounds to react with the parent material, whereas in a hot humid climate with seasonal rainfall the organic material is rapidly destroyed by oxidation and alteration. As a consequence, the kind and amount of organic products available for leaching are very different in the two environments.

Topography. Topography determines whether or not there is active vertical movement of water through the weathering material. This is particularly significant in regions of relatively high rainfall in which low, flat areas may be saturated with water almost to the surface. The prevalence of oxidizing or reducing conditions and the depth to which active oxidizing conditions penetrate depend in part on the water satura-

tion of the soils. Poorly drained areas saturated with water for long periods of the year generally have only reducing or feebly oxidizing conditions, or at best a thin surficial zone of oxidation.

Topography, by its control of the vertical movement of ground water, also influences the leaching processes. Thus, in low, flat areas with little movement of water through the soils, there would be relatively little leaching.

Topography also influences the rate of erosion at the surface, and hence the rate of removal of the products of weathering and the rate at which fresh parent material is brought close to the surface into the most active zone of alteration.

Vegetation. The significant factors with regard to vegetation are its amount and kind and the amount and kind of resulting products of its decay. In an arid area where vegetation is absent or in an area with long hot, dry intervals where vegetation is quickly oxidized, few or no organic acids are produced from the vegetation to enter into the alteration processes. Also in countries of eucalyptus rather than deciduous trees, there would be scant accumulation of leaf litter and scant production of organic decay products, even though conditions favored the abundant growth of vegetation.

Soil investigations suggest that, under cool, humid conditions with deciduous forest growth, organic decomposition products develop in the soil which have very drastic effects on parent silicate minerals. Under temperate conditions and prairie grass cover, the resulting vegetal decomposition products are different and appear to have less drastic effects on the parent minerals.

Time. Since weathering processes are relatively slow, time is a significant factor in the development of alteration products. In the initial stages of the weathering of some rocks, alkalies and alkaline earth may be present in the weathering zone, and as a consequence a certain kind of alteration product will develop. After a long time interval all the alkalies may have been removed by leaching, and a different type of alteration product will form. As a consequence, weathering products from a given type of parent material may be quite different in an initial stage and in a later stage. Bray has, for example, shown the great difference in the mineral composition of weathering products of loess in Illinois as a consequence of time. Manifestly, the factor of time is most important when weathering in general is moderately severe and when the parent rock has a composition permitting the formation of a variety of alteration products.

Soil-profile Development. Weathering processes, especially where there is vertical (downward or upward) movement of moisture, tend to

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develop a sequence of horizons within the zone of alteration. The horizons frequently grade sharply into adjacent ones and have thicknesses measured in inches or a few feet, although there are some very mature soils with horizons many feet in thickness. The horizons show differences in degree of breakdown of parent material, in kind and relative abundance of secondary mineral components, in particle-size distribution, in organic material, and/or in pH and character of alkali and alkaline-earth content. Vertical movement of water causes the translocation of soil constituents, thereby developing the sequence of varying horizons. A fairly typical profile of a podsolic type of soil is given in Fig. 117, from Lyons and Buckman. As a consequence of the difference in composition and texture, the physical properties of plasticity, tilth, etc., vary from horizon to horizon in the profile.

The soil horizons are designated from the surface downward, A, B, C, D. The nomenclature of soil horizons outlined recently by the Soil Survey Staff of the U.S. Department of Agriculture, as summarized by Winters and Simonson, is as follows: The A horizon is defined as a layer of maximum accumulation of organic matter, and/or as the surface layer that is lighter in color than the underlying horizon and has lost some of its clay and sesquioxides. The B horizon is defined as the soil layer that contains an accumulation of clay and sesquioxides with small amounts of organic material, and/or has a blocky or prismatic structure and a stronger color than the overlying A horizon. The C horizon is defined as a layer of unconsolidated and partly weathered material relatively unchanged by soil-forming processes. The D horizon is unaltered parent material.

In descriptions of weathering products it is obviously necessary to describe the profile as a whole as well as the composition and properties of the individual horizons.

Classification of Great Soil Groups of the World. The various types of soil are considered by students of soils under three main headings as follows:

1. Zonal Soils. After soil-forming processes have been at work for a considerable time, soils over wide areas, underlain by rocks of varying kinds, tend to become alike in general characteristics if the climatic influences are reasonably uniform and continuous and if erosion is not too vigorous. Such soil groups are called zonal and constitute the Great Soil Groups of the World. In these soils, climate, with its associated kind of vegetation and organic decomposition material, is the major factor in soil genesis.

2. Intrazonal Soils. These soils are associated with the zonal groups and are those that reflect the influence of some local conditions such as poor drainage, alkali salts, or some other unique characteristic superimposed on the general characteristics resulting from the climate and vegetation factors. Such soils frequently cross zonal boundaries and thus are called intrazonal.

3. Azonal Soils. These are soils without profile development, such as alluvial and colluvial soils. There is little or no alteration of parent material because of their youth or environmental setting.

The classification of the great soil groups with some of the more important associated intrazonal soils suggested by Lyon and Buckman is given in Table 45. A map showing the world distribution of the great soil groups is presented in Figure 118. A somewhat idealized diagrammatic presentation of representative profiles of five zonal soils is given in Figure 119.

Origin and Occurrence of the Clay Minerals

TABLE 45. CLASSIFICATION OF GREAT SOIL GROUPS OF THE WORLD
(After Lyons and Buckman 38)

I. Zonal humid soils

Tundra
Dark gray peaty accumulation over gray mottled mineral horizons. Substratum ever frozen and often the subsoil as well

Podsolic
Typical podsol (gray forest soil)
Brown podsolic
Gray-brown podsolic
Red and yellow podsolic (lateritic)
Prairie dark brown and reddish brown

Lateritic
Typical and well-developed laterites
Yellowish-brown lateritic soils
Reddish-brown lateritic soils
Terra rossa

Associated intrazonal groups
Plano sols—strongly leached surface soils over clay pans
Rendzinas—dark-colored grassland soils from soft limy material
Brown forest soils, similar to gray-brown podsolic but neutral instead of acidic

II. Zonal aridic soils*

Chernozem (black earth)
Chestnut and reddish chestnut
Brown and reddish-brown aridics
Reddish desert soils
Noncalcic brown soils

Associated Intrazonal Groups
Saline soils (Solonchak)—high content of soluble salts of Ca, Mg, and Na.
Mildly alkaline
Alkali soils (Solonetzs)—moderate content of soluble salts but with those of Na dominant. Strongly alkaline

* Direction of arrow indicates a progressive reduction in effective rainfall.

The general relation of the great soil groups to climate conditions is shown in Fig. 120, after Millar and Turk. 40 A Pedalfner soil is one in which there is a tendency for alumina and ferric iron to accumulate in the profile. A Pedocal soil is one in which there is a tendency for calcium carbonate to accumulate in the profile.

Description of Great Soil Groups. In zonal humid soil regions the climate varies from cold to tropical with rainfall greater than about 25 in./year. The vegetation is forest and grasses in warmer regions, and mosses, lichens, and shrubs in tundra areas. The soils are characterized generally by a concentration of iron and aluminum in certain horizons. Ordinarily there is no concentration of carbonate when the soils have reached a mature stage.

Fig. 118. World distribution of great soil groups, from Winters and Silsbee. **9**
Tundra Soils. These soils are characterized by an accumulation of organic matter giving a peaty surface overlying a bluish-gray sticky and compact subsoil. The frozen subsoil causes poorly drained, boggy conditions for most of the year. The clay-mineral content of tundra soils is frequently rather low.
Podsolic Soils. Such soils are developed under cool and damp climatic conditions providing an abundant surface accumulation of organic material. Forests are the most common vegetative cover, although podsolization does occur with grass cover. The covering vegetation must be such as to yield on decomposition organic acids and other compounds of great potency, and there must be enough rainfall to provide active leaching conditions. The environment is acid, and pH values as low as 3.5 are common in the humus and 4.0 to 4.5 in the clay component.

Under such conditions carbonates are quickly dissolved and alkaline and alkaline earths are removed from the profile. The base saturation ranges from about 20 to 80 per cent and is commonly 40 to 60 per cent. The organic and inorganic colloidal components are translocated from the upper horizon downward to about the water table. In addition leaching conditions are so intense that the inorganic colloidal complex becomes unstable in the surface horizons, and the iron and alumina are carried away to be reprecipitated at about the water table. As a consequence of the removal of aluminum and iron, a gray, highly siliceous, acid horizon develops directly beneath the surface accumulation of organic material. Because of the gray color and ashy appearance of the highly siliceous horizon, the term podsol (Russian pod, meaning under, and zola, ash) has been applied to such soils. An example of a well-developed podsol profile is shown in Fig. 117.

Brown podsolic soils are found in the Northern Hemisphere to the south of the true podsols, and where leaching is less intense. The siliceous gray A2 horizon (Fig. 117) is replaced by a friable light brown horizon containing considerable organic material. There is little breakdown of the colloidal silicates and little translocation of either the colloidal silicates or the aluminum and iron.

Gray-brown podsolic soils lie to the south of the brown podsolic soils in the Northern Hemisphere and show very mild leaching, primarily because of a vegetative cover which yields less-potent organic decomposition products and a climate which yields a smaller quantity of such products because of more complete oxidation. The gray siliceous layer is replaced by a gray or yellow-brown horizon, and considerable exchangeable calcium remains on the clay minerals. There is some downward movement of colloids, but the organic acids are too feeble to cause appreciable disintegration of the silicates.

Red and yellow podsolic soils are transitional with laterite soils in warm areas and have formed under mild climate, abundant rainfall, and a forest cover which is either mixed or largely deciduous. Leaching is marked, but the breakdown of the silicates is small. There is some translocation of colloidal silicates. The relatively rapid oxidation of the iron checks its downward movement, so that it tends to remain in the upper part of the profile.
Prairie soils are sometimes classed separately from the podsols. They form under climatic conditions similar to the gray-brown podsols but under grass instead of forest cover. Apparently the grass cover produces decomposition products of less potency than does the forest cover. The A horizon is extremely rich in organic material, and downward leaching is moderate. Long times are required to remove the exchangeable calcium and other ions, and there is little breakdown of the silicates. There is frequently considerable downward movement of colloidal silicates to form impervious horizons (pans) in the profile.

Laterite Soils. These soils develop under tropical conditions of high temperature and high rainfall that is often seasonal. The primary silicates are quickly broken down, and the extensive rainfall causes the quick removal in solution of any alkalies and alkaline earths. Iron tends to be oxidized, particularly under seasonal rainfall, and its movement along with alumina is retarded. The organic material is very rapidly oxidized so that it does not accumulate, and downward-seeping waters carry little organic acid. The downward-moving waters are almost neutral, or more often slightly on the alkaline side as a result of the presence of alkalies or alkaline earths from the primary silicates. Under such conditions of slight alkalinity the silica tends to be dissolved and removed, with attendant concentration of the alumina and ferric oxide in the upper part of the weathering zone.

Zonal Aridic Soils. In zonal aridic soil regions the rainfall is less than about 25 in./year, and the vegetative cover is grass or desert plants. There is little or no disintegration of the silicates or migration of the colloidal components. These soils are characterized by the movement of carbonate and by its concentration in some particular horizon. As the climate becomes drier, the zone of carbonate concentration gradually comes closer to the surface (Fig. 121).
Chernozem soils are found in areas of 12 to 25 in. of rainfall under grass cover and in a cool climate. Because of the cool climate, the organic material is oxidized very little, and a thick black surface horizon rich in organic material develops. There is little disintegration of the silicates, and leaching is very mild. The leaching removes the carbonates from the A2 horizon, and they are reprecipitated and concentrated in the B horizon.

The chestnut-brown aridic soils are found where rainfall is 10 to 15 in./year and the climate is warm. The vegetation is scant, and as a result the surface color is gray brown, instead of black as in Chernozems. Also the low rainfall permits slight leaching, and the horizon of carbonate concentration is close to the surface.

Gray or red desert soils develop under conditions of high aridity and in the general absence of a cover of vegetation. Because of the scant rainfall there is no downward leaching. The dominant movement of moisture through the soil is upward, owing to the dominance of evaporation, with the accumulation of carbonates and other salts at the surface.

Clay-mineral Composition of Soils. An early study of the clay-mineral composition of soils of various groups by Alexander, Hendricks, and Nelson indicated that kaolinite is the dominant clay-mineral component of red and gray podsolic soils, with illite frequently present but in quantities usually less than about 10 per cent. In Prairie soils both illite and kaolinite are usually present, with the former slightly the more abundant. Small amounts of montmorillonite are often present in the hardpan horizon of Prairie soils. In the series of Chernozem soils studies by these investigators, illite was the dominant component, and kaolinite and montmorillonite were also present in about equal amounts; and in a series of Desert soils from California, illite and montmorillonite were the dominant clay minerals.

Knox has recently made a compilation of the clay-mineral determinations reported in the literature for about 100 soils. Kaolinite was the only clay mineral reported in more than half of a total of over 20 red and yellow Podsols. In the remainder kaolinite was the dominant component, but small amounts of illite and montmorillonite were also reported. Kaolinite was reported as the dominant constituent in 6 out of 12 Gray Brown Podsols that have been studied. The remaining 6 Gray Brown Podsols are reported to contain illite and montmorillonite in varying amounts, as well as kaolinite. The analyses of 6 Planosols were reported in the literature, and they all contained montmorillonite. In all but one of the Planosols, illite was also present in about equal abundance with the

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42 Knox, E., personal communication.
montmorillonite, and in 2 of them small amounts of kaolinite were present also. A series of 3 Rendzina soils all showed illite, kaolinite, and montmorillonite, but in varying amounts. Kaolinite was the component of all the laterites whose clay-mineral composition was recorded.

The clay-mineral analyses of 15 Prairie soils were compiled by Knox, and illite is reported in 11, montmorillonite in 12, and kaolinite in only 4 of them. It seems clear from Knox's data that illite and montmorillonite are the characteristic clay minerals in Prairie soils.

Knox's work shows definitely the predominance of montmorillonite and illite in the soils of arid regions. Montmorillonite was recorded in all 7 Chernozem soils that have been reported. Illite is reported in 4 of the Chernozems, with small amounts of kaolinite in only 2 of them. Illite is reported as the only clay-mineral component in 5 out of 10 Solonetz soils that have been analyzed. Montmorillonite is reported in 5 of these soils and is the dominant component in 2 of them. No kaolinite was found in any of the Solonetz soils. In a series of 5 soils classed as White Alkali and Black Alkali, illite was present in all of them and was the only clay mineral in 3 of them. Montmorillonite was present in 2 of these alkali soils, and kaolinite was completely absent in all of them.

Recently Winters and Simonson have published compilations of data on the clay-mineral composition of the B horizon of the great soil groups which agree with the findings of Knox. According to them the composition of the B horizon of various soil groups is as follows: Tundra soils contain mainly mica and/or montmorillonite types of clay minerals; podsolic soils contain dominantly illite, with lesser amounts of montmorillonite and occasional minor amounts of kaolinite; lateritic soils are dominantly kaolinitic with minor amounts or none of the other clay minerals; Chernozem soils are largely composed of illite and montmorillonite; and Desert soils contain largely montmorillonite and illite clay minerals.

Investigations by Millot and by the author indicate that the palygorskite-sepiolite clay minerals are likely to be significant components of Desert soils.

A further generality of importance regarding soils is reported by Beavers. According to him, the organic material in many soils accumulates only up to a certain maximum amount. Additional quantities in excess of the equilibrium amount do not tend to persist. He has found that the attainable maximum may be relatively high for montmorillonite soils and that it is low for kaolinitic soils.

The authors refer to a 2:1 type of clay mineral, which would include chlorite, illite, vermiculite, and montmorillonite clay minerals.

Millot, G., Relations entre la constitution et la genèse des roches sédimentaires argileuses, "Geol. appliq. et prospe. min." vol. II, Nancy, France (1949).

Beavers, A. H., personal communication.
(Discussion of Weathering Products Formed from Various Types of Rock under Varying Conditions. Adequate information on the composition of soils, the specific influence of the various factors of weathering, and the environmental conditions favorable for the formation and occurrence of particular types of clay minerals is not available for complete and positive generalizations on the formation and occurrence of the clay minerals during weathering. However, the data are adequate for some generalizations which appear reasonably well established. These may be summarized as follows:

When a basic igneous rock contains considerable magnesium and weathers under conditions which, because of poor drainage or low rainfall, permit the magnesium to remain in the weathering zone after it is released by the breakdown of the parent mineral, montmorillonite will be the alteration product. If, however, because of high rainfall and good drainage, the magnesium is removed as soon as it is released from the parent mineral, kaolinite will be the weathering product. If the leaching of the magnesium is relatively rapid, montmorillonite will be an initial stage of weathering and kaolinite a later stage. Under long-continued weathering by processes removing magnesium, where such processes evolve in a cold, wet climate producing an abundance of organic acids (e.g., podsolic alteration) and hence a potent, acid, leaching environment, the clay minerals will ultimately be broken down, with the aluminum and iron carried downward and the silica concentrated near the surface. Under long-continued weathering by processes removing magnesium, but evolving in a wet, hot climate producing no organic acids and hence a neutral or slightly alkaline environment (lateritic alteration), the silica is carried away, and iron and alumina are concentrated at or near the surface.

An acid igneous rock containing considerable quantities of potassium as well as magnesium, under weathering conditions permitting the potash and magnesia to remain in the weathering environment after the breakdown of the parent minerals, will yield illite and montmorillonite as the alteration products. If the content of magnesium is low, illite will be the only product, and if the content of potash is low, montmorillonite will be the only product. Rapid removal of the potash and magnesia leads to the formation of kaolinite. The same sequence of events noted for long-continued weathering of the basic igneous rocks will apply to the acid igneous rocks. The other alkalies and alkaline earths which may be present appear to play a relatively minor role, except that there is a suggestion that calcium favors the formation of montmorillonite and that kaolinite does not form so long as there is any appreciable calcium in the environment.

It will be shown later that the clay-mineral components, and thus perhaps the chief silicate components, present in calcareous sediments
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(including dolomites) are illites and montmorillonites. In the weathering of calcareous sediments, there is substantially no alteration of the silicates until the carbonate is completely broken down and the calcium removed from the environment. After the removal of the calcium, alterations may be podsolic, with the development of a silica-rich surficial material, or lateritic, with the development of a zone of aluminum and iron concentration.

The weathering of a shale will progress about like that of the acidic igneous rocks. In the case of a calcareous shale, the calcium must be removed before there is any appreciable alteration of the primary silicates.

In the weathering of kaolin clays in which there is no appreciable content of alkalies or alkaline earths, there can be no formation of illite or montmorillonite, since potash and magnesia are necessary for their formation, unless some alkalies or alkaline earths are brought into the weathering zone, as, e.g., by the upward movement of moisture under hot, dry climatic conditions.

In summary, then, a significant condition in weathering is the presence of alkalies and alkaline earths, particularly potassium and magnesium, in the environment of alteration, and the length of time they remain in the environment after their liberation from the parent minerals. The kind of alkali or alkaline earth is also important, since potash leads to the formation of illite, magnesium to the formation of montmorillonite, and calcium probably to the formation of montmorillonite, with an added tendency to block the formation of kaolinite. Carbonate tends to retard the disintegration of the primary silicates.

The pH of the water moving through the soils is also important, particularly under conditions of active leaching and long periods of time. Under the latter conditions, acidity favors the removal of iron and aluminum and the concentration of silica, whereas neutral or alkaline conditions favor the accumulation of iron and aluminum near the surface.

Reversion of Weathering Cycle. A drastic change in the environment of alteration can lead to the regeneration of clay minerals or to the formation of clay minerals more characteristic of an earlier stage of weathering. Hardy et al.46 and Alexander et al.47 have shown that gibbsite developed in lateritic soils may be resilicated with the formation of kaolinite.

Regeneration of the clay minerals can be a result of man-made activities. Volk48 and Wood49 have shown independently that illite is formed

in soils under certain conditions as a consequence of the addition of potash fertilizers. Further, the formation of illite may take place quickly (in a matter of a year or so), illustrating the rapidity with which clay materials can adjust themselves to environmental changes.

Occurrence of Halloysite and Allophane in Soils. Several investigators have recorded the presence of halloysite in weathering products. Thus Bayley\textsuperscript{50} describes halloysite in some deep kaolins of North Carolina and ascribes its presence to weathering processes. Bates\textsuperscript{51} has confirmed the identification of halloysite in these same kaolins. Alexander \textit{et al.}\textsuperscript{52} and Allen\textsuperscript{53} have described weathering products which contain halloysite. Although the presence of halloysite in weathering products is well established, it is a rare component of such materials, and peculiar conditions must be required for its formation. Alexander \textit{et al.} state that plagioclase feldspar in a neutral or slightly acid environment and in the presence of water can weather to the hydrous form of halloysite.

Some few soil materials have been found by the author which contain considerable quantities of poorly crystalline or amorphous components. No detailed study has been made of these materials, and nothing is known of the conditions which determine their origin.

Nature of the Alteration Process. Correns and Engelhardt\textsuperscript{54} have concluded that weathering proceeds by the breakdown of the parent mineral to ionic solutions, and that secondary minerals are reaction products of such ionic solutions. Niggli\textsuperscript{55} states that, in the alteration of feldspar, under certain conditions, the breakdown reaches a colloidal state before the formation of the secondary products. Demolon and Batisse\textsuperscript{56} have concluded that in the weathering of a granite there is a spontaneous change to the clay minerals.

It is likely that the transition from a primary mineral or minerals to a clay-mineral weathering product does not always take place in exactly the same way. It can probably take place by means of the formation of ionic solutions with the later precipitation of the clay minerals, by the

\textsuperscript{50} Bayley, W. S., Kaolin in North Carolina, with a Brief Note on Hydromica, \textit{Econ. Geol.}, \textbf{15}, 236–246 (1920).
\textsuperscript{51} Bates, T. F., personal communication.
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formation of colloidal mixtures with later crystallization of the clay minerals, or by a direct structural change from the parent mineral to the clay mineral. The nature of the transition would depend on the parent mineral, the resulting clay mineral, and the environmental conditions. Thus kaolinite formed by the silication of gibbsite would perhaps be the reaction product of ionic or colloidal solutions and a solid, whereas the transition of muscovite and biotite to illite would almost certainly take place by a slight structural rearrangement without any breakdown to ionic or colloidal components.

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CHAPTER 14

Origin and Occurrence of the Clay Minerals (Cont’d)

RECENT SEDIMENTS

Only a very limited study has been made of the clay-mineral composition of sediments accumulating in various environments at the present time. Unfortunately many of the determinations that have been made are incomplete or are based on inadequate analytical data. Recent sediments frequently are composed of complex mixtures of relatively poorly crystallized minerals, and their analysis is particularly difficult. Unless the clay-mineral analyses are made by a combination of X-ray-diffraction, differential thermal, and chemical methods and unless the procedures are detailed, the completeness of the results is questionable. For example, the presence of montmorillonite in moderate amounts usually cannot be determined unless the X-ray analyses are supplemented by the glycol-treatment procedure. Nevertheless some trustworthy information is available on the clay-mineral composition of Recent sediments, and it is adequate for a preliminary consideration of diagenetic changes in clay minerals and of the relation of clay-mineral types to particular environmental conditions of accumulation.

Marine Environment. On the basis of their Challenger studies, Murray and Renard¹ suggested that the fine-clay fraction of the sediments accumulating on the present ocean floors was noncrystalline. At that time the idea that many clays were composed of amorphous components was widely held (see Chap. 2), largely because there were no adequate techniques available to study them.

Using modern analytical methods, Revelle² in 1936 and Correns³ in 1937 first showed that the fine-clay fraction of Recent marine sediments is substantially all crystalline. Correns³ and his colleagues found that mica (probably illite) was present in all the bottom samples collected by

¹ Murray, J., and A. F. Renard, Reports on Deep-Sea Deposits Based on Specimens Collected during the Voyage of H.M.S. Challenger in the Year 1872–1876, Challenger Reports (1891).
the *Meteor* in the South Atlantic. In addition to the mica, the clay fraction in some of the samples was composed predominantly of kaolinite, in others of halloysite, and in a few of montmorillonite. A map was presented showing the distribution of the predominant clay minerals, omitting from consideration the mica. Montmorillonite was found to be limited to relatively small regions where there were neighboring areas of basic volcanic activity. Correns himself pointed out that the differentiation of halloysite and kaolinite was not certain, and the presence of halloysite in Recent marine sediments has not yet been definitely established. It seems probable from his data that the sediments in the South Atlantic which he studied are chiefly mixtures of the illite and kaolinite types of clay minerals. Montmorillonite appears to be limited to certain areas, but this may be questioned; i.e., montmorillonite may be more widely distributed because of the great difficulty of detecting small amounts of this mineral by the techniques available when Correns did his work.

Some of the *Meteor* samples were cores, and Correns reported no variation in the clay-mineral composition of any of his cores from the top downward. He found no evidence of diagenetic changes in the clay-mineral components of his samples.

Leinz in a further study of the *Meteor* samples reported that all samples of Blue Clay showed mica and that most of them showed also a kaolinite type of mineral. Montmorillonite was found in some of the Blue Clay samples. All samples of globigerina ooze also contained mica, but only a few showed a kaolinite type of mineral reported as halloysite. Montmorillonite was also found in some of them.

Dietz determined the clay-mineral composition of 39 samples collected from various oceans of the world. Most of his samples were collected by the *Challenger*. Dietz found illite in all his samples, and it was the predominant clay mineral in 23 of them. Illite was particularly abundant in the deep-sea clays. Kaolinite, although generally less abundant than illite, was present in all the samples and predominant in 9 of them, most of which were relatively close to the shore. Small amounts of montmorillonite were found in the near-shore samples, but this mineral was not detected in most deep-sea sediments. Again it should be stated that adequate methods for detecting small amounts of montmorillonite in mixtures of poorly crystallized material had not been developed when Dietz did his work.

Dietz presented strong evidence for the development of illite on the
sea floor in sediments accumulating at the present time. It was his concept that the illite develops largely by the alteration of montmorillonite from the source material being carried to the sea.

Revelle's study of the Carnegie samples showed the finest clay fraction to be crystalline, but unfortunately his analytical data did not permit a positive identification of the predominant clay minerals. In a few samples kaolinite or halloysite was identified definitely, but most of the samples were said to be composed largely of a "beidellite-like" clay mineral. From Revelle's data it appears certain that most of his samples were mixtures of clay minerals, and that in many, if not most of them, illite was the predominant clay mineral.

Bramlette and Bradley made no serious attempt to determine the clay-mineral components in their study of the samples collected by the Lord Kelvin in the North Atlantic. They pointed out that the clay fraction possessed optical properties similar to those of beidellite or hydrous mica, and from their data it appears probable that their clay samples were a mixture of clay minerals and that illite was an important component in many, if not all of them.

Keunen obtained X-ray-diffraction data for the clay fraction of a few of the samples collected by the Snellius in the Netherlands Indies area. He found muscovite (probably illite), kaolinite, and montmorillonite in each of the samples investigated. The relative amounts of the clay minerals varied in the different samples, but too few samples were studied to permit any correlation of clay-mineral composition with type of sediment or oceanographic conditions.

Grim, Dietz, and Bradley studied a series of samples collected by the E. W. Scripps from the Gulf of California and the Pacific Ocean off the California coast. They found that all the samples contained illite, montmorillonite, and kaolinite and that generally illite was the most abundant and kaolinite the least abundant clay-mineral type. A chloritic clay mineral could be identified definitely in some samples. The clay minerals were very complex mixtures, including mixed crystallizations as well as mechanical mixtures of discrete phases. In general the crystallinity was lower, the individual size smaller, and the intergrowth more intimate in

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Origin and Occurrence of the Clay Minerals

these Recent sediments than in ancient sediments which these authors have studied.

Grim and his colleagues conclude from their data that kaolinite is very slowly being lost in these marine sediments, probably by alteration to illite or chloritic mica. They postulate that potassium is being taken up by the accumulating sediments mostly by "degraded illite," which is illite which reaches the environment of deposition with a relatively low potassium content as a result of weathering processes, and that magnesium is also being taken up by the accumulating sediments, probably in the formation of illite or chloritic micas. The widespread occurrence of montmorillonite indicates that this clay mineral is not lost completely or quickly in diagenetic processes.

Diagenetic Processes. The marine environment is alkaline; there is no leaching; and the water contains a good deal of dissolved calcium. These environmental conditions favor the formation of a montmorillonite, illite, or chloritic clay mineral rather than kaolinite. Millot has recently presented evidence from a study of the composition of many sediments to show that the presence of Ca++ tends to block the formation of kaolinite. A study of weathering processes indicates that kaolinite does not form from calcareous parent material until all the carbonate has been removed.

Correns pointed out that in environments in which the pH is less than 5, silica is insoluble and \( R_2O_3 \) is relatively soluble. At pH values from 5 to 9, the \( R_2O_3 \) is very slightly soluble and the silica becomes more and more soluble; and at pH values above 9, silica and alumina are both soluble. Therefore, at low pH values, there would be little silica in solution, and kaolinite is likely to be the stable form, whereas at higher pH values with much silica in solution, the clay minerals with higher proportions of silica to \( R_2O_3 \) are likely to be the stable form.

Millot has shown that silica sols are relatively stable and that a considerable cation content is necessary for flocculation, whereas alumina sols are not very stable, being flocculated by a relatively low cation content. Therefore, according to Millot, in an environment of low cation content, there would be a relatively large amount of available alumina with a consequent clay mineral of low silica-to-alumina ratio, e.g., kaolinite. In an environment of high cation concentration, the available silica would be relatively high, because of the flocculation of the alumina, with a consequent clay mineral of high silica-to-alumina ratio, e.g., montmorillonite.

The land-derived muds carried into the sea from many areas probably consist to a considerable extent of degraded illite, degraded chloritic mica.

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and kaolinite. The degraded minerals represent material that has been partially leached of its constituent alkalies and alkaline earths, but not sufficiently to transform it into new minerals. Such degraded minerals would have deficiencies of alkalies and alkaline earths and would quickly adsorb available potassium and magnesium with an attendant increase in the perfection of the mica structures. It seems likely that such reconstitution of the micas is a most important diagenetic change and one which would take place quickly.

It seems certain that chloritic mica and illite also tend to form during marine diagenesis from other minerals. Thus illite probably forms from montmorillonite; chloritic material appears to develop from kaolinite and possibly also from montmorillonite; and glauconite forms from a variety of raw materials. It seems that these changes, which may represent major alterations in atomic structures, would take place relatively slowly. Thus, the diagenetic alteration of kaolinite may be so slow that it frequently persists in varying amounts into ancient marine sediments.

Marine conditions vary from oxidizing to reducing, depending on the topography of the ocean floor and hence on water movement, on the rate of sedimentation, and perhaps on other factors. It is not known exactly how the variation from oxidizing to reducing conditions would influence diagenetic processes. Perhaps oxidizing conditions, by tending to fix the $R_2O_3$ in a relatively inert form, would retard diagenetic changes.

Variations in the concentration of potassium and magnesium would also affect diagenesis. Deficiencies of the alkalies and alkaline earths would retard the formation of the micas. Diagenetic changes would be expected to be most intense near shore, where the sediments first encounter the marine environment.

The nature of the marine environment and diagenesis are such that variations in the character of the source material might be reflected in the sedimentary accumulation. For example, a kaolinitic marine sediment means a kaolinitic source area, since kaolinite is not formed in the sea. Also it means relatively rapid accumulation with the persistence of kaolinite through an environment fundamentally unfavorable for it.

A completely micaceous marine sediment means a source area producing little kaolinite, or possibly extremely slow accumulation. It seems likely that source material containing a considerable amount of kaolinite would give rise to a marine sediment in which at least some kaolinite persisted.

Glauconite. Glauconite is a rather unique illite type (see page 68) of clay mineral that is formed during marine diagenesis. Many investiga-

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tors have recorded the frequent association of glauconite with organic residues, and it has been generally concluded that the presence of organic material is necessary for the formation of the mineral.

Galliher\(^{13}\) has shown that some glauconite has formed as an alteration product of biotite, with the alteration taking place under reducing conditions and slow deposition. Unless deposition is slow so that alteration takes place before burial, the biotite mica persists. Hendricks and Ross\(^{14}\) have reviewed the literature which shows that minerals other than biotite may alter to glauconite in a marine environment.

Hadding,\(^{15}\) who made an extremely complete study of glauconite, showed that glauconite occurs in flakes and as pigmentary material, in addition to the well-known large rounded pellets. According to Hadding, glauconite forms in the shallow sea in agitated waters which are not highly oxygenated. It forms during times of decreased deposition of detritus and often during negative sedimentation. Revelle\(^{2}\) has also emphasized that glauconite is currently forming off coasts lacking important rivers, where deposition is slow.

Hendricks and Ross,\(^{14}\) after a careful study of the variation in the composition of glauconites, concluded that the mineral is formed in a reducing environment maintained by bacterial action. The environment probably remains unchanged for long intervals of time. The very uniform content of magnesium and the rather constant ratio of Fe\(^{3+}\) to Fe\(^{2+}\) indicate that a critical content of magnesium and a particular oxidation-reduction potential might be required for the mineral to form. The ratio of Na\(^+\) to K\(^+\) in interlayer positions in the structure of glauconite is rather distinctive, suggesting that a certain concentration of these ions may be required for its formation.

In summary, glauconite forms during marine diagenesis, at times of slow or negative sedimentation, and in relatively shallow water. In addition, peculiar reducing conditions and particular concentrations of magnesium and alkalies seem to be essential for its formation.

Nonmarine Conditions. Lacustrine. The paucity of clay-mineral data for Recent nonmarine sediments is so great that few conclusions can be reached. Cuthbert\(^{16}\) has shown that illite is the dominant clay mineral in sediments accumulating in Lake Erie.

It would seem that there would be few diagenetic changes in fresh-

water lake sediments and that the sediments would reflect the source material supplied to the lake. Lacustrine environments in which there is any appreciable movement of water through the sediments, with some consequent removal of alkalies and alkaline earths, would be expected to show the development of kaolinite as a diagenetic mineral. As a general thing, lakes in which there is no accumulation of lime would probably show a tendency toward the development of kaolinite. In lakes where lime is accumulating, the lime would tend to block the formation of kaolinite, and any diagenetic changes would probably be very slight.

In salt lakes, the montmorillonite and illite clay mineral would form at the expense of whatever material was supplied. Investigations by Longchambon, Millot, and unpublished work by the author have shown that the sepiolite-attapulgite minerals are frequently found in Recent sediments accumulating in dry desert basins. Probably a particular composition, chiefly in regard to the abundance of magnesium, leads to the formation of these minerals.

Rivers. Holmes and Hearn have investigated the clay-mineral composition of Recent alluvium deposited by the Mississippi River and its tributaries, with the results shown in Table 46.

<table>
<thead>
<tr>
<th></th>
<th>Kaolinite</th>
<th>Montmorillonite</th>
<th>Illite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern tributaries:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ohio, Cumberland,</td>
<td>10-20</td>
<td>10-15</td>
<td>65-75</td>
</tr>
<tr>
<td>Tennessee, Duck,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and Clinch Rivers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mississippi River</td>
<td>5-15</td>
<td>25-45</td>
<td>40-60</td>
</tr>
<tr>
<td>Western tributaries:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milk, Yellowstone,</td>
<td>10-20</td>
<td>20-45</td>
<td>40-60</td>
</tr>
<tr>
<td>Missouri, Platte,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and Arkansas Rivers</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Values given are percentages.

The clay minerals in fluviatile sediments should reflect the composition of the soils from which they are derived. In the data of Holmes and Hearn, there is a relatively larger amount of montmorillonite in the western tributaries of the Mississippi River, which derive their material from dry areas which favor the formation of montmorillonitic soils.

Origin and Occurrence of the Clay Minerals

In rivers themselves one might expect a certain amount of leaching action, and if this is the case, kaolinite would tend to develop. Otherwise any diagenetic changes would probably be insignificant.

Glacial Deposits. A considerable study of the composition of the glacial deposits in North America has been made by students of soils. In unweathered till and loess, the dominant clay mineral is illite, frequently with considerable amounts of chloritic mica. Kaolinite and montmorillonite are occasionally present in small amounts.

The composition of varved glacial lake sediments is not well known, but Cooling\(^{18a}\) has shown that, in at least some varved sediments in Canada, illite is the dominant clay mineral, with montmorillonite also present in the dark layers but not in the light layers.

ANCIENT SEDIMENTS

The clay-mineral composition of sediments of widely varying modes of origin, types, and geologic age has been determined. Unfortunately many of these analyses are incomplete in that only the most abundant clay minerals were determined. However, sufficient trustworthy analytical data are available for a first approximation to the relation of clay-mineral composition and sediments of various modes of origin and of various lithologic types.

Clay-mineral Composition in Relation to Mode of Origin. Millot\(^{18}\) has recently presented thorough clay-mineral analyses of a large series of sediments from eastern France and the adjacent sections of Germany and Switzerland whose mode of origin is well established on paleontological and stratigraphic evidence. In sediments of marine origin, Millot found illite invariably present, making up from 50 to 100 per cent of the total clay-mineral content. The illite was particularly abundant in calcareous marine sediments, in which it made up from 70 to 100 per cent of the total clay-mineral content. Kaolinite was often present and made up from 0 to 50 per cent of the clay-mineral content. Millot emphasizes the point that calcareous sediments are likely to have little or no kaolinite and that calcium tends to inhibit the formation of this clay mineral. Pyritiferous marine sediments were particularly likely to contain appreciable kaolinite. Chloritic mica and vermiculite were frequently present as minor constituents.

In 26 sediments of lagoonal origin, illite was found to be the dominant clay mineral in 19, montmorillonite in 4, and attapulgite-sepiolite in 3. Chloritic mica and vermiculite were frequent minor clay-mineral components. Kaolinite was completely absent in 19 samples and in no case

\(^{18a}\) Cooling, L. F., Personal communication.
totaled more than 30 per cent of the clay-mineral content. It is probable that the sediments containing attapulgite-sepiolite represent lacustrine rather than lagoonal conditions.

In sediments of lacustrine origin where the lake is believed to have contained "aggressive" water, i.e., where there was actual leaching of alkalies and alkaline earths in the accumulating sediments because of active movement of water through them, or because of relatively low pH of the water, the dominant clay mineral is kaolinite. In such sediments the total content of illite, chloritic mica, and montmorillonite ranged from 0 to 30 per cent.

In sediments of lacustrine origin of the "nonaggressive" type, where salts and carbonate are likely to accumulate because of slight movement of water through the lake and/or relatively alkaline water, the dominant clay-mineral components are illite, montmorillonite, and sepiolite-attapulgite. The latter type of clay mineral is particularly prevalent in sediments that have accumulated in dry desert lakes.

Clay Minerals in Relation to Geologic Age. Analyses of many ancient sediments in the author's laboratory from the United States and elsewhere have shown that montmorillonite is generally absent in sediments older than the Mesozoic. Except for a few beds of probable bentonitic origin, montmorillonite has not been reported in the older sediments. This point is of particular importance, for montmorillonite is abundant in many Mesozoic and Cenozoic sediments, in Recent marine sediments, and in present-day weathering products.

It seems likely that metamorphic processes would cause the alteration of montmorillonite to a mica type of mineral, and, therefore, the mineral would tend to disappear in more ancient sediments. When the structure of montmorillonite is completely collapsed so that all the water is removed from between the unit layers, rehydration of the mineral is difficult, and the mineral has many of the attributes of mica. Further in the course of geologic time, montmorillonite would probably slowly pick up potassium and magnesium from ground waters, which might in turn obtain such constituents from the disintegration of ferromagnesian minerals and feldspars. The adsorption of potassium and magnesium would favor a shift to a mica type of mineral. Thus in the course of time, because of dehydration due to compaction, montmorillonite would tend to be altered in the direction of the micas.

There is, however, another aspect to this problem of the absence of montmorillonite in ancient sediments. It appears that certain times and certain places in the geologic past have been either particularly favorable or particularly unfavorable for the formation of montmorillonite. Thus, the Cretaceous formations of the Great Plains and the Gulf Coast of the United States contain large amounts of bentonite and montmorillonitic
Montmorillonite is developing in many soils widely scattered over the land today, and hence the argillaceous material carried to areas of accumulation at the present time generally has a fairly large content of montmorillonite. Recent sediments, therefore, have a fairly high montmorillonite content. This probably was not always the case in the geologic past. An interval of geologic time without much volcanic activity, without large areas of relatively low rainfall, and/or with large areas of lateritic weathering would produce little montmorillonite. Thus, because of variations of weathering conditions and/or volcanic activity, either on a world-wide scale or in restricted areas, montmorillonite would be expected to be absent or abundant in sediments of a particular geologic interval or of a particular geographic area.

There is a suggestion from available data that kaolinite also is less abundant in very ancient sediments than in those deposited after, say, the Devonian. Kaolinite may therefore be lost in ancient sediments, because of metamorphic processes complemented by adsorption of alkalies and alkaline earths, with the formation of micas. This would be expected to be a much slower process than the alteration of montmorillonite to the micas.

Since kaolinite is formed during weathering under certain conditions and not under others, it would be expected that ancient sediments of a particular age and/or from a particular area might have either a flood of kaolinite or none of it.

Since montmorillonite and kaolinite tend to disappear in sediments of increasing age, it follows that very ancient sediments must be composed largely of the illite and chlorite types of clay minerals. Attapulgite-sepiolite also appears restricted to relatively young sediments. No information is available on the distribution of vermiculite in sediments. Halloysite is generally absent in sedimentary rocks, except possibly in association with some coals. It has been suggested that the halloysite minerals would change under metamorphic processes to kaolinite, but there are no specific data on this point.

**Clay Minerals in Relation to Lithology.** Shales. The dominant clay mineral in many, probably most, shales that have been studied is illite. Chloritic mica is frequently present, and montmorillonite is a common component in many shales of Mesozoic or younger age. Kaolinite is a common component of some shales, but usually in minor amounts.
shales of relatively high kaolinite content, the lamination is frequently not well developed.

_Slates._ The mica clay minerals are the dominant components in the slates that have been studied. Fairbairn\(^1\) reports kaolinite in some slates and finds that kaolinitic slates have relatively low schistosity.

It appears that the illite and chloritic clay minerals in the slates have a higher crystallinity than these same clay minerals in clays. This means that the clay minerals are composed of layer units more regularly oriented and with fewer structural defects. The increased crystal perfection developed in the metamorphism of illite yields a material approaching muscovite or biotite, depending on the original composition and structure of the illite.

No montmorillonite, attapulgite-sepiolite, or halloysite clay minerals have been reported in slates. Vermiculite may occur in some slaty materials, but it is usually difficult to establish that it is not an alteration product.

_Clays._ Material which can be classed as clay has been described containing each of the clay minerals in substantially pure form. Except for mixtures of kaolinite with sepiolite-palygorskite, any combination of the various clay minerals has been described in such sediments.

_Underclay._ Many beds of coal, particularly of Carboniferous age, the world over are immediately underlain by a nonbedded carbonaceous clay characterized by many small slickensided fracture surfaces. Such material, frequently called underclay, contains either kaolinite or illite, or a mixture of these clay minerals. Occasionally the underclay is calcareous, and then illite is usually the only clay-mineral component.\(^2\)

Brindley and Robinson\(^2\) have shown that the English underclays contain kaolinite of the poorly crystalline variety. The kaolinite in the plastic underclays in Illinois is also the poorly crystalline variety. In several instances very small amounts of dickite\(^2\) have been identified in underclays. This dickite could not have had the usual hydrothermal origin for the mineral, and its genesis is obscure.

_Flint Clay._ Flint clay is a dense, hard, nonslakable, massive, nonplastic clay with flint-like characteristics. Flint clay is frequently associated with underclays, but other occurrences, as, e.g., in association with the diaspore clays of Missouri (see page 365), are also known. The


flint clays that have been studied in detail are composed of well-crystal-
ized kaolinite in extremely small particle sizes. Sometimes excess silica
or alumina is present and may serve to cement the kaolinite particles
together. In many cases, however, the precise factors which give flint
clays their distinctive physical properties have not been established.

Limestones and Dolomites. An analysis of 35 Paleozoic limestones from
Illinois showed illite in all of them. Kaolinite in small amounts was
present in about half of them. No montmorillonite was determined in
these limestones, but the analyses were made before the development of
the glycol method for the determination of montmorillonite, and small
amounts of this clay mineral would probably have been missed.

The determination of the clay minerals in limestones and dolomites is
particularly difficult since it is frequently necessary to dissolve away the
carbonate in order to concentrate the clay minerals to get adequate
analytical data, and some of the clay minerals themselves are fairly
soluble in acid (see pages 296–299).

Coal. Hicks and Nagelschmidt showed that a two-layer mineral was
the dominant clay mineral in English coals and that this mineral appeared
to be halloysite in the anthracites and kaolinite in the bituminous coals.
This relationship is difficult to understand, since it is contrary to the
usual concept of the transition of halloysite to kaolinite by metamorphic
action. Some illite is also present in the English coals. The clod and
roof shale of the coals is largely composed of illite containing some sodium
in interlayer positions. Nagelschmidt found that the sodium content of
the illite decreased from about 1.8 to 0.6 per cent with a decrease in the
rank of the coal.

Endell and Endell have shown that illite is the dominant clay mineral
in the German coals. Their analytical data indicate that there is no sub-
stantial change in the clay-mineral component with the rank of these coals.

In Illinois coals, Ball found that kaolinite was the dominant clay
mineral in the coal, both in fractures and cavities and in the coal itself.
A relatively small amount of illite is usually present also in these coals.

Salines. Unpublished work by the author and studies by Millot and
De Lapparent show that the sepiolite-palygorskite-attapulgite minerals
are frequent in the argillaceous sediments associated with salines.

23 Grim, R. E., J. E. Lamar, and W. F. Bradley, The Clay Minerals in Illinois Lime-
stones and Dolomites, J. Geol., 45, 829–843 (1937).
24 Hicks, D., and G. Nagelschmidt, The Chemical and X-Ray Diffraction Analysis
of the Roof and Clod of Some South Wales Coal Seams and of the Mineral Matter in
Coal, Med. Research Council (Brit.) Special Rept. 244 (1943).
25 Endell, K., and J. Endell, Ueber die Bestimmung der Röntgenfeinstruktur
mineralischer Bestandteile von Kohlen und Aschen sowie ihre technische Bedeutung,
Feuerungstechn., 31, 137–143 (1943).
Montmorillonite and illite clay minerals are also common. Frequently the clay minerals in such sediments are poorly crystallized, and their precise identification is difficult.

Kuhn\(^{27}\) has studied the composition of the Zechstein salt in Germany and has found that illite is the dominant clay-mineral component. He believes the mineral to be of diagenetic origin. He reports also that the crystallinity of the illite is quite low in these sediments.

Till. Any of the clay minerals may be found in glacial till, depending on the character of the source material, since there is likely to be substantially no alteration of the clay minerals during transportation and deposition. Older tills might be expected to have a relatively higher mica content, because later metamorphic changes probably would be in the direction of the formation of well-crystallized micas from any degraded mica or montmorillonite. It seems likely that kaolinite would tend to persist unless the tills were very old or had been metamorphosed substantially.

The Pleistocene till of North America has been extensively studied, and illite is the dominant clay mineral in it. Chlorite, montmorillonite, and kaolinite are frequently present, but of subordinate importance.

Gumbotil, a weathering product of till found at the surface of some pre-Wisconsin tills in North America, contains illite, with considerable amounts of montmorillonite and occasionally more kaolinite than the normal till. It also has a higher clay-mineral content than the unweathered till as a consequence of the concentration of colloidal material by downward-moving waters.

*Fuller's Earth.* This name is used for any natural earthy material which will decolorize mineral or vegetable oils to a sufficient extent to be of economic importance. The name as generally used at the present time has no genetic or mineralogical significance. An exception is the use of the term in England as a stratigraphic term for certain beds long used as commercial bleaching clays. Fuller's earths are known which are composed of attapulgite,\(^{28}\) montmorillonite,\(^{29}\) and kaolinite.\(^{30}\) Some fine silts of relatively low clay content have high decolorizing ability. On the other hand there are many silts and clays composed of montmorillonite and kaolinite and possibly also of attapulgite which are not fuller's earths.


Miscellaneous Clay Materials. Under this heading will be considered the origin and occurrence of clay minerals in argillaceous materials of unique origin or whose origin is not well established.

Bentonite. The term bentonite was first applied by Knight to a particular, highly colloidal, plastic clay found near Fort Benton in the Cretaceous beds of Wyoming; it has the unique characteristic of swelling to several times its original volume when placed in water, and it forms thixotropic gels with water even when the amount of bentonite in such gels is relatively small. It was subsequently shown by Hewett that this clay was formed by the alteration of volcanic ash in situ. Later, Ross and Shannon studied a number of clays which had been formed by the alteration of ash and redefined the term bentonite to limit it to clays produced by the alteration of volcanic ash in situ. They pointed out that such clays are largely composed of montmorillonite clay minerals and that they are generally highly colloidal and plastic. The term as now used by many mineralogists and geologists has no reference to the physical properties of the clay.

Until about 1930 bentonite was known in few places outside of the original Wyoming area, and until about 1940 the term bentonite, especially in industrial usage, was synonymous with the Wyoming material. Even today (1951) the term bentonite to most people, other than some mineralogists and geologists, carries with it the connotation of a highly plastic, colloidal, swelling clay. Also, today the term is used frequently for clays with these properties without reference to a particular mode of origin. Thus, montmorillonite clay from the Island of Ponza, Italy, is generally called bentonite and sold commercially as such, even though it is apparently of hydrothermal origin.

Because of the high commercial value of bentonite, a search for it has been made in all quarters of the globe since about 1930, and now clays composed largely of montmorillonite and formed by the alteration of volcanic ash in situ have been found in almost all countries and in rocks of a wide variety of ages. Bentonites are particularly widely distributed in the Tertiary, as, e.g., in California and the Gulf Coast states of the United States, in Italy, and in New Zealand. Bentonites are also very widely distributed in the Upper Cretaceous, as, e.g., in the Gulf Coast and High Plain states of the United States, in England, in Germany, and in Canada. Beds older than the Cretaceous appear to contain little bentonite. Some so-called metabentonite has been found in the Paleozoic rocks (e.g., the Ordovician of Illinois and of the Appalachian states). In

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31 Knight, W. C., Bentonite, Eng. Mining J., 66, 491 (1898).
such metabentonite the montmorillonite usually has been almost completely collapsed by compaction and metamorphism, so that the mineral swells very little and the clay does not have the usual high colloidal properties of bentonite.

Usually the volcanic-ash parent material of bentonites can be detected by the persistence of shared structures of the ash as pseudomorphs in the clay. Also the presence of a suite of nonclay minerals, such as feldspars, biotite, hornblende, etc., characteristic of igneous material, may provide evidence for the origin from ash.

Beds of bentonite vary in thickness from a fraction of an inch up to many feet. Rarely are beds thicker than about 10 ft, but a few are known which reach a thickness of 50 ft. The clay called bentonite which has a hydrothermal origin is found in irregular masses without any bedding. Bentonite varies in color from white to gray, yellow, green, blue, and black but is perhaps most often yellow or yellowish green. Frequently a yellow color develops on the weathered outcrop, and the weathered material may have physical properties quite different from these of the fresh material. Also the weathering outcrop frequently develops a characteristic cellular structure, because of the swelling and shrinking on wetting and drying, which permits it to be recognized easily in the field. The bentonite frequently has a characteristic waxy appearance when freshly dug. On exposure to the air, it often develops a characteristic “jigsaw puzzle” set of fractures accompanying the shrinking on drying.

Bentonites interbedded with shales, limestones, and sands are known. Perhaps most frequently it is found in a section of marine beds. Often the bentonite is immediately underlain by a hard siliceous bed in an association that suggests that there has been an enrichment of silica in the underlying bed accompanying the formation of the bentonite.

As stated above, the dominant clay-mineral component of bentonites is montmorillonite. Other clay minerals, particularly illite and kaolinite, are present in many bentonites, sometimes in amounts up to about 50 per cent of the total clay-mineral content. Nonclay minerals characteristic of igneous material as well as of detrital origin are also present in varying amounts. Some bentonites are substantially pure montmorillonite, but rarely is there less than about 10 per cent of nonclay minerals. Cristobalite is frequently present in varying amounts up to about 30 per cent of the total rock. This mineral is often intimately mixed with montmorillonite and is very difficult to identify, so that it has certainly been missed in many clay-mineral analyses of bentonites. It undoubtedly has formed from the ash at the same time as the mont-

Gruner, J. W., Abundance and Significance of Cristobalite in Bentonite and Fuller’s Earth, Econ. Geol., 35, 867–875 (1940).
morillonite. In a few cases zeolites are found in bentonites intimately mixed with the montmorillonite.

The composition of the montmorillonite itself varies greatly in different bentonites, as has been shown in detail by Ross and Hendricks. The variation may be within the montmorillonite lattice itself or in the nature of the exchangeable cations. There is considerable variation in the relative abundance of magnesium and iron and also apparently in the $R_2O_3$-to-silica ratio. That is to say, there is considerable variation in the population of the silica layer. With regard to exchangeable cations, most bentonites that have been described carry $Ca^{++}$ as the most abundant ion. Only a few are known which carry $Na^+$ as the dominant ion, and of these the Wyoming bentonite is the main example. Also only a few bentonites have been reported that carry $H^+$ or $K^+$ as the dominant ions. $Mg^{++}$ is frequently present as an exchangeable ion in relatively small amounts, and this is particularly the case when $Ca^{++}$ is the dominant ion.

The geologic column contains many beds of volcanic ash which have not altered to bentonite. In order for bentonite to form, it is probably necessary for the ash to fall in water. The kind of water, i.e., fresh or saline, undoubtedly is important in determining whether bentonite forms at all and, if it does, the precise character of the resulting montmorillonite. Since much bentonite is associated with marine formations, it seems certain that the alteration can take place in sea water. Whether or not the alteration can also take place in even more saline waters or in fresh water is not known definitely. The composition of the ash is also an important factor. Apparently the ash must have a moderate content of $MgO$, since ash devoid of magnesia does not seem to alter to montmorillonite.

The evidence strongly indicates that the alteration of the ash to montmorillonite takes place soon after accumulation or possibly almost contemporaneously with accumulation. It does not seem, at least in most cases, to be a later process and certainly is not a weathering process. The Cretaceous bentonites in Mississippi frequently grade upward without a break into glauconitic sands. The basal parts of these sands contain rounded masses of bentonite, indicating that the bentonite was already formed when the sand began to accumulate.

The process of formation of the montmorillonite is essentially a devitrification of the natural glass of the ash and the crystallization of the montmorillonite. The ash probably in most cases contains an excess

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of silica and alkalies. The silica in some cases undoubtedly remains in
the clay and gives rise to the cristobalite. Also the excess silica is prob­
ably the source of the free silica in the hard siliceous beds immediately
underlying many bentonites. The excess alkalies and alkaline earths
are probably carried away in solution in the water in which the ash fell.
The population of the exchangeable-cation positions would be a conse­
quence of the composition of the original water and the alkalies and
alkaline earths from the ash which dissolved in it.

Bentonites possess important and unique properties which give them
great commercial value in decolorizing oils, in the manufacture of
catalysts, in bonding molding sands, in the preparation of oil-well drilling
muds, and in many other relatively minor uses. The properties of
individual bentonites vary widely, and not all of them are suitable for
commercial use. Also many bentonites have properties fitting them for
one particular use, whereas they cannot be used at all for other purposes.
Thus, the Wyoming type of bentonite is excellent for drilling muds and
foundry use but is of no value for oil decolorizing or the making of
catalysts. Similarly, some bentonites from Mississippi are good for
decolorizing clays and for foundry use but are of no value for drilling
muds. The cause of the variation in properties fundamentally resides
in the composition of the montmorillonite itself and in the character of
the exchangeable ions. Much remains to be learned of the factors con­
trolling the properties of bentonites, and the subject cannot be pursued
at any length here. However, some examples of pertinent correlations
between properties and composition can be given. The very high swell­
ing and highly colloidal bentonites carry Na+ as the principal exchange­
able cation. The Wyoming bentonite is an example of such a bentonite.
That the presence of Na+ is not the sole cause of the properties of the
Wyoming clay is shown by the fact that other clays treated so that they
will carry Na+ as the exchangeable cation do not fully develop the prop­
erties of the Wyoming material. Another cause for the relatively unique
properties of the Wyoming bentonite must reside in some feature within
the montmorillonite lattice composing it.

Bentonites with montmorillonite low in iron are required for catalyst
manufacture. Decolorizing clays are usually those carrying Ca++
and/or Mg++ as exchangeable cations. Again, the montmorillonite
itself must be important, for good decolorizing clays cannot always be
prepared by a simple ion-exchange reaction. Montmorillonite clays
carrying either Na+ or Ca++ are suitable for foundry molding-sand use,
but they have quite different properties in such sands. Thus a sodium
montmorillonite provides relatively high dry strength and lower green
strength, whereas calcium montmorillonite gives high green strength
and lower dry strength.
**Highly Aluminous and Ferruginous Clays.** It is not proposed in this work to discuss in detail the highly aluminous or ferruginous material, such as bauxites and laterites, since adequate volumes on these subjects are already available. The usual clay mineral associated with deposits of the oxides or hydroxides of aluminum and iron is kaolinite. Halloysite has been reported in some high-alumina clays, but the halloysite may have been confused with poorly crystalline kaolinite. There appears to be kaolinite of two modes of origin in such materials: one which has formed prior to the development of the hydrates and is the parent material from which much of the aluminum hydrate has developed, and another which has formed after the development of the aluminum hydrates by the reaction of silica with such hydrates.

A particularly distinctive type of high-alumina clay is the diaspore and burley clay of Missouri, in which kaolinite is associated with diaspore. The origin of these clays is not entirely clear, but in general terms they seem, as suggested by MacQueen and Allen, to have formed by some kind of leaching action associated with the development of the sinkholes in which they are found. The genetic relation of the kaolinite to the diaspore is not clear.

**Indiana-type Halloysite Deposits.** The deposits of halloysite near Bedford in Indiana, first studied by Logan and later in great detail by Callaghan, typify an occurrence of halloysite known in several other places. The halloysite occurs as lenses and cavity fillings at the contact of the Mansfield sandstone of Pennsylvanian age with the underlying Chester clastics. According to Callaghan, the halloysite was precipitated from solution from ground water which derived its alumina and silica from the residual soils on the Chester beds. The formation of the halloysite was post-Mansfield. The waters were believed to be acid in nature because of a sulfate content which was derived from the oxidation of pyrite in the Mansfield sandstone.

The halloysite is relatively pure in some places but is often mixed with a good deal of alunite. Also the clay sometimes contains P₂O₅ (10% ±)

References:

Clay Mineralogy

in a mineral structurally similar to alunite. Some of the halloysite contains allophane as an additional component.

**Supergene Kaolinite Deposits.** Occurrences of supergene kaolinite are frequently found associated with metalliferous sulfide ore bodies. Such clays are developed during the downward movement of acid water produced by the oxidation of the sulfides. The conditions of origin of such clays would seem to be quite similar to those of the Indiana-type halloysite noted above. It is not known why halloysite is produced in one case and kaolinite in the other.

**Igneous Clay Minerals.** A few occurrences of clay minerals in igneous rocks have been described which suggest that some clay minerals can occur as primary igneous components. Thus Rosetti has described an association of anauxite and cristobalite in the spherulites of a rhyolite from Sardinia which seems to have this origin. Prider and Cole have described some clay minerals in a lamproite from West Kimberley, Australia, which they believe are of late magmatic origin.

It is manifestly difficult to distinguish with certainty between clay minerals of hydrothermal origin and those of possible igneous origin. There seems to be no reason why the clay minerals could not be formed directly in some igneous rocks.

**ADDITIONAL REFERENCES**

*Recent Sediments*


*Ancient Sediments*


Origin and Occurrence of the Clay Minerals


Sedletsky, I. D., Mineralogical Composition of Clays and Their Genesis, *Soviet Geol.*, 8, 82–89 (1940).


Bentonites


A vast number of chemical analyses of clay materials have been published. In many cases no attempt was made to determine the mineral composition of the material analyzed, or the material is clearly a mixture of minerals. There are, however, many analyses of materials whose clay-mineral composition is well established and which seem to be monomineral. In the tables to follow an attempt is made to present a sampling of these analyses. The objective has been to show the spread of the composition of the various clay minerals so that their range in composition is illustrated.

In the case of the vermiculite and chlorite minerals, there are substantially no data available for clay-mineral specimens, and the data given are for larger specimens.
Table A. Chemical Analyses of Kaolinite Minerals

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Kaolinite

1. Zettlitz, Czechoslovakia
2. Mexia, Texas
3. Macon, Georgia
4. St. Austell, England
5. Anna, Illinois

Analyses 1, 2, 6, and 7 from C. S. Ross and P. F. Kerr, U.S. Geol. Survey Profess. Paper 165E (1931); 3 and 4 from P. F. Kerr et al., Rept. 7, American Petroleum Institute Project 49 (1950); 5 from R. E. Grim, Econ. Geol., 29, 659-670 (1934).

Table B. Chemical Analyses of Nacrite, Dickite, and Halloysite

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Nacrite

1. Brand, Saxony
2. Anglesey, Wales
3. Ouray, Colorado
4. Liége, Belgium
5. Cadouin, France
6. Bedford, Indiana
7. Eureka, Utah

### Table C. Chemical Analyses of Montmorillonite Minerals

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**Montmorillonite**

1. Tatatilla, Mexico
2. Otay, California
3. Polkville, Mississippi
4. Montmorillon, France


### Table C. Chemical Analyses of Montmorillonite Minerals. (Continued)

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**Nontronite**

1. Manito, Washington
2. Sandy Ridge, North Carolina
3. Spokane, Washington
4. Nontron, France


**Hectorite**

1. Hector, California
2. Saponite
3. Svardsjo, Sweden
4. San Bernadino County, California

**Clay Mineralogy**

### Table D. Chemical Analysis of Iillite Minerals

<table>
<thead>
<tr>
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<td>38.18</td>
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<td>53.12</td>
<td>48.66</td>
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<td>51.95</td>
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<td>25.51</td>
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<td>28.97</td>
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<td>Fe₂O₃</td>
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<td>4.59</td>
<td>12.81</td>
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<td>1.85</td>
<td>1.24</td>
<td>1.06</td>
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<td>MgO</td>
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<td>1.70</td>
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<td>2.62</td>
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<td>CaO</td>
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<td>0.13</td>
<td>0.53</td>
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<tr>
<td>Na₂O</td>
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<td>0.17</td>
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<td>0.46</td>
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<td>0.49</td>
<td>0.00</td>
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<td>TiO₂</td>
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<td>H₂O⁻</td>
<td>7.88</td>
<td>7.14</td>
<td>11.84</td>
<td>6.70</td>
<td>6.03</td>
<td>7.73</td>
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<td>6.56</td>
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<td>Total</td>
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<td>98.78</td>
<td>100.04</td>
<td>99.52</td>
<td>99.96</td>
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<td>100.01</td>
<td>99.96</td>
<td>99.96</td>
<td>100.25</td>
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</table>

1. Alexander County, Illinois  
2. Fithian, Illinois  
3. Northeast Scotland, calculated composition of trioctahedral mica, minus impurities  
4. Scotland, weathered biotite  
5. Ballater, Scotland  
6. South Wales  
7. Geoschwitz, Germany  
9. St. Joseph Lead Co. mines, glauconite  
10. Norwalk, Wisconsin, glauconite  
11. South Tyrol, Germany, glauconite


### Table E. Chemical Analyses of Chlorite Minerals

<table>
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<td>23.69</td>
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<td>Al₂O₃</td>
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<tr>
<td>Fe₂O₃</td>
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<td>5.52</td>
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<td>26.52</td>
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<tr>
<td>FeO</td>
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<td>1.95</td>
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<td>16.36</td>
<td>26.52</td>
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<td>33.06</td>
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<tr>
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<td>99.96</td>
<td>99.96</td>
<td>99.96</td>
</tr>
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1. Leuchtenbergite, Phillipsburg, Montana  
2. Sheridanite, Miles City, Montana  
3. Chlorite, Brinton Quarry, West Chester, Pennsylvania  
4. Chlorite, Ducktown, Tennessee  
5. Prochlorite, Trumbull, Connecticut  
6. Thuringite, Schmiedefeld, Thuringia  
7. Bavalite, Bas Vallon, Brittany  

### Appendix

#### Table F. Chemical Analyses of Vermiculite

<table>
<thead>
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<td>36.12</td>
<td>35.92</td>
<td>36.54</td>
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<td>10.94</td>
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<tr>
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<td>0.82</td>
<td>0.95</td>
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<tr>
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1. Bare Hills, Maryland
2. Pilot, Maryland
3. Webster, North Carolina
4. Kenya


#### Table G. Chemical Analyses of Sepiolite, Palygorskite, and Attapulgite

<table>
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<td>6.40</td>
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<tr>
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<td>0.24</td>
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<td>2.79</td>
<td>8.36</td>
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</tr>
<tr>
<td>H₂O⁻</td>
<td>8.18</td>
<td>8.60</td>
<td>10.29</td>
<td>8.65</td>
<td>8.29</td>
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<tr>
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1. Ampandrandrava, Madagascar
2. Yavapai County, Arizona
3. Durango, Mexico
5. Taodeni, Sahara, Algeria
7. Attapulgus, Georgia

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