STRUCTURAL MINERALOGY OF CLAYS

By George W. Brindley [*]

INTRODUCTION

The investigation of clay minerals utilizing X-ray crystallographic techniques has been very actively pursued for the last 20 years and a considerable wealth of information has been collected and organized into a coherent body of knowledge. This interest is reflected in the number of books dealing with the mineralogy of clays that has appeared in recent years. The following may be mentioned [†]:

Sedletskij, I. D., Kolloidno-Dispersnaja Mineralogia, Moscow, 1945.

Marshall, C. E., The Colloid Chemistry of the Silicate Minerals, New York, 1949.

Hoyos de Castro, Angel, and González García, José, Genesis de la Arcilla, Madrid, 1949.

Kerr, P. F., et al., Clay Mineral Standards, Am. Petroleum Inst., Proj. No. 49, New York, 1950.

Jasmund, K., Die Silikatischen Tonminerale, Leipzig, 1951.

García Vicente, José, Estructura Cristalina de los Minerales de la Arcilla, Madrid, 1951.

Brindley, G. W., X-ray Identification and Crystal Structures of Clay Minerals, London, 1951.

In the present contribution, it is assumed that the reader is familiar with the main features of the structures of clay minerals, namely the arrangement of atoms in well-defined sheets and layers with the anions, mainly O, OH, and occasionally F, grouped tetrahedrally and octahedrally about the cations, mainly Si and Al in tetrahedral positions and Al, Mg, and Fe in octahedral positions, together in some minerals with interlayer cations such as K, Na, Ca, Mg. Familiarity with the main features of the kaolin- and mica-type layers is assumed and also the existence of water layers and hydration complexes between the silicate layers in such minerals as montmorillonite and vermiculite.

Even with these assumptions, some limitation of the subject matter is necessary and the discussion is therefore confined to particular aspects which are chosen partly by their relevance to the publication as a whole and partly on the grounds of personal interest.

A CLASSIFICATION OF CLAY MINERALS

Clay minerals, for the most part, belong to the group of silicates having layer structures, and their structural investigation cannot be divorced from that of layer silicates generally. A classification of clay minerals must therefore be developed within the wider context. The scheme set out in table I is largely self-explanatory. Successive subdivisions are based alternately on structural features and on chemical compositions. This is particularly important in relation to problems of clay-mineral identification, for it is clearly necessary for the methods employed to be sensitive both to structure and to composition.

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† To this list can now be added Grim, R. E., Clay Mineralogy, New York, 1953.

Structural Groups and Sub-Groups. The minerals with which we are concerned lie in the broad chemical category of silicates, which, following W. L. Bragg (1937) and others, may be classified into structural groups and sub-groups. The question of the naming of these structural groups has been discussed by Fleischer (1947), Strunz (1941), and others, and need not be considered further here. Clay minerals come mainly in the layer-silicate group and these can be subdivided according to the type of layer structure. The naming of these layer types will doubtless also be a matter for discussion. In addition to the single-layer types, a structural sub-group is also required for the mixed-layer structures, and eventually more than one mixed-layer sub-group may be necessary.

In addition to the layer-silicate clays, there are those which appear to be more closely allied to chain-silicate structures (pyroxenes and amphiboles), namely palygorskite or attapulgite and possibly sepiolite. These are less fully understood than the layer silicates and existing knowledge of these minerals up to 1950 has been summarized by Caillère and Hénin (1951).
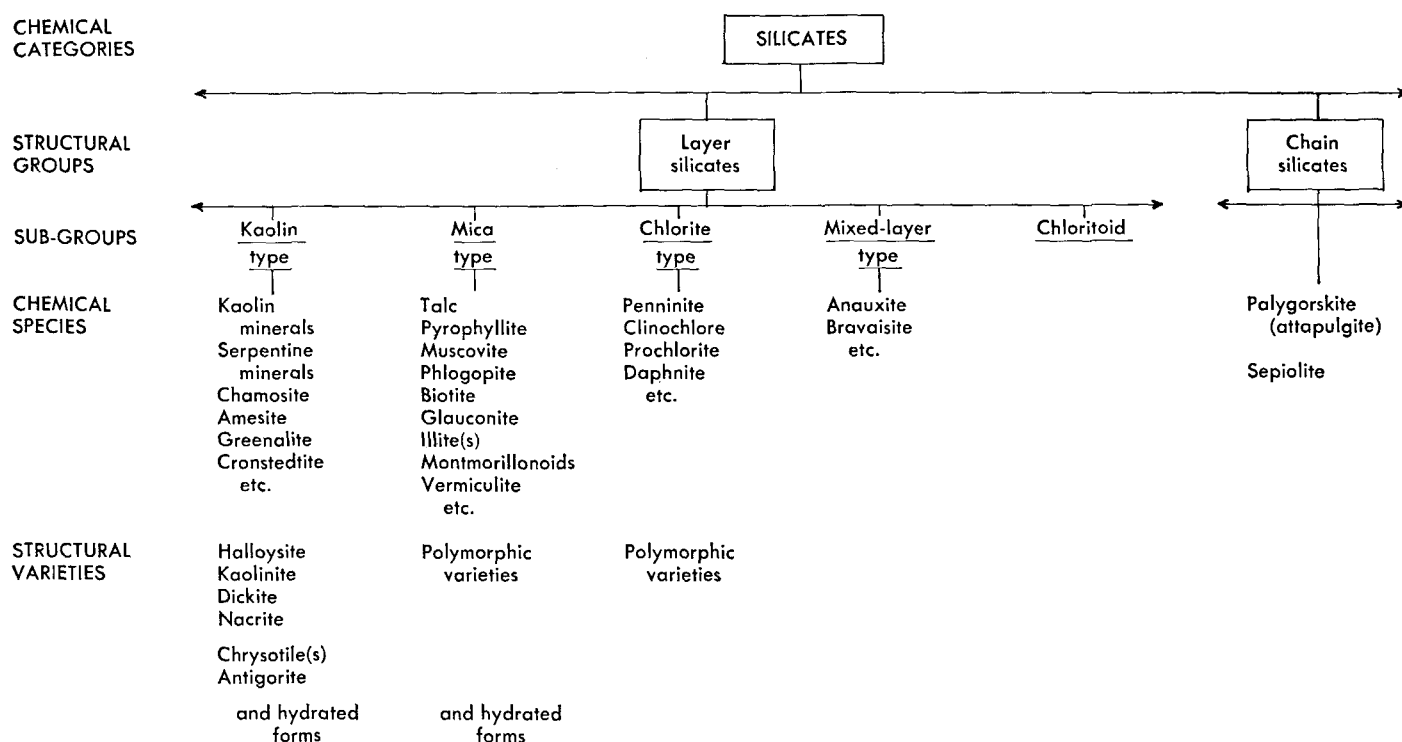
Any scheme of classification is in danger of imposing a rigidity which the subject will eventually outgrow and it is therefore desirable to retain flexibility in the scheme. This is especially necessary in connection with the classification of hydrated minerals and of mixed-layer minerals.

Hydrated minerals can often be associated most conveniently with the corresponding dehydrated forms, but on other occasions they may be treated as mixed-layer minerals. At present it seems undesirable to allocate them rigidly in either way.

In the mixed-layer group, it may eventually be useful to distinguish between randomly mixed and regularly mixed structures, and particular examples of the latter may be classified at some future date as distinct structural sub-groups. In fact, this is already true of the chlorites which consist of a regular alternation of mica-type and hydroxide-type layers, and, in view of their general importance it is most useful to regard them as constituting a particular structural sub-group. Other examples of regularly mixed layer structures, which are less well understood or which are of rare occurrence, can, for the present, be left in the mixed-layer group. As illustrations, clay minerals showing long spacing regularities may be mentioned, such as a montmorillonite with a 32Å spacing (Alexanian and Wey, 1951), a mica-type mineral with a 22Å spacing (Caillère, Mathieu-Sicaud, and Hénin, 1950), rectorite with a 25Å spacing (Bradley, 1950) and various weathered clays discussed by Jackson et al. (1952).

Chemical Species. Within each structural group or sub-group the chemical species are divisible according to composition. In some cases this gives clearly defined species (e.g. the kaolin minerals, the serpentine minerals) but in others where continuous or largely continuous composition ranges exist, (e.g. the montmorillonite-beidellite series, the chlorites) boundary lines must be drawn in a largely arbitrary manner.

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Table 1. A scheme of classification of clays and related silicate minerals.

CHEMICAL CATEGORIES			SILICATES			
STRUCTURAL GROUPS			Layer silicates			Chain silicates
SUB-GROUPS	Kaolin type	Mica type	Chlorite type	Mixed-layer type	Chloritoid	
CHEMICAL SPECIES	Kaolin minerals Serpentine minerals Chamosite Amesite Greenalite Cronstedtite etc.	Talc Pyrophyllite Muscovite Phlogopite Biotite Glauconite Illite(s) Montmorillonoids Vermiculite etc.	Penninite Clinochlore Prochlorite Daphnite etc.	Anauxite Bravaisite etc.		Palygorskite (attapulgite) Sepiolite
STRUCTURAL VARIETIES	Halloysite Kaolinite Dickite Nacrite Chrysotile(s) Antigorite and hydrated forms	Polymorphic varieties and hydrated forms	Polymorphic varieties			

There may be some disagreement about grouping together the kaolin minerals proper, the serpentine minerals, and others placed in the kaolin-type group and also about this choice of a name for the group. The structural scheme is essentially the same for all these minerals and the only point of difference is that some are dioctahedral and others trioctahedral. * This distinction, however, occurs in all the sub-groups and appears to be of relatively small structural importance. To achieve consistency, the same policy must be adopted with all the groups and the simplest solution is to place di- and tri-octahedral members always together; this also eliminates any difficulties with minerals having an intermediate number of octahedral ions. As regards the naming of the group, the term "kaolin-type" suggests the type of structure without actually taking the name of one of the members. The use of a numerical ratio, such as 1:1 and 2:1 for designating the kaolin- and mica-type layers, has some advantages but it is not easily extended to all the layer types which are involved; for example, is a chlorite layer to be designated 2:2 or 1 + 2:1?

It will be observed that in the mica-type group there have been included talc and pyrophyllite, the micas proper (muscovite, biotite, . . .), the clay micas (illites, etc.,) and the swelling minerals (montmorillonoids, vermiculite). The justification for placing all these minerals together in a single structural group instead of separating them into "10Å" and "14Å" groups or into non-swelling and swelling groups (as is usually done), is that in view of the very close inter-relations of these minerals, the simplest procedure is to regard them as

different chemical species within the mica-type sub-group, having various hydration properties.

Structural Varieties. The structural varieties of each chemical species differ in the manner in which the structural layers are arranged with respect to each other. To recognize them in clays by the X-ray powder method, it is necessary to record carefully the details of their diffraction diagrams. With well-crystallized and relatively pure materials, many of the varieties may be recognized by their powder diagrams (see Brindley, 1951a) but with poorly crystallized and/or impure materials considerable difficulties can arise. To the kaolin varieties and serpentine varieties, which can be recognized optically, separate names have been given. Polymorphic varieties of the micas, studied by Hendricks and Jefferson (1939), and of the chlorites, studied by Brindley, Oughton, and Robinson (1950), have not been given separate names and require rather detailed X-ray examination to be recognized. They are most usefully described in terms of the unit cell symmetry and the number of structural layers per unit cell, a system of nomenclature which has already been usefully applied to the polymorphs of silicon carbide (Ramsdell 1947; Ramsdell and Kohn, 1951, 1952) and of wurtzite (Frondel and Palache, 1950). Grim and Bradley (1951) have shown that some of the mica polymorphs can be recognized from X-ray powder diagrams, but no such evidence is yet available for the chlorite polymorphs which have hitherto been recognized only from single crystal diagrams.

LATTICE PARAMETERS AND CHEMICAL COMPOSITIONS OF LAYER SILICATES

A consideration of the relation between the lattice parameters and the chemical compositions of layer sili-

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* These terms signify the number of cations in octahedral coordination per half unit cell. They correspond to the terms heptaphyllite and octaphyllite.

cates is of interest in connection with (a) the identification of mineral species by means of X-rays, and (b) certain questions related to the morphology of clay minerals. The question of identification is considered in a second contribution to this symposium; here consideration is given only to the morphological aspects.

The variation of the lattice parameters with chemical composition has been discussed by several authors in *X-ray Identification and Crystal Structures of Clay Minerals* for particular mineral groups, namely the montmorillonoids by MacEwan (Ch. IV), the micas by Brown (Ch. V), and the chlorites by Brindley and Robinson (Ch. VI). The development of a more general treatment has been attempted by Brindley and MacEwan (1953) in a paper in the process of publication, which is briefly outlined here.*

Two parameters call for consideration. In the first place, in so far as the individual layers have hexagonal symmetry, a single parameter suffices to express the
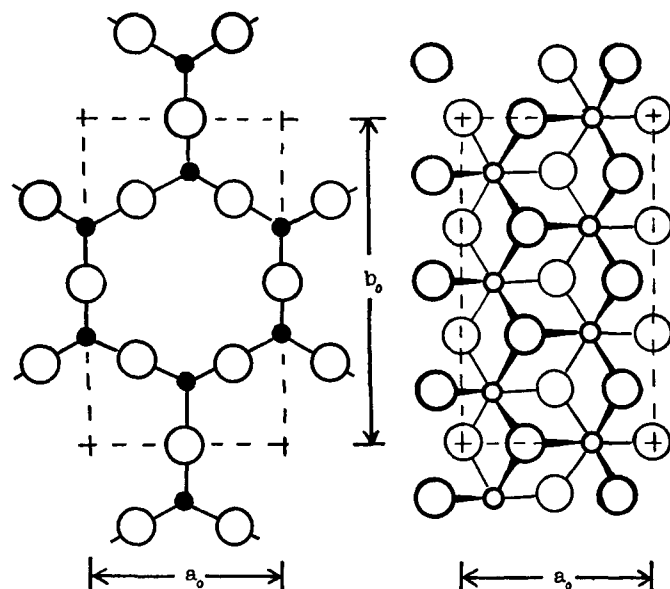

FIGURE 1. Projections of Si-O layer (left), and $X(OH)_2$ layer (right) on the ab plane of layer lattice silicates. Small black circles represent Si, small open circles X, and large open circles, O or (OH). Each Si is tetrahedrally coordinated to O; the fourth O of each tetrahedral group (not shown in the diagram) projects on to the Si atom at its center. Each X atom is octahedrally coordinated to 3(OH) above the plane of projection, shown by heavy circles, and 3(OH) below the plane, shown by light circles. The right-hand diagram represents a trioctahedral layer; one-third of the X atoms are missing in dioctahedral layers.

dimensions in the plane of the layer; b_0, (see fig. 1), is a convenient value since it can be obtained in most cases from the easily observed (060) reflection. For all layer lattice silicates the ratio of the orthogonal parameters, b_0/a_0, is equal to or very nearly equal to the value $\sqrt{3}$ which corresponds to a perfect hexagonal arrangement.

The variation of b_0 with composition will depend mainly on the effective sizes of the cations in tetrahedral and octahedral positions in the oxygen and hydroxyl networks (see fig. 1). The interlayer cations, which are

more loosely coordinated, such as the K^+ ions in muscovite which are in positions of twelve-fold coordination, are unlikely to have more than a small effect on b_0.

A second parameter which may be considered is the layer thickness. If c_0 is the third unit cell dimension and if there are n layers per unit cell, then the layer thickness is given by

c_0/n for orthogonal axes,
$c_0(\sin \beta)/n$ for monoclinic axes,
and
$c_0(1 - \cos^2\alpha - \cos^2\beta)^{\frac{1}{2}}/n$ for triclinic axes with
$\alpha \neq 90^\circ$, $\beta \neq 90^\circ$, and $\gamma = 90^\circ$.

The layer thickness depends on composition in a more complex way than the parameter b_0. The thickness of the silicate network itself depends on the sizes of the tetrahedrally and octahedrally coordinated ions. The separation of the networks from each other depends partly on the size of the interlayer cations, but also on the magnitude of the cohesive forces between these cations and the negatively charged silicate layers. It is to be anticipated, therefore, that the layer thickness will be less easily interpreted in terms of composition than the parameter b_0.

The b_0 parameter was first discussed by Pauling (1930) who compared the dimensions of the hexagonal Si-O networks in β-tridymite and β-cristobalite with those in gibbsite, $Al(OH)_3$, and brucite, $Mg(OH)_2$. On the basis of this comparison he considered that a hydrated alumino-silicate layer of the kind found in the kaolin minerals was dimensionally feasible, and that a corresponding magnesian silicate was unlikely to exist because of the misfit of the component layers, (see data in table 2). In the light of present knowledge, it seems better to start with the Si-O distance, 1.62Å, found in many silicates. This leads to a value $b_0 = 9.16$Å for a hexagonal layer of regular Si-O tetrahedra, and when this is compared with the data for $Al(OH)_3$ and $Mg(OH)_2$ (see table 2, section 3) there is no difficulty in visualizing the formation of both aluminum and magnesium layer silicates.

A difficulty in deriving any relations between b_0 values and chemical composition is to decide just how to effect a compromise between the dimensions of the component tetrahedral and octahedral sheets. Section 3 of table 2 suggests that the arithmetic mean gives values close to the observed values. An important point for consideration is the precise value for the Si-O distance or for b_0 for the Si-O tetrahedral net work, since Si-O = 1.62 or $b_0 = 9.16$ was never intended to be taken as a precise value.

Taylor and his co-workers (see, for example, Cole, Sörum and Kennard, 1949) have considered the effect of random substitution of Al for Si in feldspars and have concluded that the mean (Si,Al)-O distance increases by about 0.02Å for each Si replaced by Al in a group of four. This would give a corresponding increase in b_0 of 0.12Å. Brindley and MacEwan (1953) have therefore taken the b_0 parameter of a tetrahedral network of composition $(Si_{4-x}Al_xO_{10})$ to be

$$b_0 = T + 0.12x$$

where T is likely to be about 9.1-9.2Å, the actual value being found from experimental data.

* This has now appeared in *Ceramics—A Symposium*, published by the British Ceramic Society, 1953.

Values of b_0 for octahedral layers have been obtained from the hydroxide structures and are given in table 2, section 1.

The calculation of b_0 for combined tetrahedral-octahedral layers involves taking the appropriate mean values. Empirically the arithmetic mean has been used and the best value of T found by comparison with experimental data. For dioctahedral structures, T is found to be about 9.16Å which agrees exactly with Si-O = 1.62Å. For trioctahedral structures, $T = 9.00$Å.

Table 2. Lattice parameters in some layer minerals.

1. Octahedral layers.

	Cation radius	b_0 parameter, Å.
Al(OH)₃ gibbsite bayerite	Al = 0.57	8.62 } 8.68 } 8.65 [1]
Fe(OH)₃	Fe³⁺ = 0.67	9.00 [2]
Mg(OH)₂	Mg = 0.78	9.36
Fe(OH)₂	Fe²⁺ = 0.83	9.72

[1] Mean value.
[2] Interpolated value.

2. Si-O Tetrahedral layers.

	b_0 parameter, Å.
From hexagonal networks in β-tridymite and β-cristobalite (after Pauling, 1930)	8.71
On basis of Si-O=1.62	9.16

3. Comparison with Kaolinite and Chrysotile.

	b_0, in Å		b_0, in Å
Si-O layer	9.16	Si-O layer	9.16
Al-OH layer	8.65	Mg-OH layer	9.36
Mean value	8.90₅	Mean value	9.26
Observed value for kaolinite	8.93	Observed values for chrysotile	9.24, 9.18

With these values for T, and on the assumption that a mean b_0 parameter for the combined tetrahedral and octahedral networks is to be taken, the following formulae are obtained:

Dioctahedral minerals
$$b_0 = 8.90 + 0.06x + 0.09q + 0.18r + 0.27s$$

Trioctahedral minerals
$$b_0 = 9.18 + 0.06x - 0.12p - 0.06q + 0.06s$$
where

x = no. of Al for Si substitutions when the formula is expressed in the form $(Si_{4-x}Al_xO_{10})$
p = no. of Al atoms ⎫
q = no. of Fe³⁺ atoms ⎪ in octahedral positions
r = no. of Mg atoms ⎬
s = no. of Fe²⁺ atoms ⎭

$p + q + r + s = 2$ for dioctahedral minerals
3 for trioctahedral minerals.

A detailed comparison of b_0 values calculated from these formulae and obtained experimentally is given by Brindley and MacEwan (1953), and on the whole a close agreement is obtained. Some of the discrepancies may arise from experimental errors, but others may have real significance; for example, discrepancies found with the micas may arise from the effects of the interlayer cations. Generally the best agreement is found with minerals having no interlayer cations, such as the kaolin-type minerals and the chlorites, and with minerals like the montmorillonoids where the interlayer cations are relatively few in number and are generally hydrated.

THE MORPHOLOGY OF CLAY MINERALS

Lamellar Forms. Lamellar crystals of hexagonal outline would be expected from layer structures consisting of hexagonal networks of atoms, but when the morphology of clay minerals is considered in more detail, many questions arise which still require elucidation.

In the case of kaolinite, it is probably generally true that well-formed hexagonal flakes give clear X-ray diagrams indicating a well-ordered succession of layers. The type of kaolin mineral found in many fire clays seems usually to be very poorly crystallized and the X-ray powder diagram indicates considerable disorder in the stacking of the layers, with many displacements of layers by $nb_0/3$, n being integral (Brindley and Robinson, 1947). Both in the clay domain and on a megascopic scale, disordered sequences of this type can be obtained with material showing a well-developed morphology. One cannot therefore necessarily associate quality of morphological development with degree of crystalline regularity. Kaolinite crystals from different localities show considerable variations in their (thickness/size) ratio and in the elongation of the hexagonal forms. No explanation of these variations has yet been offered.

The poor development of montmorillonite crystals, few of which show more than an occasional 120° angle between edges, may be associated with the irregularly superposed and easily separated layers of this mineral. On the other hand, vermiculite which is similar in many respects to montmorillonite, exists as mega-crystalline material.

Tubular and Related Forms. The non-orientation of halloysite by simple sedimentation pointed to a different morphology from that of kaolinite and this has been strikingly confirmed and amplified by electron micrographs, especially by Bates and his co-workers (1950) who have indicated the existence of tubular crystals as well as split and partially unrolled tubes. The X-ray diagrams are consistent with a randomly displaced sequence of layers (Brindley and Robinson, 1948). The occurrence of tubular forms has been attributed by Bates et al. to curvature of the layers resulting from the strain imposed by binding the Si-O and Al-OH layers together. A minimum strain will exist in a layer which is curved so that the Si-O and Al-OH sheets have, as nearly as possible, their own characteristic dimensions, namely b_0 = 9.16 for the Si-O sheet and b_0 = 8.75 for the Al-OH layer. This corresponds to a diameter of about 150Å. (This is similar to, but not identical with, Bates' calculation). Following Bates, we may suppose that in hydrated halloysite a silicate sheet of this diameter forms
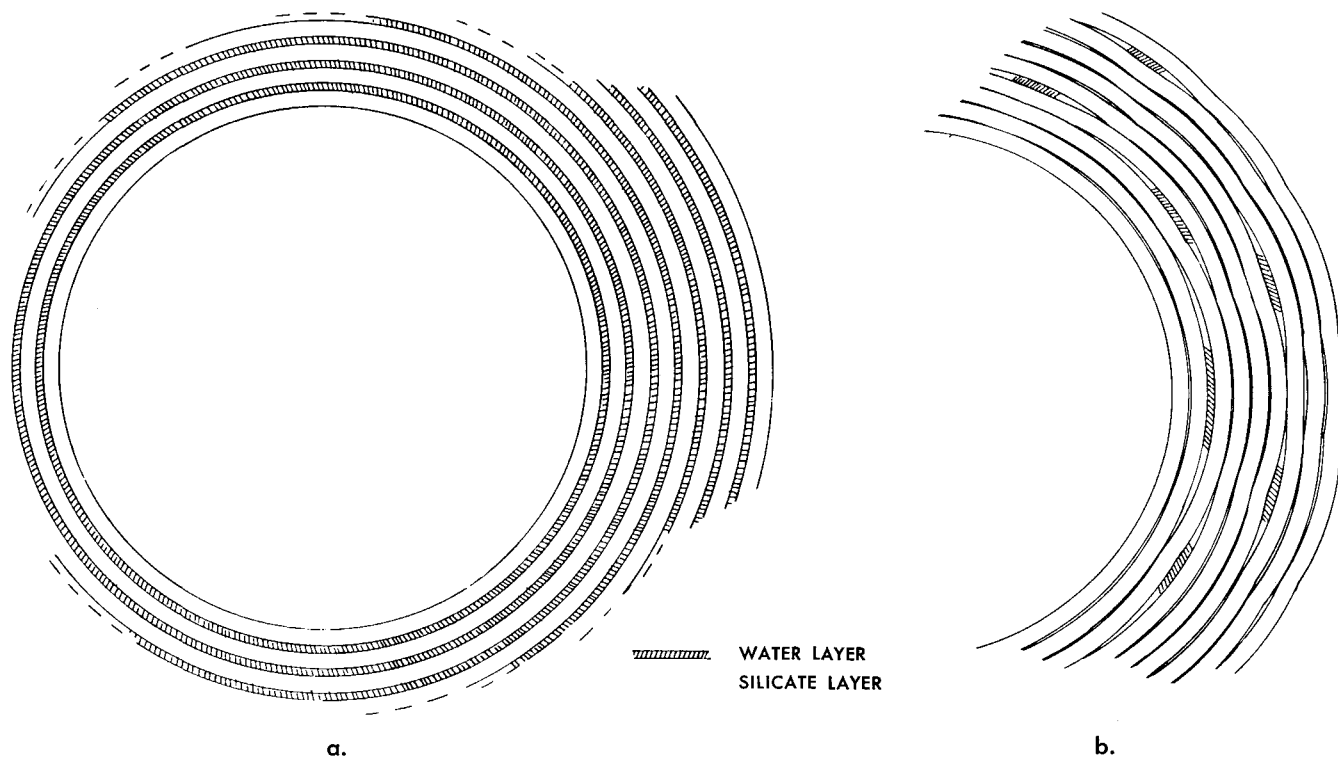
WATER LAYER
SILICATE LAYER

a.   b.

FIGURE 2. Diagram to illustrate (a) Bates' suggestion for the structure of a tube of hydrated halloysite, (b) Brindley's sugges-
tion for the structure of a curved fragment of imperfectly dehydrated halloysite; water inclusions lie in the imperfectly fitting,
curved silicate sheets. The mean layer thickness is about 7.5Å as compared with 7.15 when flat layers are packed together. The
diagrams are drawn correctly to scale as regards the water and silicate layer thicknesses and the inner tube diameter is equivalent
to about 200Å. Silicate layer is represented by white spaces between hachured areas.

the innermost layer. Alternate layers of water and sili-
cate may then be added externally with increasing radius
and therefore increasing strain, until the strain imposes
a limitation preventing further growth (see fig. 2a).
When placed in the electron microscope, the system
will largely dehydrate, probably to a metahalloysite
with a residual water content given by the composition
$Al_2(Si_2O_5)$ $(OH)_4$ $\frac{1}{4}$-$\frac{1}{2}$ H_2O, and a lattice spacing in the
range 7.2-7.5Å. The suggestion is made that on dehy-
dration, the silicate layers (with the possible exception
of the innermost layer) collapse by removal of the inter-
layer water, producing broken fragments having radii
of about 150Å, but retaining a certain amount of residual
water in the process. This is depicted in figure 2b. This
view replaces that described by Brindley and Robinson
(1946b) based on flat layers which was suggested prior
to the discovery of the tubular habit.

A similar explanation may be given of the tubular
habit of chrysotile, discovered by Bates, Sand, and
Mink (1950), but in this case the Si-O sheet will be on
the concave side of each curved layer whereas in halloy-
site the reverse is true. No evidence has yet been brought
forward for the existence of a hydrated chrysotile analo-
gous to hydrated halloysite.

Brief reference may also be made to a description by
Onsager (1952) of a possible explanation of the peculi-
arities exhibited by the single crystal photographs of
antigorite, which was found by Aruja (1945) to have an
a_0 parameter eight times greater than that of chrysotile.
The suggested explanation is that the structural layers

are curved alternately in opposite directions so that a
sine-curve distortion is impressed on the structure along
the a-axis. This requires a reversal of the structure
after every half wave.

Other Morphological Forms. The existence of lath-
like and fibrous forms has been previously attributed to
a lattice strain or curvature limiting crystal growth in
one direction and permitting growth in a perpendicular
direction. While this is feasible in the case of a kaolin-
type structure, it is difficult to see how it can apply to
mica-like structures, such as nontronite and hectorite,
which develop as fibrous forms. Beautiful ribbon-like
crystals have been observed in electron micrographs of
allevardite, a mica-type mineral studied by Caillère,
Mathieu-Sicaud, and Hénin (1950), but no explanation
has yet been given for their occurrence.

SOME STRUCTURAL TOPICS

Relations Between the Kaolin Minerals. The prin-
cipal kaolin minerals, kaolinite, dickite, nacrite, and
halloysite, are now well understood and require little
discussion. Their structural characteristics are sum-
marized in table 3.

The best crystalline kaolinite gives a clear powder
diagram in which some 60 lines have been indexed with
the triclinic parameters given in table 3 and their in-
tensities interpreted in terms of a structure with one
layer per unit cell (Brindley and Robinson, 1946a). This
is in contradiction to an earlier monoclinic structure

Table 3.　Structural data for the principal kaolin minerals.

Mineral	Layers per unit cell, symmetry	a_0 (in Å)	b_0 (in Å)	c_0 (in Å)		References
Halloysite (dehydrated)	1 layer	5.14	8.90	....	d(001), 7.2-7.5	Brindley and Robinson (1948)
Kaolinite	1 layer, triclinic	5.14	8.93	7.37	$\alpha 91.8°$, $\beta 104.5°$	Brindley and Robinson (1946a)
Dickite	2 layers, monoclinic	5.14	8.94	14.42	$\beta 96° 50'$	Gruner (1932b)
Nacrite	6 layers, rhombohedral	8.94	5.14	43.0	$\beta 90° 20'$	Hendricks (1938)

containing two layers per unit cell (Gruner, 1932a). Although the structure is essentially well-ordered, it may (and probably always does) contain some random layer displacements, as Hendricks (1942) has stated, which are more numerous than those occurring in dickite. There is a marked difference in the powder diagrams of well-crystallized kaolinite and of poorly crystallized material such as occurs in many fireclays. The essential crystallographic feature of the poorly crystallized material is the virtual disappearance of all reflections with $k \neq 3n$. This indicates the existence of a great number of random layer displacements of the type $nb_0/3$. No evidence of triclinic character remains and such lines as can be observed may be indexed with a single layer, monoclinic cell (Brindley and Robinson, 1947).*

Halloysite represents a more extreme form of disorder, from which the only reflections observable are the 00l which correspond to the stacking of layers at intervals of about 7.2 — 7.5Å in dehydrated halloysite and 10Å in hydrated halloysite, together with (hk) bands which arise from the regularity within the layers. A treatment of X-ray diffraction from this mineral taking account of its curved or tubular form has not so far been attempted, but a good general interpretation of the diffraction data has been obtained on the basis of a randomly displaced layer structure (Brindley and Robinson, 1948).

It is of interest to consider whether a series of minerals exist extending from an ideally well-ordered kaolinite to a fully disordered halloysite, with the fireclay type fully disordered in one direction (b-axis), as an intermediate stage. This question calls for a more extended survey than it has yet received. The present writer is inclined to the view that all stages probably exist between well-ordered kaolinite and a kaolin mineral highly disordered along the b-axis, but is less certain of the existence of intermediate stages between the b-axis disordered type and halloysite.

At this point reference must be made to a very careful study by Bramao, Cady, Hendricks, and Swerdlow (1952) of "kaolinite, halloysite, and a related mineral in clays and soils"; the latter is fine-grained, poorly organized material, "which may be the kaolin mineral of fireclay." In the electron microscope, it exhibits features intermediate between those of kaolinite and halloysite, and consists of "irregular layered particles having curved surfaces." In view of these statements, it is not impossible that a continuous series may exist from kaolinite to halloysite and, indeed, Bramao et al. consider a possible genesis of clay minerals from hydrated halloysite to the largely dehydrated form, to the disordered variety of kaolin mineral.

* See also Robertson, R. H. S., Brindley, G. W., and Mackenzie, R. C., 1954, Mineralogy of kaolin clays from Pugu, Tanganyika: Am. Mineral., vol. 39, pp. 118-138.

The question as to whether a name should be given to the disordered type of kaolin mineral should be viewed in relation to the situation existing in other layer-mineral groups. The occurrence of ordered and disordered (or, more ordered and less ordered) forms is very common and therefore it seems undesirable to attach a particular name to a form which appears to be characterized mainly by its disorder. The writer advocates "disordered kaolin mineral," or "b-axis disordered kaolin mineral" when a more specific description is required.

The writer, in collaboration with R. H. S. Robertson and R. C. Mackenzie, has recently examined an excellent example of a b-axis disordered kaolin mineral which under the electron microscope shows very regular hexagonal crystals about 0.2 micron in size. An account of this work will be published soon † (see also Meldaü and Robertson, 1952).

The Kaolin-Type Minerals. The principal addition to the list of kaolin-type minerals in recent years has been the mineral chamosite (Brindley 1951b). This is a fine-grained hydrated ferrous silicate frequently associated
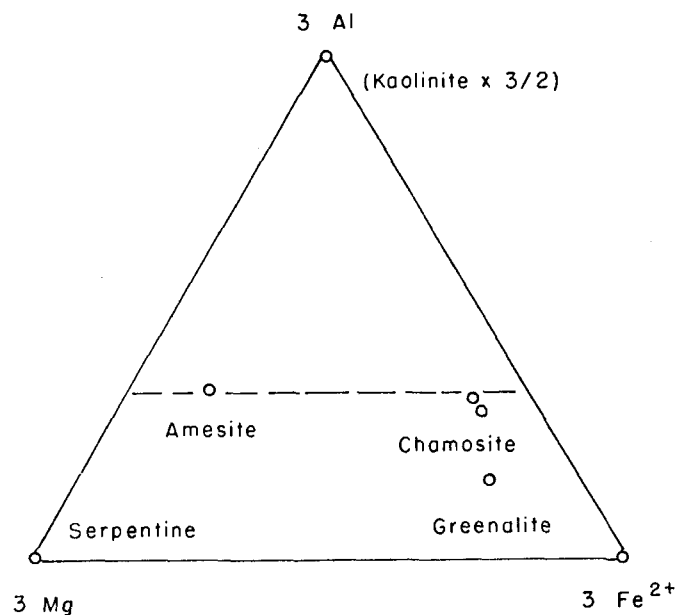
† See preceding footnote.

FIGURE 3. Composition of octahedral layers in kaolin-type minerals. Strictly the diagram refers to trioctahedral members only having the general formula $(Mg,Fe,Al)_3(Si,Al)_2O_5(OH)_4$. The only dioctahedral member, kaolinite (and its polymorphic forms), can be included if the octahedral ions, 2Al, are multiplied by 3/2. The trioctahedral members lie below the dashed line which corresponds to the composition $(Mg,Fe)_2Al(SiAlO_5)(OH)_4$. Any trioctahedral mineral lying above the dashed line would have more Al than Si atoms in tetrahedral positions.

with siderite and kaolinite; it is common in sedimentary ironstone deposits. The name, however, was originally applied to a material from Chamoson which has been shown to have a chlorite-type structure (Orcel, Caillère, and Hénin, 1950). Hallimond (1951a) has expressed the opinion that the original material may have been recrystallized and that "it would not be surprising if . . . the original chamosite turned out to be bavalite", which is a well authenticated chlorite. Taylor (1951) also has stressed the necessity for caution regarding the type material, some of which may be thuringite, which also is a chlorite. The use of the term "chamosite" for two minerals chemically similar but structurally very dissimilar creates a nomenclature problem which can scarcely be solved by taking the view that the material from Chamoson has historical priority; apart from the doubtful character of the type material (cf. Hallimond, 1951b), the term chamosite is now too widely used for the silicate mineral in sedimentary ironstones for it to be easily changed.

The discovery that chamosite is a kaolin-type mineral has provided a ferrous analogue of kaolinite and chrysotile. Its composition is somewhat variable but a typical example has the formula:

$$(Fe^{++}_{1.78}Mg_{0.41}Al_{0.43}Fe^{+++}_{0.30})(Si_{1.40}Al_{0.60}O_5)(OH)_4$$
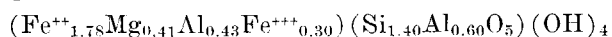
The mineral is therefore trioctahedral and mainly ferrous. The mineral greenalite, the formula of which may be written approximately as

$$(Fe^{++}_{2.2}Fe^{+++}_{0.5})(Si_2O_5)(OH)_4,$$
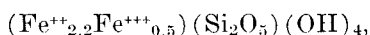
comes still nearer to being a purely ferrous iron analogue of chrysotile (Gruner, 1936).

A triangular diagram representing the compositions of the octahedral layers of kaolin-type minerals is shown in figure 3. This represents principally the trioctahedral minerals, the corner compositions being 3Mg, 3Fe^{++} and 3Al respectively. The only known dioctahedral structure is the kaolin layer itself and this may be included in the diagram by multiplying the dioctahedral ions by the factor $^3/_2$. (The same procedure may be followed with any other dioctahedral structure which may be discovered). In this representation, kaolinite, serpentine, and greenalite come at or near the corner positions, chamosites occupy a small field near the Fe^{++} corner, and amesite lies roughly between serpentine and kaolinite. The outstanding feature is the emptiness of the diagram. It may well be the case, however, that trioctahedral minerals cannot be expected to lie much nearer the Al corner than the dashed line which corresponds to a tetrahedral composition of (SiAlO$_5$); minerals nearer the Al corner would have more Al than Si in the tetrahedral layer. It is difficult, however, to understand why ferric iron substitution in dioctahedral minerals does not occur, or occurs to only a small extent. The writer is unaware of the existence of a kaolin mineral with extensive substitution of Al by other trivalent ions.

Relations Between the Mica-Type Minerals. In the structural group of the mica-type minerals, the non-swelling and swelling minerals with roughly 10Å and 14Å basal spacings have been collected together, and some justification for this procedure is required. It has been customary (cf. Brown, 1951) to separate these

minerals into the true micas, which are normally non-swelling types, at one extreme and the montmorillonoids and vermiculites, which normally swell readily, at the opposite extreme, and to place illites and kindred minerals in an intermediate position. It is becoming increasingly recognized, however, that this classification may be less fundamental than it was once considered to be. Weaver and Bates (1951), who have discussed the question generally, underline the fact that the swelling properties depend largely on the interlayer cations, which may vary with the environment; they cite many results in support of this view. Thus White (1950) has treated illite with MgCl$_2$, precipitated the exchanged potassium, and obtained a montmorillonite X-ray pattern. Caillère and Hénin (1949) treated montmorillonite with KOH and obtained an illite-type diagram. Barshad (1948) showed that biotite leached with MgCl$_2$ over long periods is converted to an expansible vermiculite, and Walker (1949) has studied similar transformations produced by weathering processes. Thus passage from a swelling to a non-swelling mineral and vice versa seems to be rather easy, and the swelling property to be connected primarily with chemical composition. Therefore, in accordance with the principles of the classification set out in table 1, these minerals must be regarded as essentially different chemical species rather than different structural arrangements. The range of basal spacings, extending from 10Å to 14Å or more, is connected primarily with hydration which is extremely variable in many of these minerals. The most logical procedure is therefore to place all these minerals in the mica-type structural group, to differentiate chemical species according to composition, and to regard hydration as a property not affecting the broad lines of the classification. This perspective does not detract from the intrinsic interest of the swelling properties, which will now be considered.

The relation of swelling to the type of interlayer cation has been discussed especially by Barshad (1950) who considers that, "The ionic radii, the valency, and the total charge of the interlayered cations, as well as the nature of the interlayered substance seem to determine the extent of the interlayer expansion of the mica type of crystal lattice." A useful synthesis of data is obtained by considering the interlayer cations in order of the potential $V = ne/r$, where ne is the ionic charge of an interlayer cation of valency n, and r is the ionic radius. This potential, conveniently measured by n/r, determines approximately the tendency of ions to form hydration shells with water molecules and therefore, under humid conditions, to expand the lattice structure. Table 4 summarizes data by Barshad (1950) and Walker (1951) for the spacings of, and water layers in, air-dry vermiculite and montmorillonite. It is clear that as n/r decreases, the hydration tendency diminishes and the number of water layers diminishes from two to one to zero.

The tendency of a lattice to swell owing to hydration of the ions is opposed by the electrostatic force binding the negatively charged silicate layers to the positively charged interlayer ions. This force depends on the magnitude of the layer charge, ne, (which also determines the number of interlayer ions)? and also on the seat of the

Table 4. Lattice spacings of, and numbers of water layers in montmorillonite and vermiculite with different interlayer cations.

Ions	H$^+$	Mg^{++}	Ca^{++}	Li$^+$	Ba^{++}	Na$^+$	K$^+$	NH$_4^+$	Rb$^+$	Cs$^+$
Radius, r, Å	0.30	0.65	0.99	0.60	1.35	0.95	1.33	1.48	1.48	1.69
n/r	3.3	3.08	2.02	1.67	1.48	1.05	0.75	0.68	0.68	0.59
(i) Data for vermiculites										
Lattice spacings { Barshad	14.33	14.33	15.07	12.56	12.56	12.56	10.42	11.24	11.24	11.97
{ Walker		14.36	15.0	12.2	12.3	14.8	10.6	10.8		
Number of water layers	2	2	2	1	1	1, 2	0	0	0	0
(ii) Data for montmorillonites										
Lattice spacings Barshad	14.5	14.8	15.1	13.4	12.9	11.9	12.0	1?.1	12.3	12.9
Number of water layers	2	2	2	1	1	1	1	1	1	1

Sources of data: Barshad (1950); Walker (1951).

charge, e.g., whether it arises predominantly in the octahedral or tetrahedral part of the lattice.

It is therefore useful to consider the magnitude of the layer charge as determined by cation-exchange measurements. Some typical values are set out in table 5, from which it is evident that there is no great difference between illites, vermiculite, and montmorillonoids as regards the charge of the layers.

The question now arises as to whether the non-swelling of such micas as muscovite and biotite is to be attributed to the greater layer charge and therefore greater electrostatic attraction or to the kind of interlayer ions. Barshad (1950) has shown that the sodium mica, paragonite, will expand in water when finely ground (to less than 0.5 micron), but muscovite when similarly treated does not expand. Crystal size therefore appears to be an additional factor.

Table 5. Layer charge on mica-type minerals.

Mineral	Layer charge, per unit cell
Margarite	4
Muscovite, biotite	2
Illites	1.0–1.5 (Mackenzie, Walker and Hart, 1949)
Vermiculites	0.9–1.4 (Barshad, 1948)
Montmorillonoids	0.7–1.0 (Foster, 1951) 0.4–1.1 (Ross and Hendricks, 1943–4)
Talc, pyrophyllite	0

A comparison of the data for vermiculite and montmorillonite in table 4 indicates somewhat greater swelling by the latter mineral. A full interpretation of this cannot be offered but it may well arise from the smaller crystal size of the montmorillonites.

SOME THERMAL AND CHEMICAL TRANSFORMATIONS OF LAYER SILICATES CONSIDERED FROM A STRUCTURAL ASPECT

Structural studies of mineral transformations are concerned with the nature of the new phases formed and with the processees by which the changes occur. Chemical and optical methods have been employed for many years in the recognition of phases and the X-ray method of identification has provided yet another method. It is particularly useful for studying fine-grained products and for intimate mixtures which cannot readily be separated. The second and possibly the more important use of X-rays lies in the possibility it provides of studying the actual transformation process itself. So far such studies have been confined to observing the orientation of a new phase in relation to the old phase. It may then be possible to arrive at a plausible picture of the mechanism of the transformation.

Thermal transformations of layer silicates are of two or possibly three kinds. Dehydration and recrystallization processes are well known, but a third may be added, namely oxidation processes.

Dehydration Processes. Dehydration processes may be subdivided into those concerned with release of water without change of silicate structure and those which involve a structural change. The former processes include release of adsorbed water from external surfaces, from internal surfaces (cf. montmorillonoids and vermiculites) and from channels in a structure (cf. attapulgite, zeolites). The latter processes involve the release of so-called "structural water," generally hydroxyl groups, with concomitant modification or recrystallization of the structure.

A partial release of "structural water" may result in a partial change of structure, but the final release of water is generally followed by recrystallization. As examples of partial release of water, the chlorites may be specially mentioned. Brindley and Ali (1950) first showed in detail that the hydroxide or brucite-type layer of the structure can be largely dehydrated without modifying the mica-type layer and without any major collapse of the usual 14Å basal spacing of the structure. The X-ray reflections are characteristically modified, especially as regards the basal intensities. The mica-type layer dehydrates at a temperature usually about 100°–150° C. higher than the first process. Chamosite provides another example of a structure which can be partially dehydrated. Two distinct stages of dehydration indicate the presence of hydroxyl ions with different degrees of binding in the lattice, and this is especially clear in the case of chlorites.

Similar deductions can be drawn with regard to adsorbed water and water of hydration which is shown by the doubled, low temperature endothermic peaks recorded in differential thermal analyses of some montmorillonoids.

Recrystallization Processes. The final dehydration of a structure often leads directly to recrystallization, with a structural reorganization. Investigations tend to show that when blocks or units of structure of an old phase can be directly built into a new phase, the transformation is rapid. Such transformations tend to develop by an orderly process. X-ray photographs of single crystals of chlorites, for example, have shown the co-existence of the old and the new phases, and in this way information is obtained of the orientation relations of the phases (c.f. Brindley and Ali, 1950). Chrysotile has been similarly studied by Hey and Bannister (1948) and by Bradley and Grim (1951). The latter have discussed generally a number of transformations of this type.

Dehydration and Recrystallization of Kaolin Minerals. Space does not permit a detailed discussion of recrystallization phenomena generally in layer silicates, but reference may be made to the dehydration and recrystallization of the kaolin structure. The practical importance of the changes in kaolinite has stimulated many investigations (c.f. Richardson, 1951) but in some respects, the results have been surprisingly discordant. Dehydration at about 550° C. leads to a disordered phase generally said to be amorphous and recrystallization commences around 900-950° C. with the formation of γ-alumina or mullite together with cristobalite. So much is broadly ascertained, but the details seem to lack precision and different workers have emphatically maintained different points of view as regards the details. Brindley and Hunter (1952) have attempted to obtain further information by studying the polymorphic variety, nacrite, which has the same layer structure as kaolinite. The only differences which can arise, therefore, between kaolinite and nacrite are those connected with crystal size.

Von Knorring, Brindley, and Hunter (1952), working on nacrite from a newly discovered source, have found that the mineral is well-crystallized and (inter alia) that on dehydration, although most of the water is lost at about 550°C, some water is retained to about 750°C. This is consistent with data for kaolinite. The retention of some water to quite high temperatures seems well established. The single crystal photographs of heated nacrite crystals (this work is not yet published in detail) show persistence of some degree of structural order almost to 900°C. The question, therefore, must be asked whether persistence of order and retention of water can be correlated. A broad diffraction ring indicating considerable disorder increases in intensity up to 900°C. At 950°C, the diffraction diagram clarifies and a powder pattern of mullite and some cristobalite is obtained.[*] It was hoped that by working with a single crystal of nacrite, a strongly orientated diagram of mullite would be obtained. This, however, has not emerged, although there are some small indications of a preferential orientation. It still remains to work out the details of these photographs, but broadly the findings are in agreement with those of Comeforo, Fischer, and Bradley (1948) who emphasized that mullite rather than γ-alumina is the essential recrystallization product. They worked with kaolinite crystals which were observed with an electron microscope and obtained evidence of the development of mullite needles having particular orientations with respect to kaolinite crystals.

Oxidation Processes—Chamosite. Oxidation processes have not been studied to any large extent from a structural standpoint, but Brindley and Youell (1952) have completed an investigation of the transformation of the normal ferrous form of chamosite to a ferric form with accompanying dehydration. Detailed X-ray and chemical data indicate two processes of dehydration, the first being essentially part of an oxidation process, as follows:

$$Fe^{++} \rightarrow Fe^{+++} + e^-$$
$$e^- + (OH)^- \rightarrow O^{--} + H$$
$$2H + O \text{ (atmospheric)} \rightarrow H_2O$$
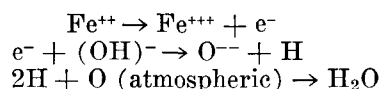
The oxidation of Fe^{++} to Fe^{+++} liberates an electron, e^-, which attaches itself to $(OH)^-$ forming an O^{--} ion and setting free H which is oxidized to water by atmospheric oxygen. The combined process can be written:

$$4Fe^{++} + 4(OH)^- + O_2 \text{ (atmospheric)}$$
$$= 4Fe^{+++} + 4O^{--} + 2H_2O$$
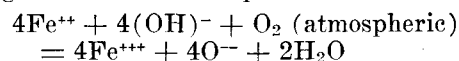
Thus the lattice loses only hydrogen, but in a certain sense the process is partly one of dehydration since $(OH)^- \rightarrow O^{--}$. The oxidation of Fe^{++} to Fe^{+++} is shown quantitatively by chemical analysis, while X-ray powder diagrams show a shrinkage of the silicate structure which is consistent with the radii of the two ions concerned, namely Fe^{++}, 0.83Å; Fe^{+++}, 0.67Å. That atmospheric oxygen plays an important part in the process is proved by the fact that in vacuo or in an inert atmosphere the reaction does not proceed in this way.

Associated with the oxidation-dehydration process, is a normal dehydration of the outermost hydroxyl sheet [*] of the structure, proceeding as follows:

$$2(OH)^- = H_2O + O^{--}$$
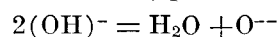
An important structural aspect of the entire oxidation-dehydration reaction which takes place at about 400°C, is that only the outermost hydroxyls take part in it. Out of the initial $(OH)_4$ of the structural formula, 3(OH) radicals are dehydrated, but the fourth persists in the structure to a higher temperature, about 450-500°C. Here we appear to have a clear indication of difference in chemical reactivity of the hydroxyl ions within the silicate layer and those in the external sheet of each silicate layer.

It is perhaps wishful thinking to correlate this behaviour of chamosite with that of kaolinite and to suppose that the retention of hydroxyl units by kaolinite is related to the inner positions of one-quarter of the hydroxyl radicals. Although this may well be partly related to the behaviour of the kaolin minerals, so far we lack any clear quantitative explanation because the amount of water retained by kaolinite and nacrite to high temperatures is a small percentage only, of the order of 5 percent, and is not a fraction which might be given a simple structural interpretation. At present, therefore, we can go no further than to note that the release of (OH) ions as water may be related to their

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[*] Further work by Brindley and Hunter has shown that γ-alumina occurs as a transient phase, and it appears to be oriented with respect to the original nacrite. It still remains to elucidate the structural significance of the results.

[*] I.e., those which lie in the external sheet of each silicate layer; the expression does not refer to the external surface of a crystal.

structural environment and that in one case, that of chamosite, we have clear evidence for such a conclusion.

Dissolution of Chlorites in Acids. Another example of chemical reactivity being related to structural environment has been obtained by Brindley and Youell (1951) from a study of the acid attack on chlorites. It was found that ions such as Mg,Fe^{++} occupying octahedral positions in the structure, were removed at the same rate when the amount dissolved was expressed as a fraction of the total amount of each ion. Al was found to be removed differently, however, and this was correlated with the fact that Al occupies both tetrahedral and octahedral positions in the lattice structure. Octahedral Al was found to be removed at the same rate as other octahedral ions and, in fact, on this basis the proportions of octahedral and tetrahedral Al were separately determined by a purely chemical method for the first time. The results were found to be in agreement with the allocation of Al to the two kinds of lattice positions from structural considerations and provided an experimental proof for the customary procedure. What is more important in the present context is that, here again, there is evidence for chemical reactivity being related to structural environment.

CONCLUDING REMARKS

In conclusion, it must be confessed that this is a very inadequate account of the structural mineralogy of clays and related minerals. The subject is now sufficiently well developed for a classification to be attempted on moderately detailed lines, but it is still growing and is likely to outgrow any classification which is too rigid in framework. It is hoped that the scheme suggested will be sufficiently elastic to accommodate new developments.

DISCUSSION

D. M. C. MacEwan:

In connection with the charge on the structure of micaceous minerals in relation to their behavior, some calculations have been done by Brown and Norrish (1952). They have recalculated a number of analyses of micas which were low in potash, and showed that, in many cases, much better agreement can be obtained with the expected complement of octahedral ions and the expected amount of OH^- ions if one assumes that the excess water is present in the form of H_3O^+ ions. In many analyses there is more water than expected on the basis of a normal structure. If the water is assumed to be present in the form of H_3O^+ ions, the analyses can be recalculated to show that there are two interlamellar cations per structural unit, in most cases, with H_3O^+ partly replacing K^+. This suggests that more micas than had been supposed are fully charged. Nevertheless, there are materials with low charge, such as Barshad has been finding, and his technique for determining exchangeable hydrogen directly may be very important.

A. Pabst:

Much longer spacings than those that have been mentioned here have been reported for chrysotile (Frankuchen and Schneider, 1944). The long spacings were interrupted as arising from "parallel fundamental fibrils—hexagonally packed in cross section". The indicated diameters of the fibrils in various samples ranged from 195 to 250 Å. It may be pointed out that this is in excellent accord with the later electron microscope work by Bates and associates (1950). The dimensions of the fibrils are similar to the dimensions found for halloysite tubes by Bates and co-workers to which Dr. Brindley has referred.

D. M. C. MacEwan:

I feel sure that you can obtain spacings greater than 30 Å from montmorillonite in certain circumstances. Norrish, working in our laboratory, has obtained spacings between 35 and 100 Å.

Stephen and I have obtained a material which we think is a type of hydrated chlorite and therefore half-way between montmorillonite and chlorite. It is a mixture of both swelling and non-swelling chloritic material. This material gives 14 Å and 28 Å spacings when it contains no water, but hydrated it gives higher spacings. We have also obtained a mixed-layer material which contains both montmorillonitic material and the chloritic material. This gives spacings of about 30 Å and 24 Å. The spacings do not necessarily follow in a rational series.

G. W. Brindley:

I think it is becoming increasingly important to extend measurements into the region of long spacings. In some of the early chlorite measurements the longest spacing recorded was around 7 Å and the 14 Å "reflection" was missed, and in some of the earliest kaolin measurements the 7 Å reflection was similarly overlooked. Several recent investigations tend to show that spacings longer than 14 or 18 Å do occur in nature. There is the work of Bradley (1950) on rectorite, which consists of a fairly regular succession of pyrophyllite and vermiculite layers with a periodicity of about 25 Å. There has also been a recent publication (Alexanian and Wey 1951) in which spacings of the order of 32 Å are recorded from well-orientated montmorillonites. Long spacings of the order of 22.5 Å have also been recorded from a mica-like mineral which has been called allevardite by Caillère and co-workers (1950). Allevardite is a rather unusual mineral which has been shown by electron micrograph to have a ribbon-like form. It is clear, therefore, that periodicities longer than the simple ones of 7, 10, and about 14 Å do occur, and it becomes increasingly important that techniques should be developed for working in this long spacing region using crystal-reflected radiation. It should be noted that with filtered radiation a peak may arise from the distribution of intensity in the white radiation that can be very confusing. We had such an experience in our laboratory. To determine the nature and origin of long spacings, one should look first for a regular succession of orders, the existence of which would indicate a *regular* succession of layers. In all probability there will not be a single layer having a thickness of 25 or 30 Å but rather a regular succession of two kinds of layers such as A-B-A-B. If successive reflections do not occur at equal intervals of sin Θ, then we probably have a disordered or partially disordered layer sequence. The general line of investigation is then to try to modify one of the component layers by dehydration or by adsorption of organic molecules. In addition one may study in detail the actual shapes or profiles of the lines.

R. C. Mielenz:

Many X-ray patterns of montmorillonite-type clays show not only a ring at approximately 13 to 15 Å but also a ring at twice that dimension ranging from 26 to 30 Å. Would someone care to discuss the significance of this determination with regard to the present concepts of the size of the unit cell of montmorillonite?

E. A. Hauser:

At temperatures above 150°C there is a complete change in the surface composition of clay minerals. This has been demonstrated by Weyl (1949) of Pennsylvania State College with his new technique which I have used quite extensively. A specific indicator will show that at a certain temperature there is a pronounced release of atomic oxygen. This release causes a complete change in the reactivity of the system and explains many of the phenomena.

REFERENCES

Alexanian, C., and Wey, R., 1951, Sur l'existence d'une raie intense à 32Å environ dans le diagramme de rayons X de plaquettes de montmorillonite orientée; Acad. Sci., Paris, Comtes Rendus, v. 232, pp. 1855-1856.

Aruja, E., 1945, An X-ray study of the crystal-structure of antigorite: Mineralog. Mag., v. 27, p. 65-74.

Barshad, I., 1948, Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analyses, differential thermal curve and water content: Am. Mineralogist, v. 33, pp. 655-678.

Barshad, I., 1950, The effect of the interlayer cations on the expansion of the mica type of crystal lattice: Am. Mineralogist, v. 35, p. 225-238.

Bates, T. F., Hildebrand, F. A., and Swineford, A., 1950, Morphology and structure of endellite and halloysite: Am. Mineralogist, v. 35, pp. 463-484.

Bates, T. F., Sand, L. B., and Mink, J. F., 1950, Tubular crystals of chrysotile asbestos: Science, v. 111, pp. 512-513.

Bradley, W. F., 1950, The alternating layer sequence of rectorite: Am. Mineralogist, v. 35, pp. 590-595.

Bradley, W. F., and Grim, R. E., 1951, High temperature thermal effects of clay and related materials: Am. Mineralogist, v. 36, pp. 182-201.

Bragg, W. L., 1937, Atomic structure of minerals: 292 pp., Oxford Univ. Press; Cornell Univ. Press.

Bramao, L., Cady, J. G., Hendricks, S. B., and Swerdlow, M., 1952, Criteria for the characterization of kaolinite, halloysite, and a related mineral in clays and soils: Soil Science, v. 73, p. 273-287.

Brindley, G. W., 1951a, Editor, X-ray identification and crystal structures of clay minerals: 345 pp., London, Mineralogical Soc. (Clay Minerals Group).

Brindley, G. W., 1951b, The crystal structure of some chamosite minerals: Mineralog. Mag., v. 29, pp. 502-525.

Brindley, G. W., and Ali, S. Z., 1950, X-ray study of thermal transformations in some magnesian chlorite minerals: Acta Crystallographica, v. 3, pp. 25-30.

Brindley, G. W., and MacEwan, D. M. C., 1953, Structural aspects of the mineralogy of clays and related silicates, in Green, A. T., and Stewart, G. H., Ceramics, a symposium, pp. 15-59, Stoke-on-Trent, The British Ceramic Society.

Brindley, G. W., Oughton, B. M., and Robinson, K., 1950, Polymorphism of the chlorites. I. Ordered structures: Acta Crystallographica, v. 3, pp. 408-416.

Brindley, G. W., and Robinson, K., 1946a, The structure of kaolinite: Mineralog. Mag., v. 27, pp. 242-253.

Brindley, G. W., and Robinson, K., 1946b, Randomness in the structures of kaolinitic clay minerals: Faraday Soc. Trans., v. 42B, pp. 198-205.

Brindley, G. W., and Robinson, K., 1947, An X-ray study of some kaolinitic fire clays: British Ceramic Soc. Trans., v. 46, pp. 49-62.

Brindley, G. W., and Robinson, K., 1948, X-ray studies of halloysite and metahalloysite: Mineralog. Mag., v. 28, pp. 393-406.

Brindley, G. W., and Youell, R. F., 1951, A chemical determination of "tetrahedral" and "octahedral" aluminium ions in a silicate: Acta Crystallographica, v. 4, pp. 495-496.

Brindley, G. W., and Youell, R. F., 1953, Ferrous chamosite and ferric chamosite: Mineralog. Mag., v. 30, pp. 57-70.

Brown, G., 1951, Nomenclature of the mica clay minerals, in Brindley, G. W., Editor, X-ray identification and crystal structures of clay minerals: Chap. 5, part II, pp. 155-172, London Mineralogical Society (Clay Minerals Group).

Brown, G., and Norrish, K., 1952, Hydrous micas: Mineralog. Mag., v. 29, pp. 929-932.

Caillère, S., 1951, Sepiolite, in Brindley, G. W., Editor, X-ray identification and crystal structures of clay minerals: Chap. 8, pp. 224-233, London Mineralogical Society (Clay Minerals Group).

Caillère, S., and Hénin, S., 1951, Palygorskite—attapulgite, in Brindley, G. W., Editor, X-ray identification and crystal structures of clay minerals: Chap. 9, pp. 234-243, London Mineralogical Society (Clay Minerals Group).

Caillère, S., Mathieu-Sicaud, A., and Hénin, S., 1950, Nouvel essai d'identification du mineral de La Table près Allevard, l'allevardite: Soc. Français Minéralogie Crystallographie, Bull., v. 73, pp. 193-201.

Caillère, S., and Hénin, S., 1949, Transformation of minerals of the montmorillonite family into 10Å micas: Mineralog. Mag., v. 28, pp. 606-611.

Caillère, S., and Hénin, S., 1949, Experimental formation of chlorites from montmorillonite: Mineralog. Mag., v. 28, p. 612-620.

Cole, W. F., Sörum, H., and Kennard, O., 1949, The crystal structures of orthoclase and sanadinized orthoclase: Acta Crystallographica, v. 2, pp. 280-287.

Comeforo, J. E., Fischer, R. B., and Bradley, W. F., 1948, Mullitization of kaolinite: Am. Ceramic Soc. Jour., v. 31, pp. 254-259.

Fleischer, Michael, 1947, Some problems in nomenclature in mineralogy and inorganic chemistry: Am. Soc. Testing Materials Proc., v. 47, pp. 1090-1108.

Foster, M. D., 1951, The importance of exchangeable magnesium and cation exchange capacity in the study of montmorillonite clays: Am. Mineralogist, v. 36, pp. 717-730.

Frankuchen, I., and Schneider, M., 1944, Low angle X-ray scattering from chrysotiles: Am. Chem. Soc. Jour., v. 66, p. 500.

Frondel, C., and Palache, C., 1950, Three new polymorphs of zinc sulfide: Am. Mineralogist, v. 35, pp. 29-42.

Grim, R. E., and Bradley, W. F., 1951, The mica clay minerals, in Brindley, G. W., Editor, X-ray identification and crystal structures of clay minerals: Chap. 5, part I, pp. 138-154, London, Mineralogical Society (Clay Minerals Group).

Gruner, J. W., 1932a, The crystal structure of kaolinite: Zeitschr. Kristallographie, Abt. A, Band 83, pp. 75-88.

Gruner, J. W., 1932b, The crystal structure of dickite: Zeitschr. Kristallographie, Abt. A, Band 83, pp. 394-404.

Gruner, J. W., 1936, The structure and composition of greenalite: Am. Mineralogist, v. 21, pp. 449-455.

Hallimond, A. F., 1951a, Discussion: Clay Minerals Bull., v. 1, pp. 136-137.

Hallimond, A. F., 1951b, Problems of the sedimentary iron ores: Yorkshire Geol. Soc. Proc., v. 28, pp. 61-66.

Hendricks, S. B., 1938, The crystal structure of nacrite $Al_2O_3 \cdot 2SiO_2 \cdot H_2O$ and the polymorphism of the kaolin minerals: Zeitschr. Kristallographie, Band 100, pp. 509-518.

Hendricks, S. B., 1942, Lattice structure of clay minerals and some properties of clay: Jour. Geology, v. 50, pp. 276-290.

Hendricks, S. B., and Jefferson, M. E., 1939, Polymorphism of the micas, with optical measurements: Am. Mineralogist, v. 24, pp. 729-771.

Hey, M. H., and Bannister, F. A., 1948, A note on the thermal decomposition of crysotile: Mineralog. Mag., v. 28, pp. 333-337.

Jackson, M. L., Hseung, Y., Corey, R. B., Evans, E. J., and Heuvel, R. C. V., 1952, Weathering sequence of clay-size minerals in soils and sediments. II. Chemical weathering of layer silicates: Soil Sci. Soc. America Proc., v. 16, pp. 3-6.

Knorring, O. von, Brindley, G. W., and Hunter, K., 1952, Nacrite from Hirvivaara, northern Karelia, Finland: Mineralog. Mag., v. 29, pp. 963-972.

Mackenzie, R. C., Walker, G. F., and Hart, R., 1949, Illite occurring in decomposed granite at Ballater, Aberdeenshire: Mineralog. Mag., v. 28, pp. 704-713.

Meldau, R., and Robertson, R. H. S., 1952, Morphologische Einflüsse auf technische Staubeigenschaften: Ber. deut. Keram. Ges., Band 29, pp. 27-35.

Onsager, L., 1952, Discussion, in Summarized proceedings of a conference on structures of silicate minerals—London, November 1951: British Jour. Applied Physics, v. 3, pp. 281-282.

Orcel, J., Caillère, S., and Hénin, S., 1950, Nouvel essai de classification des chlorites: Mineralog. Mag., v. 29, pp. 329-340.

Pauling, Linus, 1930, The structure of micas and related minerals: Nat. Acad. Sci. Proc., v. 16, pp. 123-129.

Pauling, Linus, 1930, The structure of the chlorites: Nat. Acad. Sci., Proc., v. 16, pp. 578-582.

Ramsdell, L. S., 1947, Studies of silicon carbide: Am. Mineralogist, v. 32, pp. 64-82.

Ramsdell, L. S., and Kohn, J. A., 1951, Disagreement between crystal symmetry and X-ray diffraction data as shown by a new type of silicon carbide, 10H: Acta Crystallographica, v. 4, pp. 111-113.

Ramsdell, L. S., and Kohn, J. A., 1952, Developments in silicon carbide research: Acta Crystallographica, v. 5, pp. 215-224.

Richardson, H. M., 1951, Phase changes which occur on heating kaolin clays, in Brindley, G. W., Editor, X-ray identification and crystal structures of clay minerals: Chap. 3, pp. 76-85, London, Mineralogical Society (Clay Minerals Group).

Ross, C. S., and Hendricks, S. B., 1931, Minerals of the montmorillonite group, their origin and relation to soils and clays: U. S. Geol. Survey Prof. Paper 205-B, pp. 151-180.

Strunz, Hugo, 1941, Mineralogische Tabellen; eine Klassifizierung der Mineralien auf kristallchemisches Grundlage, mit einer Einführung in die Kristallchemie: 308 pp., Leipzig, Akademische Verlagsgesellschaft.

Taylor, J. H., 1951, In discussion on Observations of the chlorites of iron ores: Clay Minerals Bull., v. 1, p. 137.

Walker, G. F., 1949, The decomposition of biotite in the soil: Mineralog. Mag., v. 28, pp. 693-703.

Walker, G. F., 1951, Vermiculites and some related mixed-layer minerals, in Brindley, G. W., Editor, X-ray identification and crystal structures of clay minerals: Chap. 7, pp. 199-223, London, Mineralogical Society (Clay Minerals Group).

Weaver, C. E., and Bates, T. F., 1951, Privately circulated report. See Weaver, C. E., 1953, A classification of the 2:1 clay minerals: Am. Mineralogist, v. 38, pp. 698-706.

White, J. L., 1951, Transformation of illite into montmorillonite: Soil Sci. Soc. America Proc. 1950, v. 15, pp. 129-133.

Weyl, W. A., 1949, Surface structure and surface properties of crystals and glasses: Am. Ceramic Soc. Jour., v. 32, p. 367.