

Information Circular No. 5

IDAHO BUREAU OF MINES AND GEOLOGY

MOSCOW, IDAHO

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Clay
Its Composition, Properties and Uses

BY

JOSEPH NEWTON

State of Idaho

ROBERT E. SMYLIE, Governor

Idaho Bureau of Mines and Geology

E. F. COOK, Director

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FOREWORD

Clay is a natural raw material which has been used by man since prehistoric times; it occurs in many different forms, and has an amazing variety of uses. Many familiar objects and materials contain clay or require clay in their manufacture; among these are paper, rubber, linoleum, enamels, paints, plastics, pesticides, medicines, fertilizers, fine porcelain, pottery, refractory brick, common brick, tile, and sewer pipe.

Idaho has abundant reserves of clay. Clay production and utilization is potentially one of the fastest-growing phases of the mineral industry in Idaho. For this reason, the present publication by Professor Newton, Head of the Department of Mining and Metallurgy at the University of Idaho, is particularly timely.

Professor Newton describes the structure and composition of clay minerals in relation to their physical properties and uses. He outlines methods of identifying various kinds of clay, and he tells of the different types of clay deposits. Finally he discusses the commercial value of the different types of clay.

The amount of published literature on clay and clay products is enormous; only a few of the available references are given in the bibliography. Each of these references, however, contains a bibliography which will enable a reader to make an exhaustive investigation of any of the topics that are introduced here.

E. F. COOK, Director
Idaho Bureau of Mines & Geology

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by

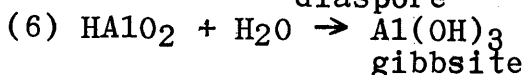
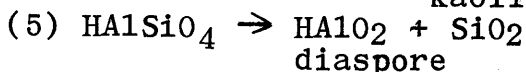
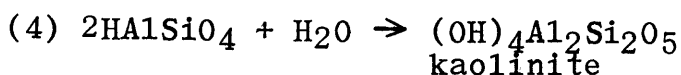
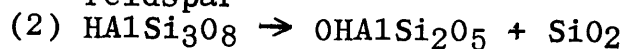
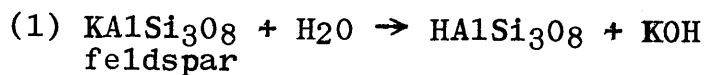
Joseph Newton

INTRODUCTION

Used by man since prehistoric times, clay has always been an important industrial commodity. Because of its many types and the many commercial uses for them, the literature on clay is voluminous, and its nomenclature and classifications are quite complex.

ORIGIN OF CLAYS

Clays are formed by secondary alteration of siliceous rocks, usually considered to have reacted with ground water. Norton (6) gives the following reactions as typical:



These equations represent the reactions involved in the weathering of one particular feldspar mineral (orthoclase). Let us consider the significance of this simple alteration to see how it can be projected to account for the more complex clays.

Two types of chemical reactions are involved: hydration (equations 1, 4, and 6) and desilication (equations 2, 3, and 5). Though the actual reactions may not take place in the order indicated, we know that these two processes must occur.

(1) Water that can be driven off by heating clay minerals, such as kaolinite, must come from outside because the parent mineral (feldspar) is anhydrous;

(2) Clay minerals contain relatively less silica than the parent rocks (in fact, there is virtually no silica left in diaspore and gibbsite);

(3) Water emerging from residual kaolin deposits contains silica in solution, which shows that it is being leached away from the rocks; in our equations it is assumed that the KOH and SiO₂ are dissolved and carried away by the ground water.

To summarize, then, the clay-forming reactions involve the addition of water (hydration) and the removal of silica (desilication). In this example, the potassium is also removed so that the end products contain only alumina (aluminum oxide), water, and silica; if diaspore or gibbsite is formed, only alumina and water remain.

For clay formation, equation 4 usually represents the end of the reaction, and kaolinite is a "typical" clay mineral. Equations 5 and 6 represent a type of weathering that produces bauxites and laterites, a process that seems to take place only in tropical or sub-tropical climates: the bauxites are composed largely of hydrated aluminum oxides; the laterites contain large amounts of hydrated iron oxides. In temperate climates, where the desilication does not go to completion, the end products (such as kaolinite) contain combined silica. The weathering that produces the bauxites and laterites, however, is essentially the same as the clay-forming reactions except that desilication is more complete.

Now let us distinguish between clay and clay minerals. Clay is the natural rock that is left as a residue from the weathering processes; clay minerals are definite minerals such as kaolinite. A clay may contain one or more clay minerals plus many residual or accessory minerals.

If our original rock was solid orthoclase weathered under temperate conditions, we would expect to get pure kaolinite; and weathered under tropical conditions pure gibbsite. With this ideal case as a starting point, let us consider some additional factors of great importance in clay formation.

1. Most rocks contain certain minerals resistant to weathering, which will remain virtually unchanged: quartz, mica, magnetite, ilmenite, and many other minerals found in clays, bauxites and laterites are simply residual from the parent rock.

2. Our equations indicate the formation of kaolinite from the potassium-aluminum feldspar, and show that the potassium is completely removed; in some cases, part of the potassium may remain in the clay mineral. Also, siliceous rocks and minerals other than orthoclase, can form clay minerals--the other feldspars, basalt, and volcanic glass, for example. Many of these parent substances contain magnesium, iron, sodium, and other metallic ions that may remain (in whole or in part) in the clay mineral.

3. The slow hydration and desilication reactions may not go to completion; in some clays, for example, we find crystals of unaltered feldspar surrounded by a coating of kaolinite, where there has not been enough time to permit complete kaolinization. Or some kaolinite in a given clay may possibly have altered to diaspore or gibbsite (equations 5 and 6).

THE CLAY MINERALS

With this brief description of the chemistry of the clay-making reaction, let us consider the nature of the clay minerals. We shall

have to dispense with chemical formulas almost completely and describe the minerals in terms of their structure.

THE BASIC STRUCTURE IN CLAY MINERALS

Kaolinite, best-known of the clay minerals requires a fairly complete description from which we can then discuss the other clay minerals by considering the ways in which they deviate from kaolinite's "ideal" structure.

A "hydrous aluminum silicate," kaolinite has already been represented by the formula $(OH)_4Al_2Si_2O_5$, but it also has other formulas: $H_4Al_2Si_2O_9$, and $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. While all of these are correct in that they give the proper chemical composition, they do not indicate the important structural arrangements.

The basic unit in all silicate minerals is the SiO_4 tetrahedron, which consists of a silicon atom (ion) surrounded by four oxygen atoms. In this very stable structure, each oxygen atom is linked to silicon by a strong electron-pair bond (one electron from silicon, one from oxygen). Because silicon is tetravalent, it can hold four oxygen atoms. Because the oxygen is divalent (has two valence electrons) an oxygen atom can be bonded to two adjacent silicon atoms in such a way that the oxygen belongs to both tetrahedra. When all the oxygen atoms are thus shared, we have a strongly bonded, three-dimensional network--the quartz crystal. In many silicate minerals the tetrahedra form long chains to produce a fibrous mineral such as sillimanite; in others, the tetrahedra form two-dimensional sheets (micas, for example). The clay minerals contain extended sheets or chains of SiO_4 tetrahedra.

Tetrahedral coordination

We speak of the silicon as having tetrahedral coordination because the four oxygen atoms are placed at the corners of a regular tetrahedron with the silicon at its center. The oxygen atoms are larger than the silicon atom which is effectively "buried" within the tetrahedron; reactions with other ions result from the free valences of the oxygen atoms at its corners.

Octahedral coordination

Aluminum ions tend to surround themselves with six oxygen and/or hydroxyl ions, and we call this octahedral coordination because the ions are disposed at the six corners of a regular octahedron. This nomenclature is initially confusing because one might think "octahedral" refers to eight atoms; an octahedron, however, has eight sides but only six corners.

The unit cell of kaolinite

The kaolinite crystal is a "two-layer" crystal and is built up of sheets which are assembled as shown in Figure 1, which shows the arrangement of the "unit cell" of the kaolinite lattice.

The five sketches indicate the arrangement in the basic two-layer kaolinite crystal of the various layers of atoms; if we were able to strip these off in succession we would find (from top to bottom) (1) oxygen ions, (2) silicon ions, (3) mixed oxygen and hydroxyl ions, (4) aluminum ions, and (5) hydroxyl ions. If these five layers were turned at right angles and fitted together, the ions would be in the positions they occupy in the kaolinite crystal. The broken lines outline the boundaries of the unit cell. Of course, the ions extend in both directions in the plane of the paper: the few atoms shown merely indicate the pattern, and the unit cells extend in both directions. Ions shown entirely within the boundary belong completely to the cell shown; ions on the edges are shared by two cells; ions on the corners are shared equally by four cells. The number of ions in the unit cell then is as follows:

Top layer	$4 + \frac{4}{2} = 6$	O^{--} ions
Second layer	$2 + \frac{4}{2} = 4$	Si^{++++} ions
Third layer	$1 + \frac{4}{4} = 2$	OH^- ions
and	$2 + \frac{4}{2} = 4$	O^{--} ions
Fourth layer	$3 + \frac{2}{2} = 4$	Al^{+++} ions
Bottom layer	$5 + \frac{2}{2} = 6$	OH^{--} ions

From this computation we can write the formula $(OH)_8Al_4Si_4O_{10}$ which if divided by two, becomes $(OH)_4Al_2Si_2O_5$, the initial formula for kaolinite.

If we re-unite these exploded fragments of the unit cell, (Figure 1) we can visualize the relative positions of the ions. Note the following:

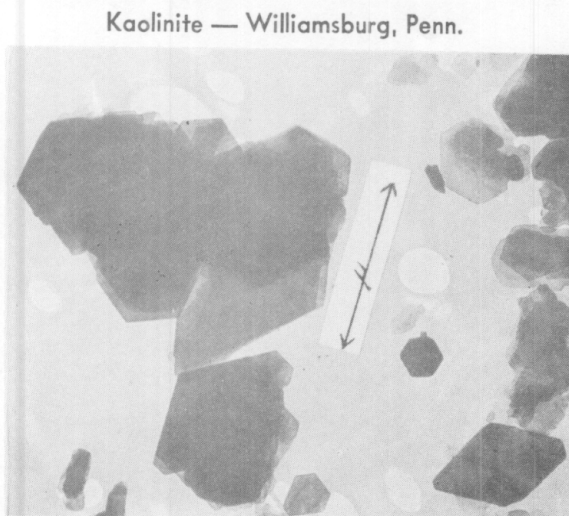
(1) Each silicon ion is surrounded by four O^{--} ions: three in the top layer and one in the middle layer.

(2) Each aluminum ion is surrounded by six large ions: three in the bottom layer and three in the middle layer. The three in the bottom layer are all OH^- ions; in the middle layer there are two O^{--} ions and one OH^- ion.

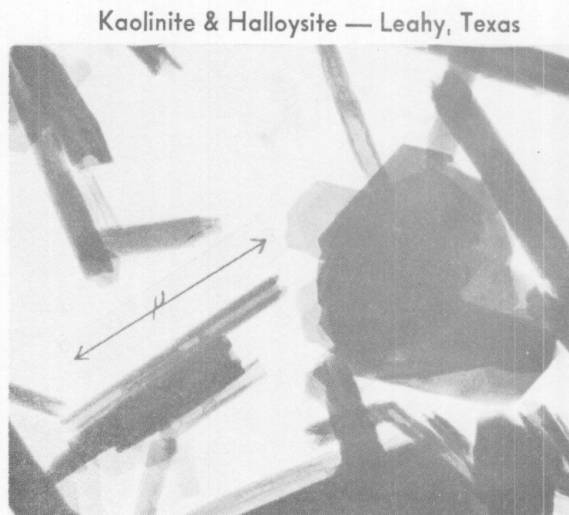
(3) Because positive and negative charges in the unit cell are equal, the crystal is electrically neutral.

(4) The ions in the middle layer belong to both the tetrahedral and octahedral systems: the O^{--} ions in this middle layer are in tetrahedral coordination with Si^{++++} , and also in octahedral coordination with Al^{+++} . This sharing of common ions strongly bonds together the two parts of the layer.

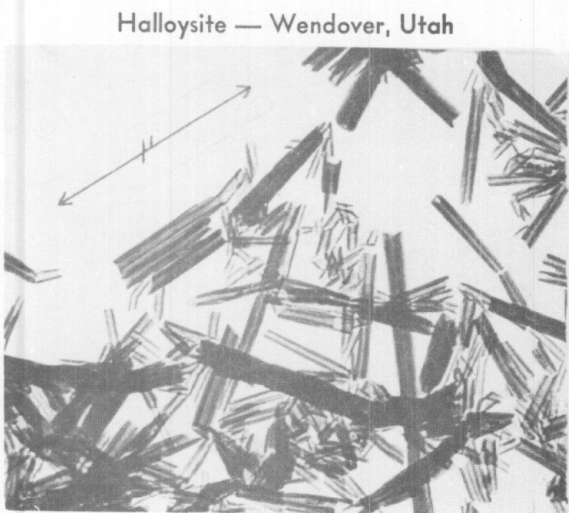
(5) The "top" of the sheet presents an unbroken array of O^{--} ions; the "bottom" is a layer of OH^- ions.



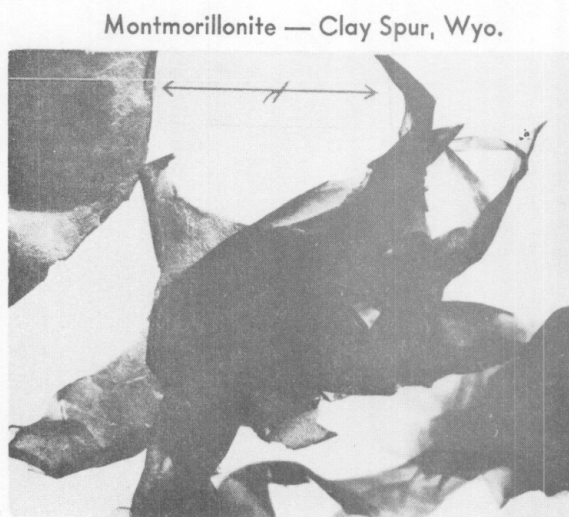
A (22,600x)



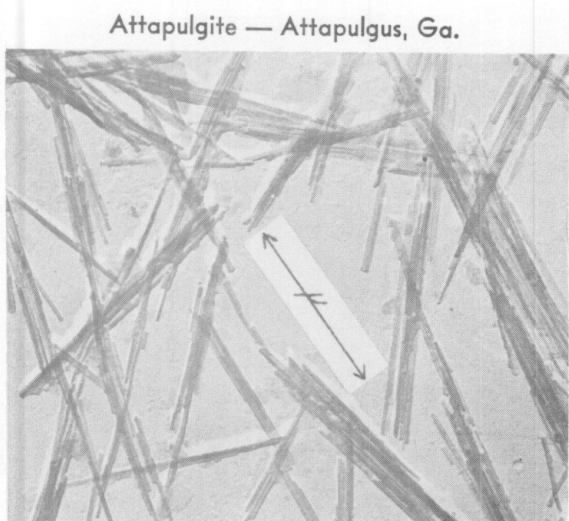
B (30,000x)



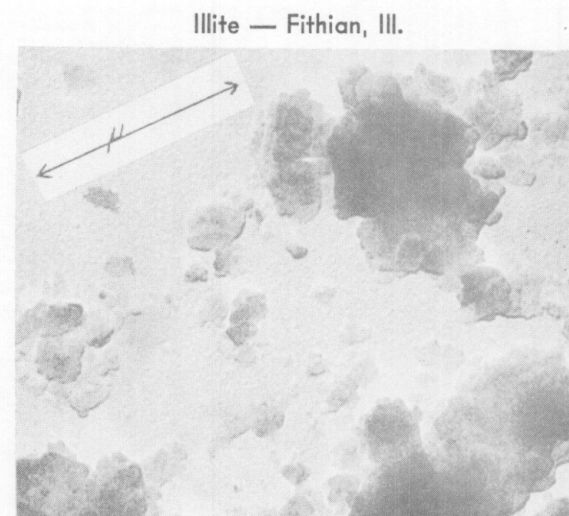
C (30,000x)



D (28,800x)



E (23,200x)



F (29,600x)

Figure 2
Electron micrographs of clay minerals.

Micrographs from: The Mineral Constitution Laboratories, School of Mineral Industries, The Pennsylvania State College; Courtesy of Dr. Thomas F. Bates.

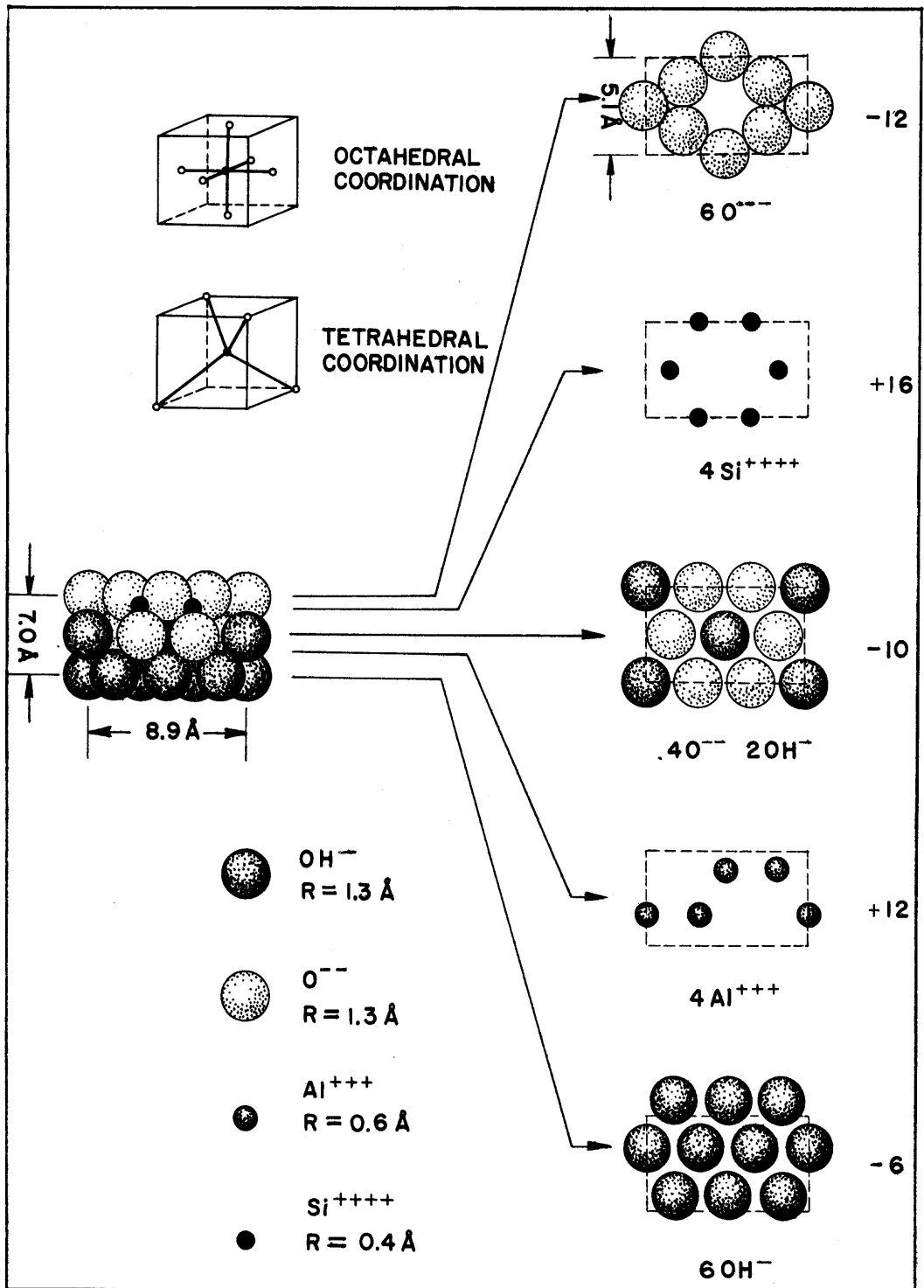


Figure 1
The Unit Cell of Kaolinite.

Reproduced by permission from Norton, ELEMENTS OF CERAMICS, 1952,
Addison-Wesley Publishing Company, Reading, Massachusetts.

(6) When kaolinite is heated, the OH^- ions react to form water, which is driven off. Though there are no water "molecules" in the crystal, OH^- ions are essential parts of the crystal.

The kaolinite crystal structure

Kaolinite crystals are "books" of these sheets stacked one above another with the OH^- face of one layer adjacent to the O^{--} face of the next layer. Electrically neutral, these sheets are held together only by relatively weak residual valences or van der Waal's forces. Figure 2 shows an electron photomicrograph of typical kaolinite crystals: flat plates with a roughly hexagonal outline.

DEVIATIONS FROM BASIC STRUCTURE IN CLAY MINERALS

Isomorphous substitution

Let us rewrite the formula of kaolinite as $(\text{Al}_2)(\text{Si}_2)(\text{O}_5)(\text{OH})_4$, listing the two cations (Al^{+++} and Si^{++++}) separately from the two anions (O^{--} and OH^-). In the ideal lattice only these four ions are present; all the Al^{+++} ions are in octahedral coordination, and all the Si^{++++} in tetrahedral coordination. As we have seen (Figure 1), this structure gives a crystal that is electrically neutral.

In most natural clay minerals, however, some of the cations are replaced by others; Fe^{+++} for Al^{+++} , Mg^{++} for Al^{+++} , etc. Even when only aluminum and silicon ions are present, we may have replacement of some of the Si^{++++} ions by Al^{+++} ; that is, some of the aluminum ions will be in tetrahedral coordination. In fact, it is doubtful if any kaolinite exists that corresponds exactly to our theoretical formula.

The extent of this isomorphous replacement of ions is extremely important because it determines the surface properties of the minerals and it accounts for the large and bewildering variety of clay, mica, and other layer-type silicate minerals. The extent of this replacement by "foreign" ions probably depends upon many factors, but certainly an important one is the chemical composition of the parent rock (if no iron is present, for example, then there would be no replacement by Fe^{+++} ions). Two phenomena about isomorphous replacement are of first importance:

1. Whenever a cation replaces another of a different valence, a residual electric charge remains in the mineral. For example, when Al^{+++} replaces Si^{++++} in the tetrahedral coordination, or Mg^{++} replaces Al^{+++} in octahedral coordination, there is a deficiency of positive charges, and the mineral particle is left with a net negative charge. As this type of replacement appears to be the most common, most of these minerals have a "built-in" negative electric charge. Cations (Na^+ , H^+ , Mg^{++} , Fe^{+++} , etc.) are attracted by these negative charges and cling at or near the surface of the sheet in sufficient quantity to make the particle electrically neutral. These "surface" ions are rather loosely held, and it is often possible to substitute one type for another; these are the exchangeable cations or exchangeable bases.

2. Although this isomorphous replacement may be very slight or quite extensive, the amount of replacement has a great effect on the nature of the mineral. Not only do a number of distinctly separate minerals result from differing degrees of replacement, but many gradations of the same mineral can exist. This phenomenon makes it difficult to classify and identify the clay minerals.

Two-layer minerals

The basic structure of a two-layer mineral (kaolinite is an example) is a sheet consisting of two tightly bonded layers. In our exploded diagram (Figure 1) where we have indicated five "layers" of ions, only two are essentially structural layers--the tetrahedral and octahedral layers which share some of the large anions. Other two-layer clay minerals that differ from kaolinite we will discuss later.

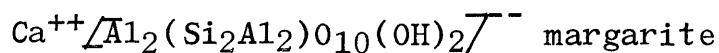
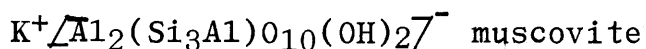
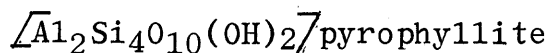
Three-layer minerals

Some clay minerals (such as montmorillonite) are composed of sheets consisting of three layers--an octahedral layer sandwiched between two tetrahedral layers. Some of the anions in the central octahedral layer are also in tetrahedral coordination with either the top or bottom layer. In these three-layer minerals, both faces of the sheet consist of an array of O^{--} ions; all the OH^- ions are buried within the sheet. Because these "oxygen" surfaces have relatively little attraction for one another, it is possible for several layers of water to enter the space between adjacent sheets of the crystal, which produces the swelling of montmorillonite and similar clay minerals.

Chemical formulas of silicate minerals

Let us write a few formulas from Kingery (3) for some of these minerals (clay minerals, micas, etc.) to indicate the wide variations that are possible. First we will consider two kaolinites: $Al_2Si_2O_5(OH)_4$, "ideal" kaolinite, and $(Al_{1.958}Fe_{0.039}^{++}Mg_{0.003})(Si_{1.982}Al_{0.018})O_5(OH)_4$, kaolinite from Pugu, Tanganyika. This latter formula was given by Robertson, Brindley, and Mackenzie (3, p. 14) as the result of the analysis of a carefully purified clay. Note that a small amount of the octahedrally coordinated aluminum is replaced by ferric iron and magnesium, and that a little of the tetrahedrally coordinated silicon is replaced by aluminum. The substitution of ferric iron for trivalent aluminum does not affect the neutrality of the crystal; but each of the other substitutions causes a deficiency of positive charge because we are replacing trivalent aluminum with divalent magnesium and tetravalent silicon with trivalent aluminum. Consequently, a net deficiency results of $0.021 +$ charges ($0.003 + 0.018$) per mol. of kaolinite; or, to put it another way, the crystal has a negative charge of 0.021 units for each mol. This negative charge is balanced by positive ions held at the surface. In this study (3, p. 14) it was shown that the amount of charge predicted by the formula was consistent with the measured "exchange capacity."

Let us now consider three non-clay minerals:



In these, the square brackets enclose the aluminosilicate sheet. Pyrophyllite is the ideal three-layer mineral; muscovite (common mica) has one-fourth of its tetrahedral silicon replaced by aluminum, with a balancing ion of potassium; margarite has one-half of the silicon replaced with aluminum, with a balancing ion of divalent calcium. Dana's Textbook of Mineralogy (1) lists many other minerals that are related to muscovite; two such are paragonite or sodium mica and roscoelite. Paragonite has the same formula as muscovite except that the balancing ions are sodium rather than potassium; and roscoelite is essentially a muscovite in which vanadium has partly replaced the aluminum. These two examples illustrate the fact that the number of possible mineral species is very large.

Now let us consider the structure of the clay mineral montmorillonite. Its formula may be written: $\text{M}_{x+y}(\text{Al}_{2-y}\text{Mg}_y)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2$ where M indicates any monovalent ion, and the quantity $x+y$ is between 0.3 and 0.5. Structurally, this mineral may be considered as intermediate between pyrophyllite and muscovite; the isomorphous substitution is less in montmorillonite than in muscovite.

Both muscovite and montmorillonite are three-layer minerals. In muscovite where the isomorphous substitution is extensive, the residual negative charge in the sheets is sufficient to hold the potassium ions firmly in position. Muscovite crystals consist of three-layer aluminosilicate sheets held together by the electrostatic action of layers of potassium ions sandwiched between them.

Montmorillonite also is a three-layer mineral, but the residual negative charge in the sheets is less than in muscovite because the sheets are held together by the electrostatic action of the "M" ions, which are fewer and farther between than the potassium ions in the muscovite crystal. Not only are the bonds holding the sheets together weaker, but the "M" ions are largely exchangeable; as a result layers of water molecules can force themselves in between the aluminosilicate sheets.

Note also that there are many possible montmorillonites. The "M" ions may be Na^+ , K^+ , Mg^{++} , Ca^{++} , or some combination of these; either x or y may vary from 0.0 to 0.5; and the sum $x + y$ may vary between 0.3 and 0.5.

One-layer minerals

Gibbsite ($\text{Al}(\text{OH})_3$) is considered to be made up of single-layer sheets in which the aluminum ions are in octahedral coordination with the hydroxyl ions, with only two-thirds of the possible

Al sites occupied. Brucite ($Mg(OH)_2$) has a similar octahedral coordination, but with all the cation positions occupied. A variant, "brucite-like" layer has the formula $(MgAl)(OH)_2$.

Mixed-layer minerals

Some minerals are made up by an ordered stacking of alternate layers of different types; chlorite, for example, consists of alternate three-layer aluminosilicate sheets and brucite-like layers. It is also possible to have a mixed-layer structure in which there is a random, irregular stacking of layers of different kinds.

Chain-structure minerals

In some clay minerals the SiO_4 tetrahedra form long chains rather than two-dimensional layers; these chains are linked together by groups of oxygen or hydroxyl ions in octahedral coordination about Al or Mg ions.

Hydration

All the clay minerals contain hydroxyl groups which, when heated, react as follows: $2OH^- \rightarrow H_2O + O^{--}$, after which the water (known as lattice water or hydroxyl water) is driven off leaving oxygen ions in the lattice. In addition, interlayer water may exist between the sheets of the crystal in certain minerals, and pore water may occupy the spaces between the individual crystals. Some interlayer water and water adsorbed on the surface of the crystals may be classified as bound water if it cannot be removed by "ordinary" drying.

Many of the common cations are hydrated when in water solution, and there is evidence that this is an important factor in the hydration of clay minerals: when ions adsorb on clay surfaces, they may carry one or more molecules of water with them.

Edge effects

The theories advanced to explain the observed surface properties of clay minerals are based on the nature of the exposed surfaces of the sheets and the amount of "built-in" charge resulting from isomorphous substitution. It must be remembered, however, that these individual crystals do not have large surface areas (rather, they are usually extremely small) and that their edges are different from the "flat" surfaces. At edges and corners, where the regular lattice structure is broken, we may have "exposed" silicon or aluminum ions, which causes a surface behavior of edges different from that of flat surfaces.

Particle size

Because most clay crystals are very small, we ordinarily express their "diameters" in microns and their lattice spacings (distances between adjacent layers) in angstrom units. Let us consider briefly a few relations between these units to fix in mind the relative magnitude of some of these dimensions.

1 millimeter = 1000 microns (μ)
 1 micron = 10,000 angstrom units

Let us compare the sizes of a "coarse" sand particle (diameter of a 10-mesh screen opening) and a very fine sand particle (diameter of a 325-mesh screen opening) with a few of the dimensions of clay particles.

	m.m.	microns	angstrom units
10-mesh aperture.....	1.651	1651	16,510,000
325-mesh aperture....	0.044	44	440,000
Usual diameter of a kaolinite crystal....	0.001	1	10,000
Wall thickness of a kaolinite crystal....	0.00005	0.05	500
Wall thickness of a halloysite crystal...	0.00002	0.02	200
Distance between planes of hydrated halloysite crystal...	0.000001	0.001	10
Distance between planes of a kaolinite crystal....	0.00000072	0.00072	7.2

These figures, of course, are averages but they indicate the relative magnitude of these dimensions and emphasize that clay minerals are extremely small as the following observations indicate:

1. In many clay "bodies" for ceramic work, we often mix "grog" (burned ceramic material which has been crushed and ground) with the clay. The grog, which remains inert when the clay is fired, is added to decrease the shrinkage of the clay. Most of the grog particles are as large as relatively coarse sand: even the smallest of the grog particles is much larger than the coarsest clay particle.
2. Most kaolinite crystals will pass readily through the aperture of a 325-mesh screen (and kaolinite is one of the "coarser" clay minerals) which means that we cannot use screens for separating clay minerals into various fractions, because a 325-mesh screen is about the finest available.
3. An average kaolinite crystal will consist of only about 70 aluminosilicate layers (500/7.2); a crystal of hydrated halloysite may have a wall thickness of only 20 layers (200/10). It is difficult to obtain accurate measurements of the wall thicknesses of these crystals, but in most cases there is no doubt that the crystal contains relatively few layers or sheets.

Clay minerals are not equidimensional, but are in the form of flat plates, warped plates, tubes, or chains. For the most part too small to be observed with a light microscope, they must be photographed with the electron microscope; and for some of the finer clay minerals, even the resolving power of the electron microscope is not sufficient.

CLASSIFICATION OF CLAY MINERALS

Let us list the common classes of clay minerals. This classification, based on structure, is essentially the same as that given by Grim (2) and Klinefelter and Hamlin (4).

TABLE 1. Classification of the clay minerals

- I. Amorphous: Allophane group.
- II. Crystalline
 - A. Two-layer type
 - 1. Equidimensional: Kaolinite group (kaolinite, dickite, nacrite).
 - 2. Elongated: Halloysites.
 - B. Three-layer types
 - 1. Expanding lattice
 - a. Equidimensional
 - (1) Montmorillonite
 - (2) Vermiculite
 - b. Elongated
 - (1) Nontronite
 - (2) Saponite
 - (3) Hectorite
 - 2. Nonexpanding lattice: Illites.
 - C. Mixed-layer types: Chlorite group.
 - D. Chain-structure types
 - 1. Attapulgite
 - 2. Sepiolite
 - 3. Palygorskite

Allophane is the name given to any amorphous clay mineral; that is one which gives no X-ray diffraction pattern. Allophanes are probably random arrangements of SiO_4 tetrahedra and metallic ions in octahedral coordination. Not only is little known about the chemical composition of allophanes, but their study is difficult because they are usually mixed with crystalline clay minerals. They are not of much commercial importance.

Except for hydrated halloysite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$), all members of the two-layer type have the same composition as kaolinite: namely, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ or $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Because of the nature of its formula, hydrated halloysite is sometimes called "four-water" halloysite; only half of the water is interlayer water, however, the other half is lattice water.

Dickite, kaolinite, and nacrite are all platy minerals. Dickite crystals are well-defined hexagonal plates, whereas kaolinite crystals, also hexagonal plates, may be elongated and less well-defined. The differences between these minerals result from different stacking of the two-layer aluminosilicate sheets.

Kaolinite crystals are usually from 0.1 to 3.0 microns in diameter, and the thickness is much less than 1 micron.

Halloysite crystals are elongated, having the appearance of small tubes, though split and unrolled tubes are also observed. The crystals have lengths of 0.1 to 1.0 micron, tube diameters of 0.05 to 0.2 micron, and wall thicknesses of about 0.02 micron. The stacking of the aluminosilicate layers is such that they curl into tubes instead of remaining flat. In the hydrated form, the aluminosilicate layers are separated by the interlayer water.

Crystals of montmorillonite, already briefly described as a typical three-layer mineral, are thin, poorly-defined plates usually much smaller than one micron. Nontronite and hectorite form thin laths or ribbons. Vermiculite consists of three-layer mica sheets separated by water layers about two molecules thick, and the lattice expansion of vermiculite is limited by this. Montmorillonites will take up thicker layers of interlayer water. We have already noted the variable composition of montmorillonite, and it is likely that minerals such as nontronite, hectorite, and saponite should be regarded as varieties of montmorillonite.

The illites or clay micas are essentially "imperfect" micas: because of less isomorphous substitution, there are not enough balancing ions to bind the aluminosilicate sheets firmly together (as in the well-crystallized micas). Illites consist of poorly-defined, thin hexagonal plates or ribbon-like particles about one micron in width; they contain little or no interlayer water.

Chlorite crystals, normally composed of alternate layers of mica sheets (three-layer aluminosilicate sheets) and brucite sheets (single-layer sheets of Mg and Al hydroxides), are altered in the clay-mineral chlorites to essentially "imperfect" or "modified" chlorites much as the illites are "imperfect" micas. Like illites, chlorite clay minerals contain little or no interlayer water.

The chain-structure clay minerals such as attapulgite, sepiolite, and palygorskite appear as fibers or rods under the electron microscope (there are also flaky forms of sepiolite). The rods will be 0.1 to 5.0 microns in length and 0.01 to 0.1 micron in width. These minerals contain "intercolumn" water that corresponds to the interlayer water found in the plate-type clay crystals.

CHEMICAL ANALYSES OF CLAYS

A great many chemical analyses of clays have been published; for example Grim (2) lists a number of representative analyses of different types of clay minerals, in which the elements are reported as oxides (MgO, Al₂O₃, SiO₂, H₂O, etc.). Let us compute the theoretical chemical analyses of five of the clays we have discussed:

- (1) Theoretical kaolinite
- (2) Tanganyika kaolinite, in which we will assume that Na⁺ is the balancing ion.

- (3) Hydrated ("four-water") halloysite.
- (4) Montmorillonite ("dry"), in which the balancing ion is Na^+ , and to which we will assign the following values: $x = 0.2$; $y = 0.2$.
- (5) Hydrated montmorillonite, in which we will assume 4 mols of water for each mol of "dry" montmorillonite.

The chemical formulas for these five minerals are as follows (the percentages are given in Table 2):

1. $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
2. $(\text{Na}_2\text{O})_{0.010} \cdot (\text{Al}_2\text{O}_3)_{0.988} \cdot (\text{Fe}_2\text{O}_3)_{0.020} (\text{MgO})_{0.003} \cdot (\text{SiO}_2)_{1.982} \cdot 2\text{H}_2\text{O}$
3. $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
4. $(\text{Na}_2\text{O})_{0.2} \cdot (\text{Al}_2\text{O}_3) \cdot (\text{MgO})_{0.2} \cdot (\text{SiO}_2)_{3.8} \cdot \text{H}_2\text{O}$
5. $(\text{Na}_2\text{O})_{0.2} \cdot (\text{Al}_2\text{O}_3) \cdot (\text{MgO})_{0.2} \cdot (\text{SiO}_2)_{3.8} \cdot 5\text{H}_2\text{O}$

TABLE 2. Calculated composition of five clay minerals

Mineral	Per cent by weight						Ratio: $\text{Al}_2\text{O}_3/\text{SiO}_2$	
	Al_2O_3	SiO_2	Na_2O	MgO	Fe_2O_3	H_2O (OH)	H_2O inter layer	
Theor. kaolinite	39.6	46.5				13.9		0.851
Tanganyika kaolinite	38.8	45.8	0.2	0.1	1.2	13.9		0.848
Hydrated halloysite	34.7	40.8				12.2	12.2	0.851
Montmorillonite	27.7	61.9	3.4	2.2		4.9		0.447
Hydrated montmorillonite	23.1	51.6	2.8	1.8		4.0	16.4	0.447

The clays that are highest in alumina are the two-layer clays such as the kaolinites and halloysites; the three-layer clays show a ratio of Al_2O_3 to SiO_2 that is about one-half that of kaolinite because each sheet contains two tetrahedral layers for each octahedral layer. The published analyses (2) of kaolinite, nacrite, dickite, and halloysite check quite closely with the figures in Table 2, though the following three exceptions are noteworthy:

1. All of these clays show small amounts of oxides other than Al_2O_3 and SiO_2 ; our Tanganyika kaolinite is closer to the theoretical composition than any of those listed by Grim (2).

2. Our analyses show that kaolinite contains 13.9 per cent water, all lattice water; the hydrated halloysite contains 12.2 per cent lattice water and 12.2 per cent interlayer water (a total of 24.4 per cent). Actual analyses report either total water or "low"

and "high" temperature water. The low-temperature water is what can be driven off at temperatures of 100° - 150° C; the high-temperature water is driven off at temperatures above 300° C.

3. Many kaolinites, nacrites, and dickites show appreciable amounts of low-temperature water. The amount of low-temperature water in halloysite is always less than our theoretical "inter-layer" water. We have shown a theoretical total water content of 24.4 per cent in halloysite; actually this percentage is usually about 17 to 19 per cent, and the low-temperature water is from 2.5 to 6.0 per cent.

The published analyses of other clay minerals may show great deviations from any "theoretical" compositions. Grim (2) lists seven montmorillonites that check fairly closely with item 5 in Table 2. Containing from about 8.5 to 23.0 per cent total water, none is as low in water as our hypothetical "dry" montmorillonite (item 4, Table 2). In all cases, however, the amount of high-temperature water is relatively greater than the lattice water (4.0 per cent) shown in Table 2. In each case, also, the alumina percentage is lower than 23.1 per cent and the amounts of other basic oxides are greater.

Analyses listed for other minerals of the montmorillonite family (nontronite, hectorite, and saponite) show much greater variations. For example, one nontronite contains 31 per cent Fe_2O_3 and only 5 per cent Al_2O_3 ; a hectorite contains 26 per cent MgO and only 0.14 per cent Al_2O_3 . These variations are so great that, on the basis of chemical analysis, such minerals would not be considered even distant relatives. All these montmorillonite-like minerals contain 15 to 20 per cent water, about two-thirds of which is low-temperature water.

The composition of the illites is similar to that of the related micas. All contain fairly large amounts of K_2O (4 to 8 per cent); the water varies between 6 and 10 per cent (mostly high-temperature water); some illites contain as much as 18.8 per cent Fe_2O_3 (which replaces Al_2O_3).

Most of the chlorite clay minerals contain between 32 and 45 per cent combined MgO and FeO , but the amount of each is highly variable. Chlorites contain about 7 to 13 per cent lattice water and practically no low-temperature water.

Vermiculites do not show such extreme variations in composition. They will contain 34 to 36 per cent SiO_2 , 20 to 25 per cent MgO , 19 to 20 per cent H_2O , and about 20 per cent combined Al_2O_3 and Fe_2O_3 . The greatest variation is in the amount of Al_2O_3 replaced by Fe_2O_3 .

The chain-type clay minerals (sepiolite, palygorskite and attapulgite) contain 47 to 55 per cent SiO_2 , with highly variable amounts of MgO and Al_2O_3 as the principal bases. Of the 21 to 30 per cent water, about 10 per cent is low-temperature (channel or column) water.

WATER IN CLAYS

The water in clay minerals is extremely important, for many of the useful properties of clays result from its presence, as we have already discussed in some detail. This section recapitulates the important facts.

1. All clay minerals contain water that is expelled when the mineral is heated: from 6 per cent in some of the illites up to 25 per cent in some of the montmorillonites.

2. As part of their crystal structure all clay minerals contain hydroxyl ions (lattice water or hydroxyl water); to expel this lattice water requires fairly strong heating, usually to about 500° C. As the lattice water (the high-temperature water) leaves, the structure of the clay crystal is destroyed and the anhydrous oxides that remain must re-combine to form new crystals or a glass.

3. Low-temperature water is that which can be expelled by heating to 100-150° C: (a) pore water, which occupies spaces between clay crystals; (b) adsorbed water, which adheres to the surface of clay crystals; and (c) layer water or intercolumn water, which is between the layers or columns of the clay crystals. When clays are heated, the pore water evaporates first; at higher temperatures the layer water and adsorbed water are given off.

4. For some clay minerals, the low-temperature water is expelled at a definite temperature, which is one of the diagnostic tests that can be used for identification. For other clays (notably the allophanes) the water is given off gradually as the temperature rises.

5. Pore water and some of the layer water is easily removed, much of it simply by drying at ordinary temperature. Adsorbed water, as well as a part of the layer water, requires heating to 100° C or even 150° C for removal. Pore water appears to be ordinary "liquid" water and can evaporate much like water in an open pan: as long as its vapor pressure is greater than the partial pressure of the surrounding water vapor it will continue to evaporate. When we have relatively thick layers of interlayer water in such minerals as montmorillonite, the water in the central part of the layer also behaves much like "liquid" water.

Adsorbed water, and the interlayer or intercolumn water that is close to an aluminosilicate layer, appear to be more strongly bound to these surfaces. Such water does not evaporate readily at room temperatures, but it may require heating to 100°-150° C to remove it. Some theories postulate that these water molecules are bound to the surface in a regular geometric pattern (effectively "crystallized") to prevent ready evaporation; also, that the balancing ions may be hydrated. The term "bound water" is used to describe such water.

6. Hallöysites, montmorillonites, and other minerals containing interlayer or intercolumn water will re-hydrate if only part of

the interlayer water has been driven off. When all traces of the low-temperature water are driven off, however, the mineral will not rehydrate.

7. Because the water in many of these hydrated minerals tends to come to equilibrium with the water vapor in the surrounding atmosphere, it is difficult to get a "true" analysis of these minerals as they occur in nature: some of the unbound water (in a montmorillonite, for example) could evaporate while the sample was being transported to the laboratory.

8. The terms "low" and "high temperature" waters, used in connection with clay analysis, are roughly synonymous with "interlayer" and "lattice" water. Some minerals, such as kaolinite, may have small amounts of low-temperature water, probably adsorbed water.

In general, there is little or no low-temperature water in the following clays: dickite, nacrite, kaolinite, illite, and chlorite.

The clays which contain considerable amounts of low-temperature water are: montmorillonites (montmorillonite, nontronite, hectorite, saponite), vermiculite, sepiolite, palygorskite, attapulgite, and allophane.

X-RAY ANALYSIS OF CLAY MINERALS

It is obvious that chemical analysis alone is not sufficient to identify most clay minerals; certainly it cannot give much information about their crystal structure. X-ray analysis has yielded most of the information we have about the crystal structure of clays.

If a beam of X-rays is passed through a crystal, the X-rays are diffracted by the planes of atoms or ions in much the same way as visible light is diffracted when it passes through a grating. The diffracted rays impinge on a photographic plate and produce a diffraction pattern that indicates the disposition of the various crystal planes and the distances between them.

Though X-ray analysis works best when it is possible to test single crystals, most clay minerals have such a small particle size that it is necessary to use the powder method in which the X-ray beam is directed through a mass of finely divided crystals. With careful X-ray analysis it is possible not only to work out the crystal structure, but also to obtain significant information about the size and shape of the individual crystals and the extent of replacement within the layers.

Theoretically, each clay mineral has its own characteristic diffraction pattern so that the X-ray method should produce positive identification. Even though much of our knowledge of clay crystals has come from X-ray studies, this method alone does not provide sufficient information for identification in most cases, chiefly for three reasons.

1. X-rays must be diffracted from a fairly large number of uniformly-spaced crystalline layers if the pattern is to be sharp; many

clay crystals are so small and poorly crystallized that they do not give good definition. In fact, the allophanes are "amorphous", which simply means that there are so few regularly-spaced crystalline layers in any aggregate that no diffraction pattern can be obtained.

2. Because many natural clays contain two or more clay minerals, the observed diffraction pattern will be a composite of two or more individual patterns. In some instances, the X-ray diffraction will clearly identify each of the minerals in such a mixture; in others, the X-ray pattern simply becomes fuzzy and difficult to interpret. Also we may have mixed-layer crystals to introduce additional complications.

3. As the spacing between basal planes of hydrated clay minerals depends upon the amount of interlayer water between these planes, the diffraction pattern will change as the amount of interlayer water increases or decreases. This phenomenon, however, can be used to confirm the presence of certain hydrated minerals.

BASE EXCHANGE

DEFINITION OF BASE EXCHANGE CAPACITY

We have mentioned the balancing ions that are held adjacent to the aluminosilicate layers by the negative charges resulting from isomorphous replacement. Not all of these balancing ions are exchangeable (the potassium ions in muscovite, for example). On many of the clay minerals, however, some or all of the balancing cations can be replaced by other cations.

The base exchange capacity or cation exchange capacity of a clay is defined as the number of milliequivalents of replaceable ions per 100 grams of dry clay. It is commonly measured by first replacing all the natural cations with hydrogen ions, and then replacing (neutralizing) these hydrogen ions with sodium ions. One process is to produce an "acid" or "hydrogen" clay (all exchangeable ions are hydrogen ions) by a process of electrodialysis, then titrate the hydrogen clay with a standard solution of NaOH, whereupon the Na⁺ ions replace the H⁺ ions at the surface, and the OH⁻ ions neutralize the liberated H⁺ ions.

EXCHANGE CAPACITIES OF COMMON CLAY MINERALS

Kingery (3) lists the following cation exchange capacities of some of the common clay minerals, arranged in ascending order of the magnitude of their exchange capacities.

Clay mineral	Cation exchange capacity in milliequivalents/100 grams
Kaolinites and two-water halloysites.....	3-15
Clay micas (illites).....	10-40
Sepiolites and palygorskites (chain-type minerals).....	20-30

Hydrated (four-water) halloysites.....	20-40
Montmorillonites.....	75-150
Vermiculites.....	100-150

Exchangeable ions are very important; many of the physical properties of clays depend on them. We can list only a few of the salient facts that extensive research has established about exchangeable ions.

IMPORTANCE OF EXCHANGE CAPACITY TO PHYSICAL PROPERTIES OF CLAY

1. Minerals such as vermiculite and montmorillonite have a very large exchange capacity as compared with kaolinite--the ratio may be as great as 50 to 1, which probably is accounted for by cations migrating in and out of the interlayer water.

2. Though our tabulation does not indicate this, the exchange capacity of minerals such as kaolinite depends on their particle size: the 1-micron fraction of a given kaolinite will have a greater exchange capacity than the 10-micron fraction of the same mineral. This effect, however, is not noticeable with minerals such as montmorillonite. The ion-exchange of minerals such as kaolinite takes place only on the "outer" surface of the particle; but with minerals containing interlayer water we may have ion exchange proceeding at both the "outer" and "inner" surfaces of the crystals.

3. The exchangeable ions are not "tightly" held to the mineral surface, but can form an "atmosphere" or double-layer of ions in the water surrounding a clay crystal; some of the cations surrounding a particular mineral may be "free-swimming" but are held in the vicinity of the surface by the negative charge in the crystal. Actually, then, clay crystals "ionize" in a water suspension, and the degree of this ionization has a very pronounced effect on the properties of the suspension.

When the double-layer is relatively "broad" and "diffused," the clay particles behave like negatively-charged ions and repel one another. Such a suspension is dispersed or stabilized: the particles will not cling to one another; the suspension has a low viscosity; and the particles remain in suspension for a long time. On the other hand, if the exchangeable ions form a thin layer held tightly to the surface so that the negative charge is neutralized or "closed off," the particles do not repel each other. Under these circumstances the suspension is unstable or flocculated: the particles are held to one another by the van der Waals forces and form relatively large flocs; the viscosity increases greatly, and the flocs may settle quite rapidly. When the flocs engulf a certain amount of water, a heavily-flocculated, thick, suspension may set up like a gel.

Divalent and trivalent ions form tighter layers than monovalent ions such as Na^+ , and relatively small concentrations of polyvalent ions have very powerful flocculating effects on clay suspensions.

In any suspension there will be an equilibrium established between the ions in the double layer and the ions in the bulk of the water surrounding the particles. The nature and concentration of the ions in the main body of water will determine the amount of ionization of the mineral particles which, in turn, will affect the stability of the suspension.

4. Our discussion so far has been concerned with cations only, but there can also be definite anion exchanges; for example OH^- ions can be replaced by F^- ions. In these cases the replaceable anions (OH^-) apparently come from the aluminosilicate layers. Anion exchange is not as well understood as cation exchange and there has been relatively little study in this field.

5. The nature of the surface exposed at edges and ends of crystals is different from that of the flat surfaces. In kaolinite suspensions, for example, it is possible to adjust the ionic environment in the water so that the crystals carry negative charges on the faces and positive charges on the edges; the resultant electrostatic attractions form large "card house" flocs which engulf large quantities of water. This type of flocculation produces a thixotropic suspension which is thick and gel-like when stationary, but becomes fluid and less viscous when it is stirred. Stirring breaks down the flimsy card house structures to release some of the enclosed water; as soon as the stirring ceases, the suspension "sets up" again.

6. The properties of a clay depend in part upon the nature of the exchangeable ions. "Hydrogen" kaolinite is different from "sodium" kaolinite. In swelling-type montmorillonite the dominant exchangeable ion is Na^+ ; non-swelling montmorillonite, essentially the same mineral, has Ca^{++} as the exchangeable ion. Thus a non-swelling montmorillonite can be converted to a swelling-type crystal by replacing the Ca^{++} ions with Na^+ ions.

METHODS OF IDENTIFYING CLAY MINERALS

DIFFERENTIAL THERMAL ANALYSIS (DTA)

DTA, a useful test in identifying certain clay minerals, was first employed in metallurgy to detect phase changes in solid metals and alloys. It works on the principle that all phase changes are accompanied by energy changes.

A thermocouple consists of two dissimilar wires joined together at the ends to form a closed loop; in such a loop there will be two junctions where the dissimilar wires are joined. If the two junctions are at different temperatures there will also be a difference in electrical potential between the "hot" and "cold" junction; the measurement of this potential difference can be used to measure the temperature difference between the two junctions. Ordinarily a thermoelectric thermometer consists of a thermocouple, lead wires, and an instrument (usually a potentiometer) to measure the electric potential. The ends of the wires are welded together to form the hot junction which is placed in the furnace; the cold junction is outside the furnace (it may be at room temperature or it may be held

at 0° C by placing it in an ice bath). Actually the wires are not connected at the cold "junction" but are attached to the potentiometer which measures the "back pressure" or potential necessary to just balance the potential generated in the thermocouple wires.

A differential thermocouple is arranged so that both junctions are in the furnace, and the electrical connections are arranged so that the potentiometer measures the potential difference between them; if both are at the same temperature, the potentiometer gives a zero reading.

In testing clay samples, one junction is embedded in a prepared clay sample and the other junction is embedded in an "inert" material, powdered Al₂O₃ for example, or some substance that does not undergo any phase change in the temperature range to be investigated. After the samples have been placed in the furnace, the temperature is slowly raised. As long as there is no change in the clay material, there is no potential difference between the two junctions, and if the result is plotted against the true temperature of the furnace it produces a horizontal line at 0 millivolts.

If any physical change occurs in the sample, however, energy is either absorbed or emitted. If energy is absorbed (endothermic reaction), the temperature of the junction in the clay remains constant, while the temperature of the other junction continues to rise; if energy is given off, the clay junction becomes momentarily hotter than its companion junction. When the complete curve is plotted (Figure 3), it consists of a horizontal line with "dips" corresponding to endothermic reactions and "peaks" corresponding to exothermic reactions.

When water is driven off, heat is absorbed. When kaolinite, for example, loses its lattice water at about 600° C, there is a pronounced dip in the curve at this point. When interlayer water is driven off, usually at temperatures of about 100°-300° C, from such minerals as hydrated halloysite and vermiculite, they show these low-temperature dips as well as the high-temperature dip representing the loss of lattice water. After all the water is gone, the anhydrous oxides recrystallize to form new compounds, which usually results in a strong exothermic reaction at about 900°-1100° C and produces a high peak on the curve.

Because each mineral has its own characteristic DTA curve, many investigators feel that the method is one of the best for identifying clay minerals. The extensive published discussions of DTA analysis by Grim (2) and others indicate this method is by no means as simple as our brief discussion would imply. With many of the energy changes very small, not only must the equipment be quite sensitive in order to detect them, but the furnace must be heated at a steady rate. And DTA curves for mixtures of minerals and mixed-layer minerals present the same difficulties as the X-ray diffraction patterns of these materials.

Figure 3 shows some simplified DTA curves, from which we may observe four conclusions.

1. Lattice water is expelled from dickite at a somewhat higher temperature than is required for kaolinite. This difference might serve to distinguish between these two minerals.

2. Halloysite loses its interlayer water at about 100° C; the lattice water is driven off at practically the same temperature as for kaolinite.

3. Montmorillonite shows two distinct dips representing the removal of interlayer water and two dips and a peak for the expulsion of the lattice water.

4. The exothermic peaks for kaolinite, dickite, and halloysite all occur at the same point, which is to be expected because all these are two-layer minerals whose dehydrated oxides would have the same composition. Note that there is no corresponding peak for the montmorillonite, which could also be expected because montmorillonite is a three-layer mineral whose dehydrated oxides will be different from those produced from the other minerals.

DEHYDRATION CURVES

Dehydration curves indicate the temperatures at which water is expelled from clay minerals as well as the amount of water removed. In a sense, they give much the same information as the DTA curves, but the experimental procedure is different.

To plot a dehydration curve, clay samples are heated at various temperatures until they reach constant weight. When the weight loss is plotted against temperature, we should obtain a step-like curve, though actually many experimental curves bear only a faint resemblance to it.

ELECTRON MICROSCOPY

In most cases clay minerals are too small to be resolved by a light microscope. For some clay minerals the electron microscope produces excellent pictures of the individual crystals, indicating their size and shape. For other clay minerals it is difficult to obtain sharp pictures even with the electron microscope.

SUMMARY

The previous discussion has indicated that there is no simple way to identify clay minerals; in many cases it is necessary to obtain evidence from a number of sources--chemical analysis, X-ray tests, DTA curves, dehydration tests, electron photomicrographs, adsorption of certain organic ions or molecules, and optical tests. In some cases even the full battery of tests is not sufficient to positively identify the clay mineral (or minerals).

PROPERTIES OF CLAY MINERALS

Before we proceed to consider the clays themselves, let us briefly summarize the characteristics of clay minerals which set

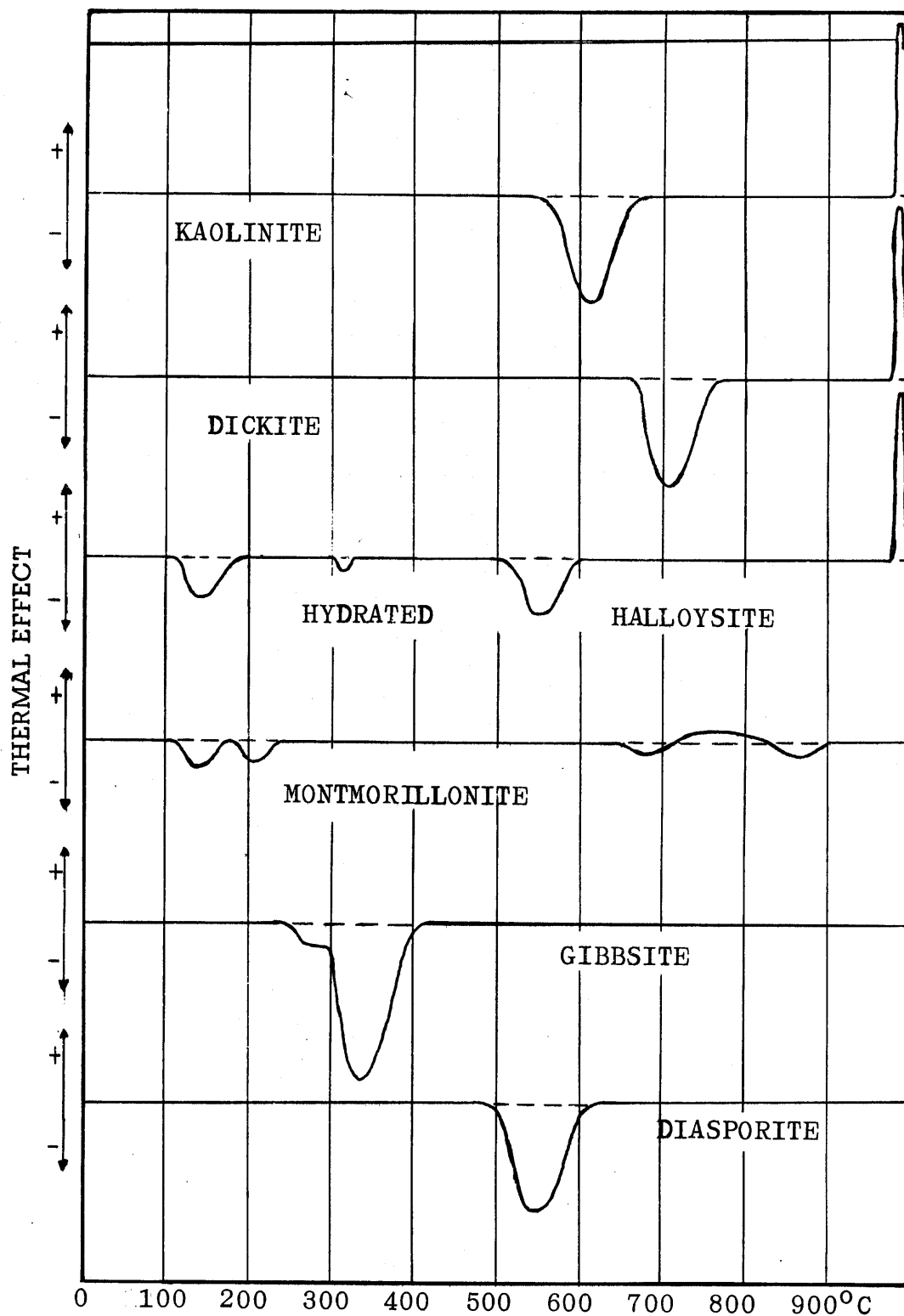


Figure 3.

Generalized DTA curves for several clay minerals.

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them apart from most other substances and account for many of their useful properties.

PARTICLE SIZE AND SURFACE

We have noted that clay crystals are usually very small: in some cases they may not be more than one or two layers thick. The basic reason for their small size is the relatively feeble forces that hold the component layers (sheets) or fibers together. Probably the "natural" crystals of clay are larger than the ones we observe when the clay is dispersed, because the crystals break down so easily.

Some of the kaolins and flint clays are fairly hard and compact rocks that require crushing and grinding to disintegrate. Other clays will disperse or disintegrate spontaneously (slake) when covered with water. In many cases the dispersion can be accomplished by agitating the clay particles in water (blunging).

With such small particle sizes, these clay minerals have large specific surfaces, ranging from about 10 M²/gram for kaolinite to 100 M²/gram for clay micas and montmorillonites, a single pound of which has a total particle surface of about 11 acres.

ISOMORPHOUS SUBSTITUTION

Isomorphous substitution provides a built-in electric charge in clay particles which is neutralized by balancing ions held at the crystal surface. The crystal surfaces are actually ionized and some or all of the balancing ions are exchangeable. The surface chemistry, degree of hydration, stability of suspensions, and plasticity are all related to this surface ionization.

CHEMICAL INERTNESS

The aluminosilicate layers or columns are quite resistant to chemical attack: the exchangeable ions may "react" readily, but the main body of most clay crystals is fairly inert to many chemical reagents.

PLASTICITY

When certain clays are mixed with the correct amount of water, they form a plastic putty-like mass (paste) that can be readily molded. Plastic bodies have a definite yield point and a definite extension before fracture, which means that a certain load or stress must be applied before deformation starts, and that the body will deform permanently without fracture.

Although the mechanism of plasticity is not completely understood, apparently it depends on the continuous matrix of water which surrounds the clay particles and is adsorbed to their surfaces: the deformation takes place through the water layers, but the matrix holds together and does not form cracks or fractures. Plasticity is essential for clay bodies that are to be shaped by such processes as molding in a die or throwing on a wheel.

The more plastic clays, known as plastic or fat clays, exhibit a large volume shrinkage in drying. Lean or non-plastic clays show much less shrinkage. High plasticity is associated with small particle size; in fact, there is some evidence that a great many non-clay materials will exhibit plasticity if they are ground fine enough.

There is no routine test that will determine or measure the plasticity of a clay body. An expert must tell by the "feel" when a clay body has the proper "consistency" for molding or throwing.

CLAY DEPOSITS AND TYPES

RESIDUAL AND TRANSPORTED CLAYS

Residual clay is clay that is still "in place" where it has been formed by weathering of the parent rock. Transported clay is clay that has been carried from its original source and deposited elsewhere by either wind or water. Apparently the transport may occur before the clay-forming reactions are completed, the final conversion to clay taking place after the material has been deposited.

Residual clays are generally quite impure because all the unweathered minerals in the parent rock remain in the clay deposit: a residual clay may contain as little as 10 per cent clay minerals. Transported clays are usually much purer than residual clays.

The complete geological classification of clays is more complex, taking into account the nature of the parent rock, the nature of the weathering process, and the method of transporting. Though clays are formed for the most part by weathering as we have described it, there is evidence that some clays are primary minerals in igneous rocks.

IMPORTANT COMMERCIAL TYPES OF CLAY

Classification and consumption

Clay deposits (as distinguished from clay minerals) can be classified in a number of ways. We have mentioned briefly the classification based on geological occurrence, but they can also be classified on the basis of (1) commercial usage, (2) nature of the clay mineral, (3) plasticity, (4) refractory properties, or (5) purity.

To begin with, let us consider the important commercial types of clay, Table 3 lists some production statistics and prices of clay for the year 1957 as given in The Minerals Yearbook (5). Of some of the many other names applied to clays given in Table 3, we shall refer in later sections.

The difficulty of making a systematic classification of clays is pointed up by the data in Table 3: the "miscellaneous" category includes two-thirds of the total tonnage. But let us consider briefly the important industrial uses of the clays listed in Table 3 before considering each type in more detail.

Total consumption of all clay was 45.7 million tons with a gross value of 156 million dollars. Miscellaneous clay amounted to two-thirds of the total tonnage but represented only 24 per cent of the gross value. Miscellaneous clay and fire clay together comprised 90.3 per cent of the total tonnage; the four other groups accounted for only 9.7 per cent of the tonnage but represented 43 per cent of the gross value. None of these clays has a high unit value, and the average value of a ton of "miscellaneous" clay is very low.

TABLE 3*. Some statistics on U. S. clay production in 1957

Tonnages are for domestic clays sold or used by producers

Type of Clay	Short Tons	% of Total Tonnage	Gross value dollars	Unit value, dollars per short ton
Miscellaneous clay	30,495,000	66.6	37,580,000	1.23
Fire clay including stoneware clay	10,805,000	23.7	51,311,000	4.75
Kaolin or china clay	2,184,000	4.8	35,598,000	16.25
Bentonite	1,451,000	3.2	17,830,000	12.28
Ball clay	409,000	0.9	5,521,000	13.52
Fuller's earth	366,000	0.8	8,057,000	22.01
Total	45,710,000	100.0	155,897,000	

*From Minerals Yearbook 1957, Vol. I, U. S. Bureau of Mines

Miscellaneous clay

Deposits are widely distributed in this country, 45 of our 50 states reporting production in 1957. Heavy clay products (building brick, sewer pipe, tile, etc.) accounted for 58 per cent of the tonnage. Cement manufacture used 29 per cent, and light-weight aggregate 12 per cent. These three uses accounted for 99 per cent of the total consumption of miscellaneous clay.

Fire clay

Fire clay is used primarily in the manufacture of refractories (52 per cent) and heavy clay products (43 per cent), which account for 95 per cent of its total use.

Kaolin (china clay)

Kaolin is one of the main ingredients in porcelain and china, but this is by no means the principal use for this type of clay. In 1957, 54 per cent of the kaolin was used in paper manufacture (30 per cent for coating and 24 per cent for filling); 14 per cent was used in the rubber industry; 12 per cent for refractories; and only 4 per cent for pottery. The remaining 16 per cent had a wide variety of uses including the manufacture of insecticides and paint fillers.

Bentonite

Bentonite is used for rotary drilling mud (38 per cent), foundry-sand bond (26 per cent), and filtering and clarifying (14 per cent). Many miscellaneous uses account for the remaining 22 per cent.

Ball clay

Ball clay is used mainly in pottery, which accounts for 60 per cent of its consumption.

Fuller's earth

Fuller's earth has several important uses; 92 per cent of the consumption in 1957 was accounted for by: absorbents (42 per cent), rotary drilling mud (20 per cent), insecticides and fungicides (18 per cent), and mineral-oil refining (12 per cent).

TESTING OF CLAYS

In addition to the many different tests to identify clay minerals, a number of tests are applied to the clays themselves. Klinefelter and Hamlin (4) discuss these tests in some detail, but we shall give brief descriptions of two of them.

PLASTICITY: THE ATTERBERG TEST

The Atterberg test (4) measures the amount of water required to plasticize 100 grams of clay. The dry, powdered (-20 mesh) clay sample is placed in an evaporating dish into which water is allowed to drop very slowly from a burette. As the water is dropping, the operator works the mass with a spatula until a plastic state is reached. When the clay is in its "plastic state" it forms a smooth and yielding paste that does not stick to the spatula and that yields a clean cut when the spatula is drawn through it. If the clay slumps after being cut, or if it sticks to the spatula, too much water has been added.

The result of this test is reported as water of plasticity, the amount of water added expressed as a percentage of the dry weight of the clay. Nonclays such as bauxite and marl show low values, from a few per cent to 40 per cent. Highly plastic clays have a value of about 60 per cent; and the lean (less plastic) clays, about 30-40 per cent. Most of the kaolins, ball clays, and plastic common clays fall in the range of 30 to 65 per cent. Values above 80 per cent almost always indicate one of the montmorillonite-type clays (bentonite, subbentonite, fuller's earth), and the value may go as high as 200 per cent or more.

This test also gives some qualitative information about the clay: texture, grain size, grittiness and workability.

One of the best to distinguish between kaolinite- and montmorillonite-type clays, this test is not sufficiently accurate to be used for production control in the ceramic industry.

PCE: PYROMETRIC CONE EQUIVALENT TEST

PCE, the standard method for determining the refractory properties of a clay, compares essentially the softening temperature of a sample of clay with that of a standard pyrometric cone. The clay

to be tested is moistened with water, shaped into a small triangular-based cone, and dried; if the clay is not plastic it is necessary to add a small amount of dextrin or other organic binder to the mixture. After drying, the test cones are mounted on a plaque with standard pyrometric cones of the same size, placed in a furnace, and heated until the cones soften and bend through 180 degrees so that their points just touch the plaque. The cone number of the unknown is the same as that of the standard cone that softens at the same time.

Pyrometric cones are widely used in the ceramic industry though basically they are temperature-measuring devices, their softening point depends on both the temperature and the rate of heating. Following are some examples of cone numbers and the equivalent temperatures, taken from tables in Norton (7) and Klinefelter and Hamlin (4).

Only a few representative PCE cones are listed in Table 4. There is one cone for each 20° C interval (approximately) of temperature. Because these cones are made of various mixtures of oxides and silicates, the softening process involves their chemical reaction; and the observed softening temperature, therefore, depends on the rate of heating: the slower the rate, the lower the softening temperature. For example, the softening point of cone 10 as given by Norton (7) is 1260° C when the heating rate is 20° C per hour, and 1305° C when the heating rate is 150° C per hour.

PCE furnaces are of three types: electric (carbon resistance), gas-fired, and oxyacetylene-fired furnaces. The ordinary gas-air flame will only work up to about cone 32; for tests on refractory clays require very high temperatures.

TABLE 4. Pyrometric cone equivalents

Cone Number	Softening Temperature	
	°C (heating rate 150° C per hour)	°F (heating rate 270° F per hour)
022	605	1120
017	770	1420
010	895	1640
01	1145	2090
1	1160	2120
6	1230	2250
12	1337	2439
19	1541	2806
28	1646	2995
35	1785	3245
39	1865	3389
42	2015	3659

SIZE ANALYSES

Size analyses of clays are made by screen analysis, elutriation, sedimentation, and centrifuging.

SCREEN ANALYSIS

A screen analysis must be performed by wet-screening or by a wet-dry method. A sample of 100 grams is mixed with water and stirred until it is evident that all lumps of clay have disintegrated; then it is carefully washed on the finest screen (usually 325-mesh). The granular oversize remaining on this screen can then be washed through a set of coarser screens, or it can be dried and dry-screened; the undersize can be dried and weighed directly, or it can be treated by elutriation or some other method for "sub-sieve" sizing. Regardless of the procedure used, it is essential that the clay be dispersed in water and washed on the finest screen. Dry clay particles will adhere to larger mineral particles, which will adhere to one another to form coherent aggregates, which will stick to the screen wires to completely "blind" a screen.

ELUTRIATION

Most of the common methods for sub-sieve sizing depend on the settling rate of mineral particles in a fluid medium (water, kerosene, air). Motion of a particle through a fluid medium is opposed by the fluid resistance. A falling body reaches a terminal velocity determined by both its diameter and specific gravity: the smaller and lighter the object, the more slowly it will fall.

In elutriation the particles are introduced into a steadily upward-rising current of water or air (or other fluid), which produces (1) particles with terminal velocities less than the velocity of the rising fluid, that rise and are carried over the top; and (2) particles with greater terminal velocities that sink against the steady current. If all particles have about the same specific gravity, the elutriator column will make a separation based on size only. By using several different current velocities it is possible to separate a sample into a number of sized fractions.

One of the best methods for sub-sieve sizing, elutriation is slow and tedious, however, (especially in removing very fine sizes), and requires special equipment.

SEDIMENTATION

Sedimentation, based on the rate at which particles settle in still water, is the simplest method of sizing and does not require much equipment except beakers or other settling vessels. One method is to agitate a clay suspension, allow it to stand quietly for a definite time, and then decant or siphon off the supernatant liquid. Another method more commonly used is the pipet method, which involves removing samples of the suspension from different depths and determining the weight of suspended material in each of these samples. This process gives information from which a size distribution curve may be plotted.

CENTRIFUGING

Centrifuging, essentially an accelerated sedimentation test, is especially useful in removing particles one micron or less in diameter.

INTERPRETATION OF SIZING TESTS

Screen analyses are most useful to determine the nature and distribution of the accessory minerals in clay, for most of the clay minerals pass freely through the finest screen. Coarse fractions can be examined microscopically to identify the minerals and estimate their relative abundance. If the clay washes away easily from the accessory minerals, the clay can probably be purified by a simple washing operation.

Elutriation, sedimentation, or some similar process must be employed to determine the size distribution of the sub-sieve material. In most clays, practically all the clay minerals will be in the sub-sieve range, but it does not necessarily follow that the sub-sieve material is all clay. Very small crystals of mica or other minerals may also be present.

COLOR OF CLAYS

Clays exhibit a wide range of colors: some of the kaolinites are white and some of the ball clays are black; there are clays of various shades of red, yellow, buff, gray, and blue. For ceramic use, the color after burning is most important, for some dark blue or black clays may be white or cream-colored after burning.

When clay is used directly as in paper filling or coating, the "raw" color is most important. These clays should be white and show a high reflectivity of incident light. A simple way to evaluate the color of a given clay is to compare it with a standard clay of acceptable whiteness. When dry samples of a standard clay and the unknown are placed on a white surface (such as a piece of white blotting paper) and pressed flat with a spatula so that they form a junction, differences in color are easily distinguished. Because apparent color of a clay sample depends on the particle size and the moisture content, samples to be tested should pass a 200-mesh screen and contain no more than 2% moisture.

Paper clays are usually tested by some sort of reflectance meter or brightness tester that measures the per cent of incident light reflected from a flat layer of clay. For paper fillers the reflectance should be 80 to 84 per cent, and for paper coating 84 to 88 per cent.

CHARACTERISTICS AND USES OF MAJOR CLAYS (USBM CLASSIFICATION)

KAOLINS OR CHINA CLAYS

Kaolins, either residual or transported, are weathered products of feldspathic rocks. The clay mineral is kaolinite, from which refined kaolins yield the closest approach to unadulterated clay mineral of any commercial type of clay. Though a few kaolins are pure enough to be used in the crude state, most of them are refined by washing or some other beneficiation method.

There is some variation in color, but the refined kaolin of commerce is nearly white or light cream in color. Refined kaolin is light and fluffy; lumps are readily crushed with a light pressure of the fingers and will readily slake (disintegrate) when placed in water. Kaolins have low plasticity, and the water of plasticity will usually be between 25 and 40 per cent. Because of relatively coarse constituent minerals, kaolin does not have the smooth, greasy "feel" characteristic of highly plastic clays such as the ball clays.

The British call the clays from the Cornish and Devonian granites "china clay" and all other similar clays "kaolins." On the European continent the term kaolin is used exclusively, and in the United States the two terms are practically synonymous. The main source of kaolin in the United States is the Tuscaloosa formation which runs in a belt across the central part of Georgia and into South Carolina.

Kaolins (and other two-layer clays) are highly refractory, with PCE values of cone 33 to cone 35. When used for refractory purposes, most kaolins burn to a good white color.

BALL CLAYS

Ball clays are basically the same as kaolins, consisting principally of kaolinite. A Florida clay, which appears to be intermediate between kaolin and ball clay, is known as Florida ball clay, ball-china clay, Florida kaolin, or Florida plastic kaolin.

Transported clays, ball clays are usually found in swamps. Containing a large amount of organic matter, the raw clay varies in color from pink and buff through the various shades of gray and black, though commercial ball clays are roughly classified as blue or black clays. Most ball clays are white or light cream after firing: the carbonaceous matter burns off and the carbon reduces any ferric iron present to the ferrous state.

Much finer grained than the kaolins, ball clays also are more plastic (water of plasticity is 40 to 65 per cent), show greater shrinkage on drying and firing, and develop much greater dry strength.

Ball clay is tough and hard in the dry state, but when moistened with water is soft and greasy to the touch. A lump immersed in water may take several hours to slake. The fired structure of ball clay is dense and vitreous, with PCE values of cone 30 to 34, roughly the same as kaolin's.

The principal use of ball clay is as a plasticizer in ceramic bodies: whiteware, refractories, and other ceramic bodies. Ball clay makes up from 7 to 30 per cent of these bodies and gives them the required plasticity.

Most domestic ball clay comes from Tennessee and Kentucky. English ball clay is imported in considerable quantity.

FIRE CLAY

Fire clays are formed in swamps and basins and are usually associated with coal measures. The principal domestic supplies come from Ohio, Pennsylvania, Missouri, Kentucky, California, Indiana, and Illinois.

As the name implies, these clays are used mostly for refractory ceramics: firebrick, crucibles, retorts, saggars, muffles, etc. The many types of fire clays may be designated as plastic or non-plastic; siliceous, ferruginous, calcareous, or carbonaceous in composition; and fine or coarse in texture. Klinefelter and Hamlin list the following commercial classes of fire clay: (1) Plastic, (2) Semiflint, (3) Flint, (4) Nodular flint.

Called flint clays because they are hard and exhibit a conchoidal fracture, they are highly refractory and exhibit little plasticity. The nodular clays, containing nodules of gibbsite or other aluminum hydrates, are even more refractory than the flints because they have a higher percentage of Al_2O_3 . The PCE values of most flint clays are cones 35 to 36 with some as high as cone 38.

Plastic fire clays have PCE values between cones 26 to 30, and the PCE values of the semiflints are from cones 30 to 35. In general, the less plastic the clay, the more refractory it is.

Fire clays may contain one or more of the two-layer clay minerals: kaolinite, dickite and halloysite. It appears that the flint clays consist largely of halloysite, whereas the predominant mineral in the plastic clays is kaolinite. Fire clay usually burns to a buff or yellow color.

BENTONITES AND FULLER'S EARTH

These clays consist predominantly of some form of montmorillonite, depending for their useful properties on the fine particle size and large ion-exchange capacity of the three-layer montmorillonite crystals. From volcanic shards found in the deposits, domestic bentonites are known to be largely derived from volcanic ash. If fuller's earth, which does not contain these volcanic shards, forms from volcanic ash, the decomposition of the parent material has been complete.

Swelling bentonites consist largely of sodium montmorillonites which will swell from 1 to 15 times their volume when immersed in water, and remain a gelatinous suspension almost indefinitely. Wyoming, South Dakota, and Montana are the principal sources of swelling bentonite.

Non-swelling bentonites are calcium montmorillonites, essentially the same as swelling bentonites except that the replaceable ions are mostly calcium. In the trade, these are known as sub-bentonites or metabentonites. Mississippi and Arizona supply most of our domestic supply.

Fuller's earths, which consist largely of magnesium montmorillonites, are often difficult to distinguish from the non-swelling bentonites. Georgia and Florida are the principal domestic sources of fuller's earth.

These clays are powerful plasticizers, and 2 to 3 per cent of bentonite is as effective as 10 per cent of ball clay in a ceramic body. The use of bentonite in ceramic work is limited, however, because of its excessive drying shrinkage, and because its color after firing will discolor whiteware. These clays are not refractory: bentonites have PCE values of cone 04 to 05 (about 1900° F).

Some swelling bentonite is used in ceramic bodies and as a suspending agent in glazes and enamels, but, by and large, the principal uses of these clays are nonceramic.

Swelling bentonite is used in drilling muds (for oil-well drilling) to stabilize the suspension; as a binder in foundry sands; as paper filler; and for many other purposes.

The non-swelling bentonites and fuller's earths are also used in drilling muds and foundry sands. Because natural fuller's earth and acid-treated subbentonite have the property of adsorbing certain organic molecules, they are widely used for clarifying mineral and vegetable oils. Acid-treated subbentonite is much the better of the two for clarifying petroleum oil, while fuller's earth is used to clarify such products as cottonseed oil. This grease-adsorbing property of fuller's earth has been known for a long time: the Romans used it as a grease adsorbent in textile work and as a medical carrier.

MISCELLANEOUS CLAYS

This term includes "brick" clay and "common" clay. It usually refers to any buff- or red-burning clay which is suitable for making brick or other heavy clay products. Many of these clays grade into the fire clays, but they are usually much less refractory.

Enormous quantities of these clays are used: this "miscellaneous" class accounts for about two-thirds of the tonnage of all clay produced, but its unit price is the lowest of all.

Let us now consider one or two categories not included in the U. S. Bureau of Mines classification.

OTHER CHARACTERISTICS AND USES OF CLAYS

STONEWARE CLAYS

These are low grade fire clays or semirefractory clays that are fairly plastic and can be fired at relatively low temperatures. They are used for making jugs, cooking and domestic utensils and ornamental pottery. The usual color of the fired ceramic is "stoneware gray." These clays are included in the fire clays in the U. S. Bureau of Mines statistics.

HALLOYSITES

We use the term kaolin to indicate a "rock" and kaolinite to indicate a clay mineral. Halloysite indicates both rock and clay mineral. A further complication is the fact that some writers use the name endellite or metahalloysite to refer to the hydrated form of the mineral.

Halloysite "rock" may be soft, porous, and dull-looking (this variety may resemble kaolin very closely); or it may be dense, waxy, and hard, with a conchoidal fracture. Either variety may be white, buff, or pinkish in color. The most positive identification is the tube-like structure of the mineral, revealed by the electron microscope.

Halloysites can be used for almost the same purposes as the kaolinites: paper coater and filler, ceramic uses, etc. Because many clays contain both halloysite and kaolinite, one theory of clay genesis postulates that halloysite is an intermediate product in the formation of kaolinite.

ALUMINUM FROM CLAY

Much research work has been done on the production of pure Al_2O_3 from clay; this can serve as raw material for the production of metallic aluminum. Our domestic aluminum industry depends very largely on imported bauxite as raw material, and there would be many advantages to be gained from a successful process for utilizing our clays as a source of metallic aluminum.

So far, no such process has been placed in commercial operation, but there are indications that one may be developed in the near future. If clay is used as a source of aluminum, it seems likely that the material used will be the relatively pure kaolinites and halloysites--these two-layer minerals have the highest ratio of Al_2O_3 to SiO_2 , and are relatively free of iron and other contaminating elements.

PROPERTIES OF CLAYS OF IMPORTANCE IN ASSESSING THEIR

COMMERCIAL POTENTIAL: SUMMARY

Let us recapitulate some of the uses and properties of various clays, the points that must be considered in assessing the potential commercial value of any clay deposit.

1. Clays used in making common brick, sewer tile, and similar objects ("miscellaneous" clays) are difficult to appraise because they exhibit such wide variations in properties. For common brick, for example, the clay must be plastic enough to be readily molded, it must burn at a reasonably low temperature, and it must have a "pleasing" color when burned. Such clays should not be highly refractory.

These "common" clays are widely distributed and, as we have noted, they have a low unit value. The geographical location of

these clay deposits is very important because low-value clays cannot be profitably shipped for any distance. Plants for the manufacture of brick, sewer tile, and other heavy clay products are located adjacent to the clay deposit; usually they have no facilities for storing crude clay and the mine itself serves as a storage bin.

2. Fire clay can be simply described as a buff-burning refractory clay (high-grade kaolins, ball clays, and halloysites are also refractory but burn white). About the only test necessary to evaluate a fire clay is the PCE test. If the clay has a PCE value below cone 19 it is worthless as a fire clay. If the PCE value is above 27, the clay is "refractory" or "high heat duty"; if the PCE value lies between cone 19 and cone 26 the clay may be designated as a "low heat duty" fire clay.

The unit value of fire clay is about four times the value of the average common clay, a price still too low to permit any extensive transportation. Commercial deposits of fire clay must be located close to the manufacturing plants that use the clay.

3. Stoneware clays may be very desirable for art work, manufacture of household utensils, etc., but this market is quite limited.

4. Common clay, fire clay, ball clay, and stoneware clay are used almost exclusively for ceramic purposes; there are no important non-ceramic uses for these clays.

5. High-grade kaolinites and halloysites, bentonites, and fuller's earths have extensive commercial uses other than as refractories. With a higher unit value, these clays can bear the additional cost of purification and transportation.

6. Though bentonites are used in small amounts in some ceramic bodies to improve plasticity, almost all bentonites and all the fuller's earths are used for non-ceramic purposes.

7. Kaolins, ball clays, and halloysites are highly refractory but they are too expensive to be used for making refractories such as fire brick.

8. Kaolins and halloysites for paper coating and filling must be white in color and have a high reflectivity. A quick comparison with a standard sample will indicate if a clay is off-color or not. Such a test will eliminate unsuitable clays, but more elaborate tests are required to determine if a given clay is actually suitable for paper clay. Final evaluation should be made by a paper manufacturer.

9. Kaolins, halloysites, and ball clays for use in whiteware ceramics may be colored in the raw state, but they must burn to a white or light cream color.

10. Montmorillonite clays (bentonites and fuller's earths) may be identified by their high values for water of plasticity; swelling bentonites are easily identified.

11. For many of the uses of clays, special tests are made by the industrial users of the material. Some bentonites, for example, are better than others for drilling mud; some subbentonites are superior to others for oil clarification, etc. Some of the properties of clays will indicate their suitability for a given use, but in the final analysis, there is only one way to determine this: that is actually to try a sample of the clay for the purpose to which it is to be used.

12. Finally, it must be remembered that (as in the case of many non-metallics) the clay producer must search out his markets. Any commercial user of clay will expect not only to get the material at a competitive price, but will also expect regular deliveries of standard grade material. There is no "market" for "clay." Each type of clay has its own specialized uses, and it is imperative that the producer establish contracts with industries that will buy his particular clay or clay products at a price that will enable him to mine it profitably.

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