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CLAY MINERALOGY TECHNIQUES
- A REVIEW -

by
Merrill F. Aukland

COLUMBUS
1956

SECOND PRINTING 1959

STATE OF OHIO

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INTRODUCTION

The study of clays and the clay minerals is of considerable magnitude when it is realized that it is a subject pertaining to several closely integrated sciences and applied sciences. Among the sciences are chemistry, physics, mineralogy, and geology; and in the field of applied science, ceramics, engineering, and agriculture. It has been found from experience that much of the interest in clay minerals stems from problems having to do with the structure, physical properties, origin, and occurrence of clay minerals. It is the purpose of this paper to briefly review some of what has been done and to present in abbreviated form the status of clay mineral research currently.

For the past three years the Ohio Geological Survey has sponsored a clay mineral research program in conjunction with a program of research on clay minerals that is being currently conducted by the Department of Mineralogy of the Ohio State University. The principal methods of investigation being used are x-ray diffraction and differential thermal analysis. At the present time a detailed investigation of a single stratigraphic member is being undertaken. Eventually the Ohio Geological Survey hopes to expand this program of research on clays to other geologic horizons. Needless to say, much data such as on firing properties and other properties have been greatly minimized inasmuch as there are a number of standard references that treat these subjects more fully.

An appendix for "Outline of Identification of Minerals in Clays" is included.

DEFINITIONS

The word clay is derived from an old English word 'claeg,' Dutch and German klie, from 'kli,' meaning 'to stick to' from the German verb form kleben. Most important to this discussion is the application to the words 'clay mineral.' One of the most acceptable definitions of a clay is one which is used to designate a rock with specific physical properties and a certain general chemical composition. It may also be used as a particle-size term to pigeon-hole fractions of rocks that are less than a certain size grade. There is some latitude in the upper limit of grade sizes depending upon the field of application. To the geologist, the upper limit is 4 microns, while soil scientists and others may establish the limit at 2 microns.

Clay, more specifically as a rock term, is difficult to define precisely. It is a naturally occurring material, very fine-grained and essentially composed of the silicate minerals. These silicate minerals are the clay minerals for the most part, although Grim (1955) would exclude such materials as bauxites and diatomaceous earths. In addition, clays are earthy and with the exception of the flint clays are usually plastic when wet. There are a number of natural rock materials which do not quite fit into such a classification but this problem seems to be more related to taxonomy. Soils are not indurated and the shales as more compact forms would be possible examples of disagreement. Grim points out that he has found the expression 'clay material' very useful in writing about clays to groups of diverse interests. His definition for such usage implies any argillaceous material composed primarily of the clay minerals, whether or not it is weathered or whether it is plastic or laminated.

It is the view of a number of clay specialists such as Grim, Ross, and Kerr that the definitions of the clay minerals are in good agreement among the experts. Needless to say, there are notable exceptions to this generality such as halloysite and the mica clay minerals. It is also a fact that not all clay scientists or clay technologists are in accord with many views of the chosen few. Frequently the 'ivory towers' become quite sullied by the more mundane pursuits of the technologist and justly so for it would be a very sad situation for the practitioner to bow to the theorists at all times.

CLASSIFICATION AND NOMENCLATURE OF CLAY AND CLAY MINERALS

Any attempt to completely review the numerous classifications of the clays and clay minerals would be impracticable. In general, clays are classified on the basis of geologic occurrence, physical and chemical properties, structure and morphology, genesis, and use.

The following chart is a simplified grouping of the clays into three clay mineral groups based upon a general chemical composition and geologic occurrence, as follows:

Important Clay Mineral Groups (Grim and Bradley, 1940)

<u>Name</u>	<u>Chemical Composition</u>	<u>Occurrence</u>
Kaolinite	$(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$	China clay, fire clay, ball clay, etc.
Illite	$(\text{OH})_4\text{Ky}(\text{Al}_4 \cdot \text{Fe}_4 \cdot \text{Mg}_4 \cdot \text{Mg}_6)$ $(\text{Si}_{8-y} \cdot \text{Al}_y)\text{O}_{20}$	Shales, fire clay, ball clay, etc.
Montmorillonite	$(\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{20} - x\text{H}_2\text{O}$	Bentonites, gumbotil, loess, etc.

The more specific crystalline character of each of these groups will be treated more fully under the structure of clay minerals in this paper. The above list is very general and by no means describes the members of each of these groups.

A different method of classifying clays has been attempted by Ries (1924) who developed the following based upon the chemical disintegration of aluminous rocks:

A Genetic Classification of Clays

- I - Residual clays - formed by weathering in situ
 - Kaolins
 - Red-burning clays
- II - Colloidal clays - landslide masses
- III - Transported clays
 - Sedimentary
 - Marine
 - Lacustrine
 - Floodplain
 - Estuarine
 - Delta

Glacial

Wind-formed - loess deposits

Such a classification has an important sequel in that the various modes of origin yield different types of clays, and since usefulness dictates in a large way the worth of the raw material, they are classified according to types based on use as follows:

Types of Clay Based Upon Utility

<u>Type</u>	<u>Chief Use</u>	<u>Chief Characteristics</u>
Kaolins China clay Paper clay	Whiteware, porcelain fillers, paper making, sanitary ware	High-grade, fine-grained, white-burning
Ball clay	Whiteware, mixing	White-burning
Fire clay Flint clay Diaspore	Refractories, insulators	High alumina
Stoneware clay	Stoneware, bird baths	Dense burning
Paving and sewer-pipe clay	Paving bricks, sewer-pipes, conduits	Low alumina, sandy
Brick and tile	Brick, tile, partition block, pressed brick	Impure clays
Bentonite	Iron and steel making	Very hygroscopic
Fuller's earth	Filtering, bleaching, light-weight aggregate	Absorptive properties
Surface clay	Drilling muds	Low to medium viscosity

The two preceding clay classifications are only as valuable as the initial evaluation of any particular clay deposit may have been at the time of discovery, including such factors as accessibility, purity of the raw material, transportation facilities, and nearness to market. A geologic study of a clay deposit involves at least two distinct problems: first, the correct determination of the geologic setting; and second, the uniformity of the particularly desirable physical properties of the clay under investigation for its intended use. Clay deposits are notoriously variable and a casual examination may reveal opinions that are not substantiated upon further detailed investigation. In other words, the outward appearance of uniformity does not necessarily indicate the true or consistent behavior of the clay body with respect to its desired physical properties. The fact that very small variations in composition may cause large variations in the physical properties is an important corollary. This means that important changes in physical properties are often not accompanied by noticeable changes in the gross lithologic character of the natural clay body. This is an exceedingly important fact which has led many a geologist or prospector astray because he assumed that clay was an inherently inert, uniform material that could be completely evaluated in the field by a superficial study. Nothing could be further from the truth for it can be seen that the initial observations, classification, and evaluation of the clay at the time of discovery must be made carefully. The geologist must be ever cognizant that the geologic occurrence, genesis, and morphology of a clay has a direct bearing upon the eventual utility of the raw material and likewise he must bear in mind the technological problems of beneficiation that face the plant superintendent, ceramic engineer, or technologist.

A more refined classification of the clays breaks them down into their clay mineral composition based upon the structure of crystal and chemical units that comprise the clay. Inasmuch as the clay minerals are the essential constituents of clay materials Grim (1947) has suggested three general kinds of clay minerals:

- (1) Minerals in which the individual ultimate units have a sheet or flake shape.
- (2) Minerals in which the ultimate units are fibrous or lath shaped.
- (3) Minerals that are amorphous.

More specific treatment of these characteristics is taken up in the section on structure of the clay minerals, since this is one of the more important features of this discussion. The sheet or flake-shaped structures are the most abundant and best known of the clay minerals and are usually subdivided into three clay mineral groups: kaolinite, illite, and montmorillonite. Illite is sometimes known as the hydrous mica group and montmorillonite as the expanding lattice group. Attapulgite belongs to the fibrous group of clay minerals and possibly indianaite is amorphous. For purposes of further discussion this paper shall be restricted for the most part to (1) above. It should be made clear, however, that the fire clays belong to mixtures of kaolinite group clay minerals and illite group clay minerals, generally speaking, and should also be included in a discussion of such minerals. There is yet much to learn about the fire clays, underclays, or coal formation clays as they are variously known. Since it is always easier to study chemically pure well ordered crystalline material by x-ray, thermal, and other means, these chemically impure clays often offer complex problems, many of which remain to be solved.

Based upon the generalizations above, Grim (1947) presented the following tabular summary of the clay minerals:

Clay Minerals

1. Kaolinite group
 - (a) equidimensional flake-shaped units
 - kaolinite
 - dickite
 - anauxite
 - (b) lath-shaped units
 - halloysite
2. Montmorillonite group
 - (a) equidimensional flake-shaped units
 - montmorillonite
 - (b) lath or needle-shaped units
 - nontronite
 - hectorite
3. Illite group

Insufficient data to accurately describe subdivisions
4. Miscellaneous fiber-shaped units
 - attapulgite
 - sepiolite-like
5. Amorphous
 - indianaite ?

The reader is next referred to the "Glossary of Clay Mineral Names" by Kerr and Hamilton (1949) for a brief summary of additional information. This information is quoted for the three general clay mineral groups as follows:

Glossary of Selected Clay Mineral Terms

Kaolin - "The name kaolin is a corruption of the Chinese word 'kauling' meaning 'high ridge,' the name of a hill near Jauchau Fu, where the material is obtained. Kaolin, as commercially used, is best considered by the geologist as a rock, composed essentially of one of the kaolin minerals. Mineralogically the term was once used to refer to a single clay mineral but the word is now used (with the suffix - ite) as a group name for at least four separate clay minerals: kaolinite, nacrite, dickite, and anauxite. Halloysite, endellite, and allophane although structurally and chemically different are sometimes included. Ross and Kerr (1931) suggest that the name kaolinite be kept for the characteristic mineral of kaolin, and that the other two chemically similar minerals of the kaolin group be called nacrite and dickite."

Montmorillonite - "A name proposed by Damour and Salvétat (1847) for a clay mineral from Montmorillon, France. It occurs as the essential mineral in the rock bentonite and occurs in soils as well as in association with mineral deposits. Thus montmorillonite has a well-recognized importance. Other names of minerals that were considered by Dana (1892) to be at least in part montmorillonite, are confolsenite, described by Dufrenoy (1856), from Confolens, at St. Jean-de-Cole near Thiviers, France -- and delanouite, described by Kennigott (1853) from Millac near Nontron, France. Smectite and galapectite are two names that antedate montmorillonite, however, galapectite, although in part montmorillonite, is probably correlated with halloysite rather than montmorillonite. Smectite has fallen into disuse since the time it was proposed, while montmorillonite has been generally accepted. Nontronite, beidellite, hectorite, and saponite are related structurally to montmorillonite and belong to that group."

Illite - "A name proposed as a general term (not a specific mineral name) for the widely distributed clay mineral constituents of argillaceous sediments apparently related to the mica group. This name, illite, was proposed by Grim, Bray, and Bradley (1937) while working on clays, soils and shales from Illinois, and was intended as recognition of a state in which clay study has received much encouragement."

It may readily be seen from these accepted definitions that the clay minerals are far from known even generally, let alone, specifically.

PHYSICAL PROPERTIES OF CLAY MATERIALS

General

Before one can cope with the vast subject of the physical properties of clays, it is necessary to appreciate some of the factors that control the properties of the clay materials. They have been set forth by Grim as follows:

Factors Controlling the Properties of Clay Materials

- a) Clay-mineral composition
- b) Nonclay-mineral composition
- c) Organic material
- d) Exchangeable ions and soluble salts
- e) Texture

A brief word on each of the above factors will suffice. The clay-mineral composition refers to the identity and relative abundance of each of the clay-mineral constituents. Mixtures of different clay types, even in small amounts, will affect their behavior. The problem of nonclay-mineral types is primarily concerned with the identity of the nonclay minerals, their relative abundance, and the particle-size distribution of each species present. Organic material is present in clays in two ways: it may be present as discrete particles of wood, leaf matter, spores, etc.; or as organic molecules adsorbed on the surface of the clay-mineral particles. Certain of the clay materials contain water soluble salts which may have been incorporated at the time of accumulation or may have developed as some post depositional process. Such salts are commonly chlorides, sulfates, and carbonates of alkalis, alkaline earths, aluminum, and iron. The last factor, texture, 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.

The first observation that clays become hard and mechanically strong during drying probably antedates historical record but the fact remains that this is still one of the most important properties of clays. From a scientific point of view, this is in a large way due to the inherent shape of clay particles. It should be made clear at this point that many early workers in clay mineralogy were of the opinion that clays were of amorphous construction. This, of course, has been largely disproved except for a very few clay minerals. When clay is mixed with water, the latter acts as a lubricant, and the sheet-like clay particles move in the direction of the crystal plane without losing cohesion which is manifested by electrical charges of the ions in solution. This brings about a deformation of the clay which can be molded when wet and when dry the resulting form is permanent. As the water evaporates during the drying process, the lubricant disappears and the crystal sheets come into direct contact with each other, thereby creating a rigid condition. Almost everyone has attempted to pry two clean glass plates apart that have been placed one on top of the other. In direct contrast to the sheet-like structures of the plastic clay materials are the crystals of three-dimensional non-plastic materials that are in point contact with each other much like rubber balls stacked in a tetrahedron. From this comparison, it is known that since there is much less surface contact involved in the latter, there is less cohesion between the balls. Not all of the crystal sheets in a plastic clay lie parallel to one another. The number of crystals in direct contact with each other is greater, the smaller the size of the individual crystals and the more tightly they are packed in the same space. In dried articles made of a plastic type of clay more particles are in direct contact than in those made of non-plastic clays. It is therefore obvious that the mechanical strength of dry articles made of plastic clay is greater than those made of non-plastic clays.

Next, we must consider the problem of how the elimination of water takes place. It takes place in two phases, the first of which is the evaporation of the water that surrounds each of the tiny clay particles like an onion skin. When this occurs the clay particles approach closer to each other and shrinkage takes place. If the crystal arrangement of the packing of the particles were homogeneous, the body would continue to shrink until all the particles were in contact with each other to the same degree, but this is seldom the case since clays are rarely pure materials. Since impurities create imperfections in the ideal sheet structure, this means that not all the clay crystals lie parallel to each other, thus at certain points the crystals and their intermediate water layers are not stacked together. Pockets are thus formed which are filled with water also and hence this must be evaporated and the pockets subsequently filled with air. There are various tables available to demonstrate the relationship of plasticity, shrinkage, water of formation, and drying time.

Because of the technical importance of plasticity, a large literature has developed around the mechanical properties of clay-water systems. The concept is based upon general colloid-chemical principles and three fields of investigation have been most fruitful: viscosity in dilute sols, thixotropy in sols and gels of intermediate concentration, and plasticity of the pastes. Of the three concepts only viscosity is well-defined physically.

Particle Size and Composition

The general theory of the nature of internal forces which cause clay suspensions to assume peculiar viscosity and thixotropic properties is of keen interest. Of the former, particle size and particle shape are the controlling factors whereas the thixotropic qualities are explained on the basis of the nature of the relatively weak Van der Waal's bond. Thixotropy is defined as the limiting slope of the viscosity-reciprocal shear curve when the latter approaches zero. There is no doubt that a better understanding of oil migration should result from the mathematical study of clay particles.

Although numerous definitions of plasticity are in existence, no satisfactory basis for a quantitative evaluation is known. The idea of permanent deformation under stress is present in most definitions but the quantitative approach is neglected. More work must be done on plastic flow, particle-size effects, swelling, and swelling effects according to Marshall (1949).

In view of the above, relatively small amounts of certain components may exert a very great influence on some of the properties of a clay according to Grim (1948). All of the clay minerals form suspensions in water if their particle size is sufficiently small and if there is the proper electrolyte content. The montmorillonite minerals, attapulgite, and perhaps the sepiolite-like minerals are more easily placed in suspension than the other clay minerals. This is because they break down more easily in water to exceedingly small particles due to their absorptive power for electrolytes, and because of their influence on the state of the water surrounding the particles, which was more simply explained above. As a result, when certain montmorillonite clays carry sodium as an exchangeable cation, their suspensions in water have a high degree of thixotropy which is detrimental to some ceramic applications. Small amounts of montmorillonite clay add greatly to the suspension forming characteristics of the other clays.

Average Size Composition of Selected Clay Samples

<u>Mineral</u>	Grade limits (mm)-composition (%)				
	1/256	1/256- 1/512	1/512- 1/1024	1/1024- 1/2048	<1/2048
Kaolinite	27.0	10.8	13.4	12.3	36.5
Halloysite	49.7	8.2	6.3	4.5	31.3
Dickite	84.9	9.0	2.2	1.1	2.8
Montmorillonite	39.7	14.6	14.1	7.0	24.6
Nontronite	21.6	14.6	15.8	11.2	36.8
Illite	31.3	20.0	17.1	5.4	26.2
Attapulgite	25.8	4.9	18.8	5.2	45.3

Mineralogic Composition of Size Fractions of Clays

Particle size, microns	Minerals in order of quantity		
	Predominating constituents	Common constituents	Rare constituents
> 0.1	montmorillonite beidellite	mica and intermediates	illite (tr)
0.1-0.2	mica and intermediates	kaolinite montmorillonite	illite quartz (tr)
0.2-2.0	kaolinite	illite micas halloysite	quartz montmorillonite feldspars
2.0-11.0	micas illites feldspars	quartz kaolinite	halloysite (tr) montmorillonite (tr)

- from Calif. Bureau of Mines

Bonding Strength

The much greater plasticity of clays over minerals of small grain size is due, as we have seen, to the sheet or flake-like structure of the clay minerals. It should be noted, however, that this property of very small grain size being conducive to plasticity is peculiar to not only clay minerals. In fact, almost all minerals can acquire a certain degree of plasticity by grinding. It is important to realize that this bonding is of a physical nature rather than that of a chemical bond such as is found in polymerized plastic materials and paints.

The bonding strength for various clays are as follows:

Bonding Strengths for Clay Minerals - Grim and Cuthbert

	Clay 8%	Opt. H ₂ O (1)	Max. GCS (2)	Opt. H ₂ O	Max. DCS (3)
Kaolinite Grundy County, Ill.		1.7%	14.6%	4.5%	77
Illite Grundy County, Ill.		1.9	12.7	4.5	90
Montmorillonite Belle Fouche, Wyo. Pontotoc, Miss.		2.07 2.65	24.1 30.5	3.0 5.0	100 90
Halloysite Eureka, Utah		2.95	21.3	5.0	30

- (1) Optimum H₂O content is the amount of tempering water necessary for maximum compression strength in mixtures of 8% clay and 92% standard testing sand.
- (2) Green compression strength.
- (3) Dry compression strength.

It is seen from this chart that there is a definite relationship between the bonding strength of a clay and the plasticity range. In other words, deformation under mechanical stress is a property of plasticity in which the material does not lose its cohesive strength while a new shape is being imparted to the mass.

When clays are used as ceramic materials, they are used alone or in mixtures for their effects upon the working properties, the drying strength, and the compressive strength of the ceramic body. Some clays are used primarily because they offer an inexpensive body constituent or filler of a desired chemical composition and a minute grain size. For example, china clay probably serves its purpose more effectively as a filler in certain wall tiles than as a contribution to the plasticity of the mass. Other types of application are the various uses of clays in refractory ware, either as raw or calcined flint clay, as a grog.

It has already been demonstrated that when clay is mixed with sufficient water, a mass is formed which exhibits plastic flow that has a yield stress and a measurable mobility. The ceramist is also interested in another factor, extensibility. This is a term used to express how far the clay can be deformed before rupture. This is of major concern to the technologists. Norton (1942) listed the variables in clays that influence this property of extensibility: particle size, type of clay mineral, soluble salts, adsorbed ions, particle shape, and organic matter. Norton made the following statement:

"In the future the manufacturer of ceramics is going to demand a tailor-made clay which has all these variables under a reasonable degree of control. While at present it is not feasible to produce clay in large quantities with an exact control of properties this can be done quite readily in the laboratory."

Inasmuch as the clay producers for a variety of reasons have not been able to meet Norton's challenge, the ceramic manufacturer is faced with the following problems:

- (a) purifications of clays for ceramic use
- (b) aging and bacterial action
- (c) modification of working properties
- (d) effect and amount of exchangeable ions
- (e) clays as colloidal electrolytes
- (f) slip casting
- (g) chemical treatment
- (h) clays as suspending or binding agents
- (i) differential thermal analysis
- (j) drying of clay wares
- (k) atomistic approach of W. A. Weyl.

Much could be said about each of these problems but that is not the function of this paper.

Firing Properties

Any discussion of clays would not be complete without some consideration of the effect of heat on clays, the firing of clays. The firing behavior of any clay at a given temperature is determined by its mineral constitution, particle-size distribution, firing atmosphere, and the amount and kind of accessory minerals present in the raw material or added to the ceramic body. It has been found, for instance, that decomposable minerals contribute to the bloating of clays in making light-weight aggregate for concrete.

Firing Products of Selected Clays

High alumina clay	900°C	1000°C	1100°C	1200°C	1300°C
Kaolinite	mullite			mullite cristobalite	
Endellite	mullite			mullite cristobalite	
Diaspore	alpha- alumina				
Gibbsite	gamma- alumina	alpha- alumina			
Beidellite					mullite cristobali
Nontronite					mullite cristobali spinel

- after Bradley & Grim (1951)

Differential Thermal Analysis

It is distinctly more to the point, however, to understand more about the specific changes that take place as the clays and clay minerals are heated. Differential thermal analysis is today widely used to study the characterization of clay materials. DTA, although not a very accurate or quantitatively definitive technique, shows important changes that take place within the clay material. Limited primarily by the sensitivity of the apparatus being used, the resulting thermal curve records all the transformations in which heat is taken up or given off. This record includes the dehydration of clays, the decarbonation of carbonates, the reversible change from alpha-to-beta quartz, the burning of materials, and the recombination of elements into more stable forms. When employed alone the technique can be used to determine the nature of nearly pure compounds and when used in conjunction with x-ray diffraction, microscopy, and chemical analysis it may be used to study more complex combinations. Before any specific character information can be had it is essential that the instrument be standardized. Not only must the DTA apparatus be standardized but also the processing of the samples such as disaggregation, particle size, and packing in the specimen holder. Mackenzie (1950) has suggested a number of factors to be considered for international standardization. It can not be too strongly advised, however, that the universal acceptance of international standards will not in any way obviate the necessity for making individual apparatus standards. The writer suggests the use of apparatus described by McConnell and Earley (1950) which is three-point multiple type recorder. This DTA set-up can be seen at the Department of Mineralogy, Lord Hall, The Ohio State University, Columbus, Ohio. The Ohio Division of Geological Survey has been sponsoring for several years research on Ohio clays by DTA and x-ray diffraction methods. They are currently carrying on an investigation of the character of the Lower Kittanning fire clay with respect to the mineralogic variation of the member laterally, from one end of the State to the other, and vertical variations from the base of the fire clay to the top of the stratigraphic section. Numerous thermal curves have been run and many x-ray pictures are on file. It is hoped that these and many more future patterns will serve as a basic reference file to the Ohio ceramic industry. It is hoped and believed that there is a definite correlation between such data and the use to which the clay material is being put. Would it not be worth while to be able to run an unknown sample of fire clay through DTA and x-ray techniques and then find that such material could be used for a specific type of manufactured product? This could be accomplished by using the basic reference file of information as a comparison index. Bowen (1954) has provided a convenient compilation of "Data for Interpretation of Differential

Miscellaneous Differential Thermal Curves

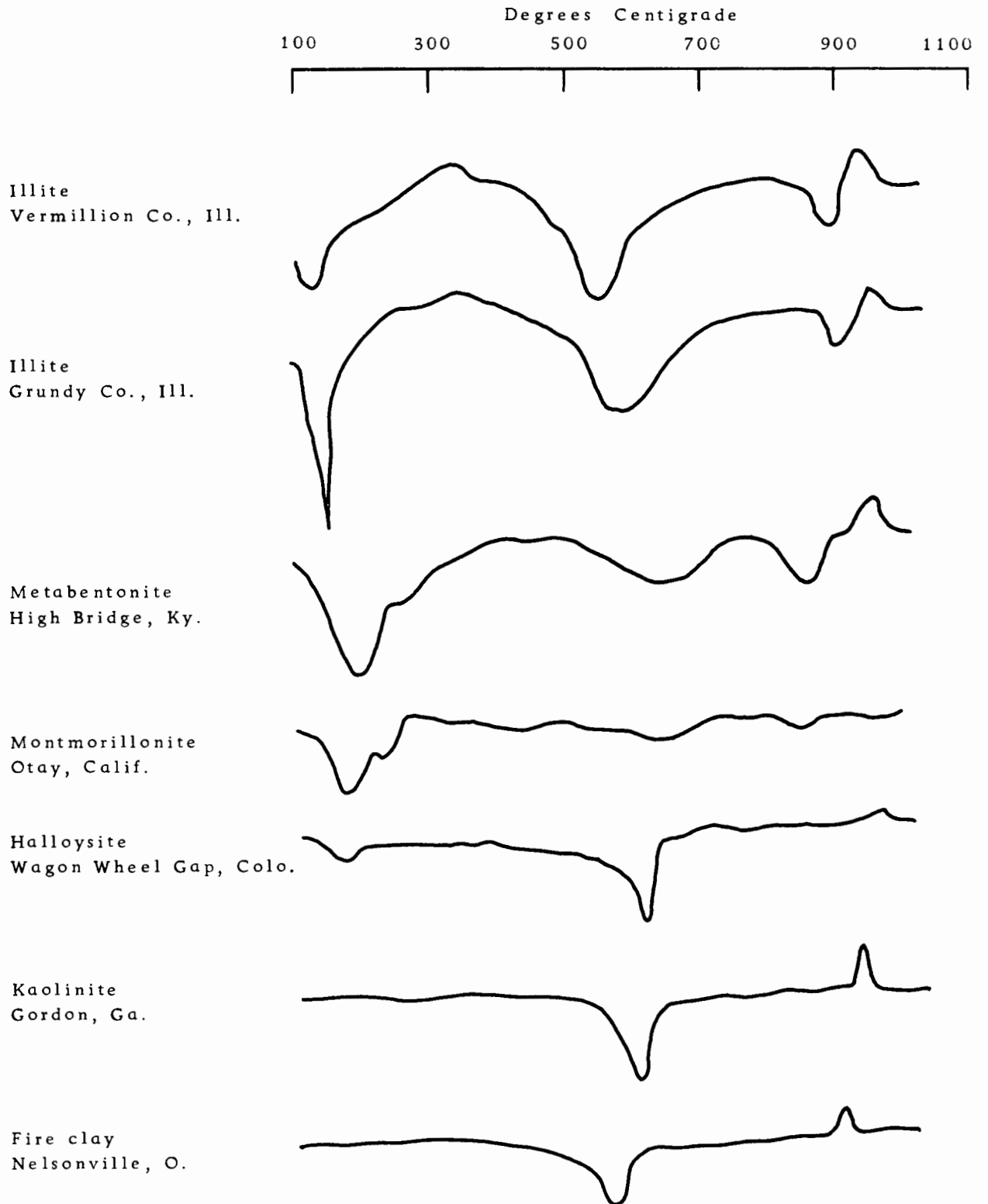


Figure 1

Thermal Curves." In the final analysis, therefore, the value of DTA procedure is to provide a rapid method of getting important information regarding the properties of a clay or a shale. The speed of the method makes it feasible for use as a plant production check on the variations in the ceramic properties of clays that look alike in the outcrop but are actually quite variable. In other words, as Grim and Rowland (1944) have said, the DTA method can be used as a control and as a prospecting method. They performed numerous tests and recorded the results as follows: differential thermal analyses of common clay-mineral and non-clay mineral components of clays and shales, differential thermal analyses of prepared mixtures of clay minerals and non-clay minerals, and differential thermal analyses of clays of various types. Interpretation of thermal curves like the Lower Kittanning offers certain inherent difficulties inasmuch as the fire clays are not pure clay minerals but mixtures of clay minerals and non-clay mineral components. For instance, with an increase in quartz impurity, there is an accompanying lowering of the peak intensity for the endotherms and exotherms of the kaolinite.

X-Ray Diffraction

The study of clays and clay minerals has probably been made easier by the application of x-ray diffraction techniques. The x-ray method is probably the most widely used for identification of clays. In order to become adept at this technique it is of prime necessity that the reader become familiar with the theory of the production and properties of x-rays, the Bragg reflection law, and the powder and single crystal methods of taking x-ray photographs. Although it is possible to make use of single crystals in the study of clays, by far the most important method is powder x-ray diffraction. The powder method was devised by Debye and Scherrer (1917) and by Hull (1917). Many special cameras and techniques have been developed. A cylindrical powder camera is often used of the type sold by the North American Phillips Company, Inc. X-ray diffraction methods are based upon satisfaction of the Bragg law which for powdered crystalline materials states that the angle theta varies when placed in a monochromatic beam with the random orientations that the particles of crushed material will reflect from each of the possible planes of reflection for the material. The theta values are computed for all the reflecting planes from measurements of the line positions. Identification of the lines is easy for the high symmetry crystal systems but for the lower symmetry crystals it is very complex. However, once the pattern has been interpreted and the values and calculations recorded, all future pictures of the same material can be compared against the known standards such as those published on cards by the ASTM. Again it should be noted that data for impure materials such as the fire clays is vastly complicated and much remains to be done.

Levinson (1956), who has studied the polymorphs of mica very extensively, has suggested several problems that remain to be solved in the study of fire clays:

- (1) Possible difference in structures and compositions of the two texturally distinctive micas that occur in the underclays. Consideration of mixed-layer types might arise as a consequence of further study.
- (2) More information on the kaolinite might permit characterization of the very well-crystallized and the poorly crystallized types and thus indicate structural or compositional differences.
- (3) The changes in clay mineral ratios in different size fractions might prove of practical interest in predicting firing properties.
- (4) A reliable method for estimation of quartz has not been developed for applications to mixtures of this sort.

He further postulates that the ability to determine the mineralogical composition, and hence utility, of a clay by DTA and x-ray methods is not an end in itself, and should not be thought to eliminate other useful tools such as the classic petrographic microscope.

X-ray Data for Interpretation of Powder Diagrams of
Clay and Clay Minerals

Well-crystallized Kaolinite		Poorly crystallized Kaolinite		Montmorillonite		Illite	
d	I	d	I	d	I	d	I
						9.98	s
7.15	10+	7.15	10				
4.45	4	4.45	8	4.60	vs	4.97	w
4.35	6	4.36	2			4.47	s
4.17	6	4.14	2			4.11	vw
4.12	3						
3.837	4						
3.734	2					3.70	vw
3.566	10+	3.57	10			3.40	vw
3.365	4					3.31	m
3.138	2					3.20	vw
3.091	2					2.98	w
2.748	2					2.84	vw
2.553	8	2.55	7	2.55	s	2.56	s
2.521	4						
2.486	9	2.50	7			2.44	w
2.374	7	2.375	7			2.38	m
2.331	10	2.325	8b				
2.284	9						
2.243	1					2.24	m
2.182	3			2.217	vw	2.18	w
2.127	2					2.11	w
2.057	1						
1.985	7					1.98	m
1.935	4	1.977	4				
1.892	2						
1.865	1						
1.835	4						
1.805	1						
1.778	5	1.785	3				
				1.689	m	1.65	w
						1.64	m
				1.489	vs	1.50	s
						1.34	vw
				1.286	m	1.29	m
				1.241	m	1.24	w
				1.118	vw		
				1.027	vw		
				0.9745	w		
				0.8625	mw		

Explanation of Symbols

d = plane spacing
I = intensity
s = strong
m = medium
w = weak

Optical Properties

In this latter regard it would be well to dwell on the subject in more detail. Grim (1952) has stated that some workers have used petrographic methods as the sole means of making a clay mineral analysis, whereas others consider this method as obsolete and useless for such fine-grained materials. There is little doubt but that the value of the method lies between these two

extreme views. It is often possible for a careful worker to determine with reasonably accuracy the indices of refraction, birefringence, optical sign, and axial angle of the clay mineral components of clay materials. It is not always a simple matter and may require supplementary techniques. The next question that arises is, of what use can be made of optical data? Numerous published tables of the optical properties of the clay minerals are available and can be used to make the correct identification with very little additional information. It is also of value in thin section studies of clay materials where information on the texture and fabric and paragenesis may be revealed. Grim feels that a preliminary investigation of clays by the microscope is an essential before planning further detailed studies. As an entity in itself optical identification should be used with caution and almost always should be supplemented with some other analytical technique if for no other reason than to be used as a check.

Some Optical Properties of the Clay Minerals

Mineral	alpha	gamma	birefringence	sign	2V
kaolinite	1.553-1.563	1.560-1.570	.006-.007	(-)	42°
dickite	1.560-1.562	1.566-1.571	.006-.009	(+)	52°-80°
nacrite	1.557-1.560	1.563-1.566	.006	(-) (+)	40°
allophane	n-1.468-1.512				
halloysite 4H ₂ O	mean value	1.526-1.532			
halloysite 2H ₂ O	mean value	1.548-1.556	.002-.001		
montmorillonite	1.480-1.590	1.515-1.630	.025-.040	(-)	0°-30°
nontronite	1.565-1.600	1.610-1.640	.035-.040	(-)	moderate
illite	1.545-1.630	1.570-1.670	.022-.055	(-)	small
chlorite	1.570-1.640	1.575-1.645	.003-.007	(-) (+)	small
vermiculite	1.525-1.526	1.545-1.585	.020-.030	(-)	small
sepiolite	1.490-1.520	1.505-1.530	.009-.015	(-)	0°-60°
attapulgite	1.510-1.520	1.540-1.555	.025-.032	(-)	small
palygorskite	mean value	1.500-1.555	.025-.035	(-)	small to large

Summary of Physical Properties

This brings to a close the discussion of the properties and ways of investigating these properties as far as this paper is concerned. To give the impression that these findings and methods are the only ones would be far from the truth but the writer has attempted to summarize some of the better known ideas. There are many other facets of study such as dye adsorption, particle-

size distribution studies, infrared analysis, electron microscopy, and further studies on chemical analyses, that could well be the subject for much more discussion.

Chemical Analyses of Some Clays and Clay Minerals

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
SiO ₂	46.90	44.75	40.80	44.46	51.14	51.22	59.48
Al ₂ O ₃	37.40	39.48	35.70	36.58	19.76	25.91	23.51
Fe ₂ O ₃	0.65	0.53	--	0.36	0.83	4.59	2.71
FeO	--	--	0.04	0.07	--	1.70	--
MgO	0.27	0.19	tr	0.18	3.22	2.84	0.54
CaO	0.29	0.13	3.96	0.19	1.62	0.16	0.34
K ₂ O	0.84	--	0.20	0.51	0.11	6.09	2.21
Na ₂ O	0.44	--	0.20	0.01	0.04	0.17	0.26
TiO ₂	0.18	--	0.02	0.15	--	0.53	1.56
H ₂ O-	--	0.61	1.95	4.05	14.81	--	--
H ₂ O+	12.95	14.40	17.68	13.38	7.99	7.14	--
Total	99.92	100.09	100.55	99.94	99.52	100.35	90.61

- (1) Kaolinite - Zettlitz, Czechoslovakia
 (2) Nacrite - Brand, Saxony
 (3) Dickite - Ouray, Colorado
 (4) Halloysite - Bedford, Indiana
 (5) Montmorillonite - Montmorillon, France
 (6) Illite - Fithian, Illinois
 (7) Fire clay - Nelsonville, Ohio

Staining Tests for the Clay Minerals - after Mielenz et al

Clay mineral	Untreated clay	Acid - treated clay	
	Benzidine	Safranine	Malachite green
Kaolinite	no reaction	Red-purple red. Strong to weak pleochroism from reddish purple parallel to cleavage to yellowish red perpendicular to cleavage	Blue-green blue and blue-green. Strong to weak pleochroism from yellowish green parallel to cleavage to blue perpendicular to cleavage
Halloysite	no reaction	Blotchy stain: purple, purple-blue purple, and red-purple red. Not pleochroic	Blotchy stain: yellow-green yellow, blue-green, and green-yellow. Not pleochroic
Dickite	no reaction	Crystals not stained	Crystals not stained
Nacrite	no reaction	Crystals not stained	Crystals not stained
Montmorillonite	purple-blue	Purple-blue	Yellow-red yellow
Nontronite	blue-green	Red-purple red	Green blue-green and blue-green blue
Illite	no reaction	Red-purple red	Green blue-green
Attapulgite	no reaction	Red-purple red	Blue-green and blue-green blue
Pyrophyllite	no reaction	Not stained	Not stained

Note - For technique see Faust, G. F., Staining of Clay Minerals as a Rapid Means of Identification in Natural and Beneficiation Products, 1940, U. S. Bur. Mines Rept. Inv. 3522.

ORIGIN AND OCCURRENCE OF CLAY AND CLAY MINERALS

This problem is best approached by making an attempt to understand how clays and clay minerals are formed in nature and by mineral synthesis. In nature, the alkalic feldspars and micas tend to alter to kaolin minerals, whereas ferromagnesian minerals, calcic feldspars, and volcanic glasses tend to alter to members of the montmorillonite group. Presence of magnesium ions in the altering system is most favorable for the formation of the montmorillonite minerals.

Illite is the most abundant clay mineral of the recent marine sediments, whereas kaolinite is less common and montmorillonite rarely found. Kaolinite is the most stable of the clay minerals, according to Ross (1943) who postulates that the formation of kaolinite or montmorillonite during weathering seems to depend upon the stability of the minerals in the parent rock. If the

ferromagnesian minerals and the feldspars are decomposed at the same time, ferrous and ferric iron, magnesium, alumina, and silica will be released and montmorillonite follows. If the ferromagnesian minerals are the first to break down, then the magnesium is removed in solution and iron either removed or precipitated as hydroxide or oxide under greatly oxidizing conditions. When the feldspars decompose, no magnesium and iron are available, and kaolinite will form. Moreover kaolinite will form when the leaching is effective and weathering is thorough, whereas montmorillonite results in soils where the drainage is poor and the oxidation restricted. Kaolinite forms under both oxidizing and reducing conditions, such as the fire clays, in the presence of organic matter and organic acids. One of the problems in the formation of underclays is the nature of the chemical balance during the transition between or during the coexistence of the two environments.

Clay minerals also occur in hydrothermal veins and mineral deposits. Members of the kaolinite, illite, and montmorillonite groups have all been found under such conditions. The formation of clay minerals under hydrothermal conditions depends upon the pH of the solutions. Frederickson (1952) states that the clay minerals are very sensitive to small changes in the composition, temperature, and pH of the surroundings and hence are excellent indicators, but much remains to be proved as yet. According to Bray (1937) and Wood and DeTurk (1940), the clay minerals are not necessarily stable products of weathering but are part of a system in dynamic equilibrium with its environment. The rate at which many of the clay minerals react to environment is often very rapid, Bray and DeTurk (1938).

Kerr (1955) also thinks that clays may be good indicators of earth processes. They form through a wide range of temperature conditions from the compressed action of water at one extreme, to the action of normal atmospheric agents at ordinary temperatures. These conditions are grouped by Kerr under the heading of two distinct geologic processes, hypogene and supergene. He lists the following evidence for data on temperatures that prevail during hypogene processes:

- (1) Measurements in drill holes penetrating hydrothermally active areas.
- (2) Measurements of surface emanations.
- (3) Temperatures recorded during experiments in clay mineral synthesis.

Unfortunately the supergene processes have not been studied experimentally as much as those by hypogene processes. However, we have the advantage of more direct observation under normal atmospheric conditions. Such as conditions of clay mineral development under normal surface conditions and those of diagenesis under saline conditions. Clay mineral development under the first condition may require very long periods of time even from a geological point of view. Under slightly favorable conditions, leaching and deposition together with weathering and soil formation do take place. Keller (1952) has attributed such an origin to the genesis of the fire clay deposits of Missouri. He points out that geologic field evidence is contrary to an origin for the diaspore deposits at suggested high temperatures of 275° C, and high pressures of 130 atmospheres, at which conditions the clay mineral is stable in the laboratory. It is suggested that the structure and energy of an octahedral alumina sheet are inherited from kaolinite or other clay minerals and the extensive modification of the alumina linkage is minimized, thereby meeting the low energy requirements for the hydrothermal synthesis of diaspore. Such chemical processes are rather complex but it is thought that weak concentrations of acid or alkali solutions along with small amounts of alkali or alkaline earth elements may produce clay deposits, given sufficient time. To these conditions may be added the variable factors of more concentration of chemical action or moderate temperature increases which may shorten the time factor.

Diagenesis under marine conditions has been suggested as a possible process for the formation of clays under a supergene environment. If this theory is correct, small flakes of mica, kaolinite, and other minerals deposited on the ocean floor may change to illite, glauconite, or montmorillonite. Grim et al (1949) in their discussion of the formation of recent marine sediments off the coast of California attribute broad-range depth characteristics to kaolinite, illite, and

montmorillonite. Kaolinite is thought to be gradually eliminated by a diagenetic process with increase in depth. The nature of underclays would seem to substantiate this. Well-crystallized kaolinite in the New Jersey sediments is thought to be due to fresh-water lake conditions in Triassic shale hollows. Kaolinite in many coastal sediments shows a decrease in crystallinity because the waters were not fresh with an increase in chlorite and hydromuscovite as the ordering of the kaolinite declines. Under nearly pure marine conditions illite forms. This would suggest that Ohio fire clays are probably formed under conditions that are not purely marine or purely fresh water but under some transitional phase inasmuch as the clays are most often kaolinitic with poor crystallinity and accompanied by quantities of hydromuscovite.

STRUCTURAL MINERALOGY OF CLAYS

The study of clays and clay minerals has been greatly enhanced by the application of x-rays to the investigation of them for over twenty years. A vast literature has been compiled and organized into a well-integrated set of data for reference. Clay minerals, as we have seen, are silicates having layer structures for the most part. The atomic lattice of most clay minerals may be broken down into two basic structural units. The first unit consists of two sheets of closely packed oxygens or hydroxyls in which aluminum, iron, or magnesium atoms are linked in octahedral coordination, so that they are equidistant from six oxygens or hydroxyls. When aluminum is present, only two-thirds of the possible positions are filled to complete the structure, which is the gibbsite structure with the formula $\text{Al}_2(\text{OH})_6$. When magnesium is present all the positions are filled and the structure is that of brucite with a formula of $\text{Mg}_3(\text{OH})_6$. The normal oxygen spacing is 2.60A, and a common hydroxyl spacing is about 3A for many clay minerals. The second unit is made up of silica tetrahedra. In each tetrahedron a silicon atom is equidistant from four oxygen atoms or hydroxyls. These tetrahedra are linked in a hexagonal network which is repeated indefinitely to form a sheet structure. The bases of all tetrahedra lie in the same plane. Therefore, the structure of the clay minerals can be said to be made of a perforated plane of oxygens which is the plane of the bases of the tetrahedra; a plane of silicon atoms with each silicon in the cavity at the junction of three oxygen atoms; and a plane of hydroxyl atoms with each hydroxyl directly above the silicon at the tip of the tetrahedra. The total thickness of these units in the common clay mineral structure is 4.93A.

Although most clay minerals fall into the above category, some of the clay minerals are fibrous and are composed of different structural units. These minerals are similar to the amphiboles which are double chain structures of composition Si_4O_{11} . The chains are bound together by atoms of aluminum and/or magnesium placed in such a manner that each atom is surrounded by six oxygen atoms. These oxygen atoms have only one link to the silicon atoms and are therefore at the edges of the chains and at the tips of the tetrahedra.

The writer will briefly review the general structural features of the principal clay mineral groups, kaolinite, montmorillonite, and illite, in that order.

The structure of kaolinite was first suggested by Pauling (1930) and worked out in greater detail by Gruner (1932) and Brindley et al (1946). The structure is composed of a single tetrahedral sheet and a single alumina sheet of octahedral linkage combined in a unit so that the tips of the silica tetrahedra and one of the layers of the octahedral sheet form, (Fig. 2). All the tips of the silica tetrahedra point in the same direction and toward the center of the unit made of silica and octahedral sheets.

In the layer common to the octahedral and tetrahedral group, two-thirds of the atoms are shared by the silicon and aluminum, and then they change from hydroxyl to oxygen positions.

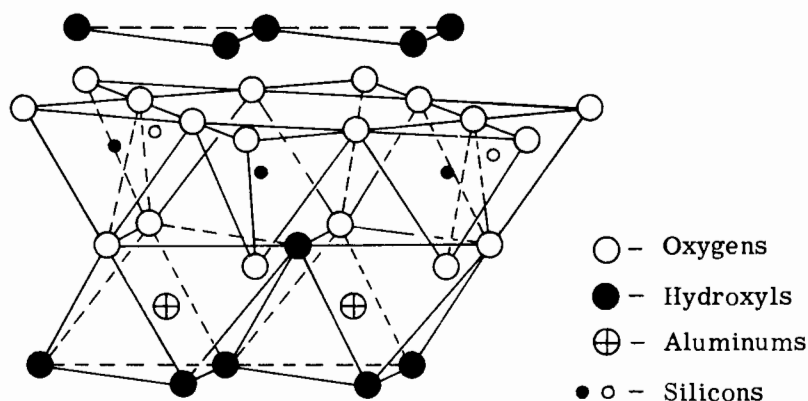


Figure 2. - Structure of kaolinite (Grim).

The charge distribution in the layers is as follows:

6	O^{--}	12	-
4	Si^{4+}	16	+
4	O^{--}	10	- (layer common to tetrahedral and octahedral sheets)
	$-2(OH)^-$		
4	Al^{3+}	12	+
6	OH^-	6	-

It is seen that the charges are balanced. The structural formula is $(OH)_8Si_4Al_4O_{10}$ and the theoretical percentage composition in oxides is SiO_2 - 46.54%; Al_2O_3 - 39.50%; and H_2O - 13.96%.

The minerals of the kaolinite group, kaolinite, dickite, nacrite and halloysite, consist of sheet units which are continuous in the a and b directions and stacked vertically in the c direction. Any variation between the members of this group exists in the manner in which the unit layers are stacked above each other and in the position of the aluminum atoms in the possible positions for them in the octahedral layer.

The specific mineral, kaolinite, has been studied by Brindley (1950) and others by x-ray methods. The following data is significant: the mineral is triclinic; a - 5.16Å; b - 8.94Å; c - 7.38Å; alpha - 91.8° ; beta - 104.5° ; and gamma - 90° . This information is applicable to the well-crystallized kaolinites. However, it is known that many investigators of the fire clays have found that the kaolinitic mineral is frequently poorly crystallized. Whether this occurrence should be known by a different species name or whether it is a disordered kaolinite is a controversial issue. Such identification for purposes of comparison are made by studying the relative intensities and d-spacings of appropriate powder pictures. Brindley feels that the mineral chamosite which is a fine-grained hydrated ferrous silicate frequently associated with siderite and kaolinite belongs to this group, (Fig. 3).

For purposes of speculation it is of interest to consider whether a series of minerals exists between an ideally well-ordered kaolinite to a fully disordered halloysite with the fully disordered fire clay as a transition stage. This thought calls for more investigation than has been accomplished. Dickite and nacrite have structures that are similar to kaolinite with the former being made up of two unit layers and the latter of six unit layers. Occasionally kaolinite type minerals are discovered that appear to be monomineralic species on the basis of x-ray diffraction but have a considerably higher silica-to-alumina molecular ratio. These silica-rich kaolinites are called anauxite.

The montmorillonite minerals commonly occur in extremely fine particles so that single crystal rotation studies are nearly impossible. For this reason almost all data must be taken from powder pictures. The generally accepted structure for the montmorillonites has been worked out by Hofmann, Endell, and Wilm (1933) and subsequently studied by Marshall (1935),

CLAY MINERALOGY TECHNIQUES

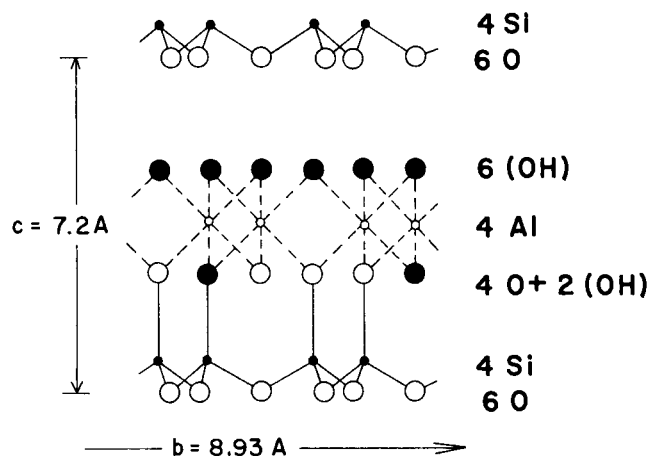


Figure 3. - Diagram of the crystal structure of kaolinite (after Gruner).

Hendricks (1942), and others: Montmorillonite was found to be composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet with all the tips of the tetrahedra pointing in the same direction and toward the center of the unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedra 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. The montmorillonites have a very weak bond which results in an exceptional basal cleavage. The unique feature of this structure is that water and other molecules can enter between the unit layers, causing the lattice to expand in the c direction. Because of this phenomenon the vertical dimension of the unit cell is variable from 9.6a when no water or other molecules are between the unit layers to an almost complete separation of the unit layers at the other extreme. Pyrophyllite is used as an example (Fig. 4).

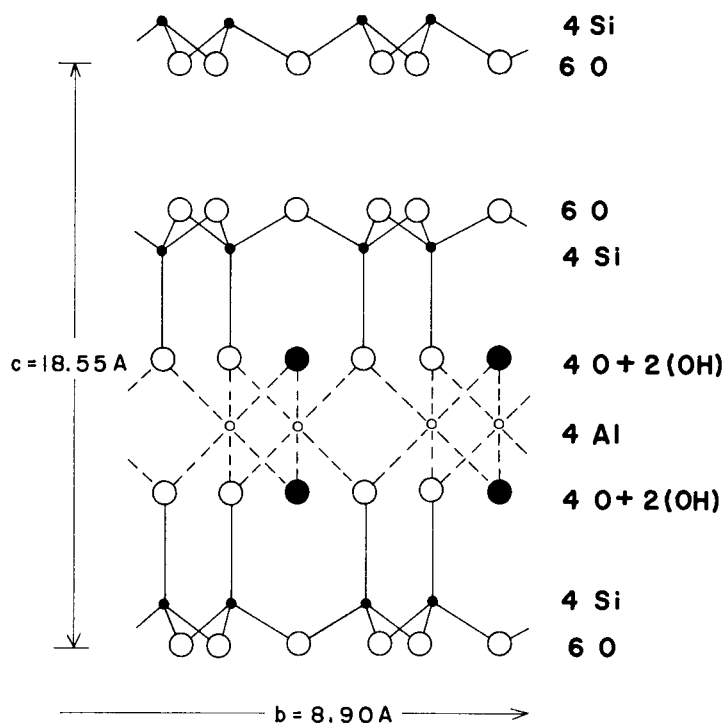


Figure 4. - A diagram indicating the crystal structure of pyrophyllite (after Pauling).

Where the kaolin group is a 1:1 lattice type with one silica and one alumina layer present, the montmorillonite group is a 2:1 lattice type; but one must be cautious in making use of such a numerical ratio since varieties such as chlorite are not so readily designated by a simple numerical ratio.

It has long been known that the property of base exchange which exists in natural soils and in water softening agents such as the zeolites is particularly applicable to the montmorillonites. Jenney (1932) determined the exchange capacity for various cations in beidellite and the order of ease of entry was $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{H}$ and $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{La} < \text{Th}$, the former being monovalent and the latter divalent. In the divalent series the order depended to some extent upon the cation originally present, whereas the monovalent series was constant. In accordance with these observations, Marshall (1935) determined the chemical compositions of different members of this group by placing the exchangeable cations along with the water molecules between adjacent alumina silicate units. This enabled him to deduce that the cation exchange capacity varies little with the particle size. As the result of this and other papers it is thought that in the mineral montmorillonite some of the Al from the middle layer is replaced by Mg. Beidellite has a predominant replacement of Al for Si; nontronite has a large replacement of Al by Fe; and saponite (magnesium bentonite or magnesium beidellite) has a large replacement of 3 Mg for 2 Al.

In nearly all theoretical deductions made with respect to base exchange, the basic assumption has been that the ions of a single kind all belong to one set, that is, all are held by bonding energies of the same magnitude. According to Marshall, this is tantamount to regarding the clays as possessing a single dissociation constant which is far from the truth. Based upon Pauli's exclusion principle, Mattson and Bradfield (1926) applied the technique of purification of clays by electro dialysis. This process does not consist simply of a removal of mobile cations to the cathode chamber and of mobile anions to the anion chamber, but shows that some of the basic constituents, such as iron and magnesium, are often found at the anode while silicic acid moves freely with the bulk of the bases to the cathode.

The theoretical formula of the montmorillonites without considering complex lattice substitutions is $(\text{OH})_4 \text{Si}_8 \text{Al}_4 \text{O}_{20} \cdot n\text{H}_2\text{O}$, and the theoretical composition of the oxides is SiO_2 - 66.7%, Al_2O_3 - 28.3%; and H_2O - 5%. It must be remembered that this formula probably never really exists in nature because of the complexity of the possible lattice substitutions. Also, unlike typical kaolinite, the lattice is always chemically unbalanced. McConnell (1950) has suggested a revision in the structure of montmorillonite which would be more favorable for balance.

The illite minerals, which are very similar to the micas, are of the 2:1 lattice type. They are often small particle size and plate-shaped clay minerals which have the ability to fix potassium irreversibly. They are characterized by numerous polymorphic variations which have been studied by Pauling (1930), Mauguin (1927), Jackson and West (1930), and Hendricks and Jefferson (1939). The basic structural unit is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedra in each sheet of silica point toward the center of the unit and are combined with the octahedral sheet in a single layer with replacement of OH by O. The potassium cations occur between the unit layers where they barely fit into the perforations of the surface O layers. Adjacent layers are stacked so that the potassium cation is equidistant from 12 oxygens, six in each layer.

The illite clay minerals differ from the well-crystallized micas in a number of ways. There is less substitution of Al^{3+} for Si^{4+} ; in the micas one-fourth of the Si^{4+} are replaced, whereas in the illites only about one-sixth are replaced. In some ways, the illite structure may be regarded as a minor modification of the montmorillonite lattice. They are probably best distinguished from each other in nature where they are found under different geochemical conditions. Although illite forms under widely varied conditions, it is probably most abundant as a secondary mineral in sediments, particularly those of recent marine genesis. It is conceivable that all gradations exist between illite and well-crystallized micas on the one hand and montmorillonite on the other hand but before any specific relations can be established more information is necessary. Such data must come from electron micrographs, x-ray diffraction, particle size measurements, and base exchange studies. One of the prime difficulties encountered in the study of this mineral is to obtain a pure sample. Most of the illite clay minerals are dioctahedral which makes them more nearly related to muscovite than to the biotite micas which are trioctahedral.

Grim (1939) has given the general formula for the illite group as follows: $(OH)_4 Ky (Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6) (Si_{8-y} \cdot Al_y) O_{20}$. It can be seen from this formula that this group of clay minerals is extremely complex to the extent that some workers doubt the validity of a true mineral group with a distinctive structure. These doubters regard illites as mixed clay minerals of other established members.

Finally, it must be said with respect to the structure of the clay minerals such as sepiolite, attapulgite, palygorskite, and others that they probably belong to other groups not here discussed.

The term fire clay or underclay deserves some attention inasmuch as they are commonly associated with cyclical deposition in the coal measures. Such is the case with many of the Pennsylvanian age clays of eastern and southeastern Ohio. The Ohio Geological Survey is currently carrying on an investigation of the clay mineral character of the Lower Kittanning member. These coal formation clays have been found to contain not only one or two or more clay minerals but also the following minerals as impurities or accessories: quartz, limonite, rutile, muscovite, sericite, pyrite, siderite, tourmaline, zircon, calcite, dolomite, and ankerite. McCaughey (1923) states that these accessory minerals occur as separate grains in the sand separate or as tiny grains dispersed through the clay aggregate. It is commonly thought that the underclays are predominantly kaolinitic with varying amounts of illite, dickite, and halloysite for the most part.

CONCLUSIONS

Any attempt to conclude that all that can be said of the clays and clay minerals has been said in this paper would indeed be a gross injustice. Nothing could be farther from the truth for the literature references alone would fill a large-sized book. The writer has made some attempt to touch upon some of the data and facts that have been accumulated which pertain to the clays. I believe that the reader can appreciate what an enormous amount of work has been done in the past, something of what is being done at present, and even more important a realization that we have just begun to really know about these minute earth materials.

It seems to the writer that there is yet a vast frontier to be more fully developed as far as the clay materials are concerned. For instance, there is still very little known about fire clays as far as genesis is concerned. X-ray and differential thermal data is of very limited use simply because we do not know as yet how to interpret much of the material. The use of pure materials is a valuable starting point but we must learn more of nature's complex mixtures.

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APPENDIX

OUTLINE FOR THE IDENTIFICATION OF MINERALS IN A CLAY

I. General Examination

A. Investigation of Clay Source

1. Type of Deposit: Indicate whether residual or sedimentary clay. Certain worthwhile generalizations may result from such an examination such as type of clay, possible clay minerals present, impurities, etc.
2. Geological Investigation: The geological age must be determined and the general stratigraphic relationship to other geologic formations or members must be established. The type and extent of the deposit can often be judged from a knowledge of the occurrence. Evaluation for possible further detailed field study such as bore hole or core examination can be obtained.
3. Nature of Locality: The geological environment of the clay may provide useful information on the nature of the impurities, e. g., sandstone areas usually will have clays containing appreciable quantities of quartz whereas clays from limestone regions will probably have a high Ca CO₃ content.

B. Examination of the Bulk Clay

This phase should never be omitted. Much information such as influence of micaceous minerals on bedding planes or stratification can readily be seen by eye or hand lens. Clay-ironstone nodules, color, presence and nature of organic materials may be observed.

C. Microscopic Examination of Clays

Much important information may be had from such an examination. Both thin section and grain mount studies are possible, and one or the other should always be made prior to other more detailed studies.

II. Treatment of Clay

The following methods have been used successfully on clays of many types. With certain modifications these methods may be universally adapted to the study of clays.

A. Dispersion

When dispersing clays it is important to break down the raw material into its fundamental particles in such a way as to avoid disruption

and decomposition of the fragile mineral particles. Vigorous stirring of the unground sample in distilled water with various dispersing agents such as Calgon T, sodium oxalate or ammonium hydroxide produces excellent results. Particularly resistant clays may be heated in water to assist in the dispersion. The stirring should be continued until no clay lumps remain on decantation. It is suggested that at least a gallon of water for every 2 pounds of clay be used.

B. Sedimentation

The suspension is poured through a nest of sieves, either ASTM or Tyler, such that the largest is about 50 mesh and the smallest about 270 mesh. The larger mesh will retain a high proportion of clay-ironstone nodules, small pyrite concretions, occasionally large mica flakes, and other aggregates.

The suspension which passes through the sieves is allowed to settle for 24 hours and after decantation almost all of the remaining quartz and heavy minerals remain in the sediment. Washing this residue removes any retained clay or fine-particled mineral, which can be returned to the sediment.

C. Centrifuging

The decanted liquid is then separated into fraction ranges by centrifugal means. Earlier stages of fractionation may be effected by use of a Broadbent model which is capable of sedimenting large volumes of suspension. Further stages of fractionation are brought about by an air driven turbine Sharples supercentrifuge operating under continuous feed conditions. The latter is capable of developing a "G" or 50,000 which is about 100 times that of the Broadbent type. Particles down to 0.05 microns can thus be separated from suspension. It is the usual practice to split the sediment up into 8 or 9 fraction sizes, each consisting of particles with an ever-decreasing maximum grain size. Various minerals tend to predominate in narrow particle ranges. By recentrifuging, the particles can be separated into closely monodispersed fractions along the wall of the centrifuge rotor. By introducing a celluloid liner into the rotor enables the sample to be withdrawn and the grain size at any particular point may be estimated from published nomograms.

III. Additional Methods of Separating Minerals

Although sedimentation and centrifuging methods have done much towards completely separating the minerals in a clay, it is often impossible to isolate pure specimens of minerals by these methods alone. This is particularly true in fractions of larger grain size where three or four minerals sometimes predominate over a specific particle range. In such cases supplementary separation methods must be employed. Perfect quantitative results are rarely accomplished by these methods.

A. Selective Chemical Action

This may be used where one component of a mixture of minerals is unattacked by chemical agents used to remove the rest. The chemical method for estimating quartz by fusion in potassium

bisulfate is an example. Other methods employ the reverse principle of dissolving one component preferentially to others such as the dilute acid solution of carbonates.

B. Heavy Liquid Separation

The use of organic liquids such as bromoform, acetylene tetrabromide, methylene iodide and thallium formate, with increasing values of specific gravity, respectively, is well known. In general, this method is limited to effective separation of only large-sized particles. The smaller sizes tend to flocculate in organic liquids and restrict free sedimentation.

C. Froth Flotation

By use of a suitable frothing agent such as pine oil, cresylic acid, mixtures of fuel or pine oil with branched-chain alcohols, or amino acids some separation of minerals may be made. The amino acids are suitable for separation of mica and quartz.

D. Electrostatic Separation

Many minerals, if allowed to fall freely between two oppositely charged plates, will move towards one or the other. Muscovite mica, for example, can be appreciably detected by relatively low voltages. The electrostatic separation of feldspar from quartz is used commercially. Unfortunately however, most of the minerals found in clays behave similarly in an electric field and a very high voltage is required to obtain satisfactory separation.

E. Magnetic Separation

This has limited use with respect to clays. Should any large sized particle of hematite or magnetite be present this method is applicable.

F. Elutriation

This method has proved useful for separating fine-grained fractions from the centrifuge into very closely monodispersed ranges, with subsequent purification of mineral species.

A stream of water or air is passed upwards through a bed of dispersed particles and, if the flow is carefully regulated, particles within a narrow size can be extracted. Large particle separation is not very effective.

IV. Methods of Identifying and Estimating Minerals

Although minerals can be isolated in a state of nearly pure content, the problems of estimating their content in the original clay still remains. For each mineral identified it is usually necessary to devise or use a suitable test or reaction that is quantitative in character and free from interference by impurities.

A. Chemical Tests

These are usually rather limited, but they have proved of great value in many instances. For example, mica and illite are particularly difficult to estimate but by determining the ratio of potassium and sodium in the pure mica mineral, a reasonable figure for its content in the original clay can often be derived.

B. Differential Thermal Analysis

This method affords easy identification and rapid estimation of many minerals found in clays. Numerous published reference curves are available for comparison standards. The presence of organic matter, impurities, and closely related thermal effects of different minerals can mask the results in certain complex mixtures. These effects may be minimized or nearly eliminated by using neutral or reducing atmospheres such as devised by R. L. Stone at the Ohio State Engineering Experiment Station. Preheating the sample is also effective. Although the D. T. A. method provides excellent qualitative results it has been found to be limited with respect to quantitative data. Used in conjunction with x-ray diffraction on the x-ray spectrometer better results may be obtained. Recent experiments with thermogravimetric apparatus improve the quantitative aspect of the problem.

C. X-ray Analysis

Usually of more value in the identification than in the estimation of minerals although recent workers have suggested the use of relative intensities obtained by x-ray spectrometry especially in evaluating the ratios of the true clay minerals. More information is necessary to estimate quantitatively the amounts of the non-clay mineral constituents, particularly colloidal silica. A. S. T. M. reference cards are available for comparison of x-ray data on many materials.

D. Petrographic Microscope

Yields excellent results on all coarse grained fractions. Numerous tables of optical data such as Bulletin 848, U. S. G. S. , are available for reference. Thin section identification is of great value when possible. Recent studies suggest the section be only .020 mm for best results.

E. Electron Microscope

An invaluable method to obtain direct measurements of clay minerals as well as a suitable technique to view texture, fabric, and particle shape determinations. Needless to say, the principal objections to this method would be the prohibitive cost and the high degree of specialization.

F. Other Special Techniques

1. Dye absorption
2. Oriented particle analysis
3. Infrared investigations

V. Computation of Mineral Content of Clays

By using one or more of the techniques above, the amount of each mineral isolated and identified from the clay can be estimated with reasonable accuracy. Another important conclusion which can be derived is the grain size range over which a mineral exists in the raw bulk material. Standard reference data and procedure are available to plot this information.