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:

Sedletsjik, I. D., Koloidno-Dispersnaja Mineralogia, Moscow, 1945.
Garcia Vicente, Jose, Estructura Cristalina de los Mina­rales de la Arcilla, Madrid, 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. At present it seems necessary to distinguish between randomly mixed and regularly mixed layer structures, 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 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- 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 (Caillére, 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 serpentinite minerals) but in others where continuous or largely continuous composition ranges exist, (e.g. the montmorillonite-bidellite series, the chlorites) boundary lines must be drawn in a largely arbitrary manner.

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.

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.
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 "10A" and "14A" 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 (Frodel 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-
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 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 \((006)\) 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

\[
\frac{c_0}{n} \text{ for orthogonal axes,}
\]

\[
\frac{c_0}{n} \left( \sin \beta \right) \text{ for monoclinic axes,}
\]

and

\[
\frac{c_0(1 - \cos \alpha - \cos \beta)^{1/3}}{n} \text{ for triclinic axes with} \quad \alpha \neq 90^\circ, \beta \neq 90^\circ, \text{ and } \gamma = 90^\circ.
\]

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 \( \beta \)-tridymite and \( \beta \)-eristobalite with those in gibbsite, \( \text{Al(OH)}_3 \), and brucite, \( \text{Mg(OH)}_2 \). 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, 1.62\( \AA \), found in many silicates. This leads to a value \( b_0 = 9.16 \AA \) for a hexagonal layer of regular Si-O tetrahedra, and when this is compared with the data for \( \text{Al(OH)}_3 \) and \( \text{Mg(OH)}_2 \) (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 network, 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, Sörn and Kennard, 1949) have considered the effect of random substitution of Al for Si in feldspars and have concluded that the mean \((\text{Si,Al})-O\) distance increases by about 0.02\( \AA \) for each Si replaced by Al in a group of four. This would give a corresponding increase in \( b_0 \) of 0.12\( \AA \). Brindley and MacEwan (1958) have therefore taken the \( b_0 \) parameter of a tetrahedral network of composition \((\text{Si}_{1-x}\text{Al}_x\text{O}_{10})\) to be

\[
b_0 = T + 0.12x
\]

where \( T \) is likely to be about 9.1-9.2\( \AA \), the actual value being found from experimental data.
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 9.16 Å which agrees exactly with Si-O = 1.62 Å. For trioctahedral structures, \( T = 9.00 \) Å.

Table 2. Lattice parameters in some layer minerals.

1. Octahedral layers.

<table>
<thead>
<tr>
<th>Cation radius</th>
<th>( b_0 ) parameter, Å.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃ gibbsite</td>
<td>Fe³⁺ = 0.67</td>
</tr>
<tr>
<td>bayerite</td>
<td>Fe⁺⁺ = 0.78</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
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2. Si-O Tetrahedral layers.

<table>
<thead>
<tr>
<th>b₀ parameter, Å.</th>
</tr>
</thead>
<tbody>
<tr>
<td>From hexagonal networks in ( \beta )-tridymite and ( \beta )-cristobalite</td>
</tr>
<tr>
<td>On basis of Si-O = 1.62</td>
</tr>
</tbody>
</table>

3. Comparison with Kaolinite and Chrysotile.

<table>
<thead>
<tr>
<th>( b_0 ), in Å</th>
<th>( b_0 ), in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O layer</td>
<td>9.16</td>
</tr>
<tr>
<td>Al-OH layer</td>
<td>8.65</td>
</tr>
<tr>
<td>Mean value</td>
<td>8.95</td>
</tr>
<tr>
<td>Observed value for kaolinite</td>
<td>8.93</td>
</tr>
<tr>
<td>Observed values for chrysotile</td>
<td>9.24, 9.18</td>
</tr>
</tbody>
</table>

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**

\[ b_0 = 8.90 + 0.06x + 0.09g + 0.18r + 0.27s \]

**Trioctahedral minerals**

\[ b_0 = 9.18 + 0.06x - 0.12p - 0.06g + 0.06s \]

where:

- \( x = \) no. of Al for Si substitutions when the formula is expressed in the form \((Si_{4-x}Al_x)O_{19}\)
- \( p = \) no. of Al atoms
- \( q = \) no. of Fe³⁺ atoms
- \( r = \) no. of Mg atoms
- \( s = \) no. of Fe⁺⁺⁺ 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 inter-layer cations. Generally the best agreement is found with minerals having no interlayer cations, such as the kaolinite-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 150 Å. (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...
Part I

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WATER LAYER

SILICATE LAYER

FIGURE 2. Diagram to illustrate (a) Bates' suggestion for the structure of a tube of hydrated halloysite, (b) Brindley's suggestion 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 silicate 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 $\text{Al}_2\text{(Si}_2\text{O}_4\text{)}\text{(OH)}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, and a lattice spacing in the range 7.2-7.5Å. The suggestion is made that on dehydration, the silicate layers (with the possible exception of the innermost layer) collapse by removal of the interlayer 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 halloysite the reverse is true. No evidence has yet been brought forward for the existence of a hydrated chrysotile analogous to hydrated halloysite.

Brief reference may also be made to a description by Onsager (1952) of a possible explanation of the peculiarities exhibited by the single crystal photographs of antigorite, which was found by Arija (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 kaolinite-like 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 principal kaolin minerals, kaolinite, dickite, nacrite, and halloysite, are now well understood and require little discussion. Their structural characteristics are summarized 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 intensities 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
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 \( nhk/3 \). 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 — 7.5\( \AA \) in dehydrated halloysite and 10\( \AA \) 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, Cadj, Hendricks, and Swerdlov (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.

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 Meldahl 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 containing two layers per unit cell (Gruner, 1932a).

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† See preceding footnote.
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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 (Oreel, Caillère, and Hénin, 1950). Hallimond (1951a) has expressed the opinion that the original material may have been reconstituted and that "it would not be surprising if...the original chamosite turned out to be bavellite", which is a well authenticated bavellite. Taylor (1951) 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:

\[(\text{Fe}^{2+}_{1.7}\text{Mg}_{0.41}\text{Al}_{0.52}\text{Fe}^{3+}_{0.30})(\text{Si}_{1.46}\text{Al}_{0.60}\text{O}_{2})\text{(OH)}_{4}\]

The mineral is therefore trioctahedral and mainly ferrous. The mineral greenalite, the formula of which may be written approximately as

\[(\text{Fe}^{2+}_{2.2}\text{Fe}^{3+}_{0.5})(\text{Si}_{3}\text{O}_{8})\text{(OH)}_{4},\]

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, 3Al and 3A1 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 1/3. (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 (SiAlO₃); minerals nearer the Al corner would have more Al than Si in the tetrahedral layer. It is difficult, however, to understand why ferrous 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 10A and 14A 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 MgCl₂, 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 MgCl₂ 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 10A to 14A 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
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 4. Lattice spacings of, and numbers of water layers in montmorillonite and vermiculite with different interlayer cations.

<table>
<thead>
<tr>
<th>Ions</th>
<th>H⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Li⁺</th>
<th>Ba²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>NH₄⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius, r, Å</td>
<td>0.26</td>
<td>0.65</td>
<td>0.99</td>
<td>0.90</td>
<td>1.35</td>
<td>0.95</td>
<td>1.33</td>
<td>1.48</td>
<td>1.48</td>
<td>1.69</td>
</tr>
<tr>
<td>n/Å</td>
<td>3.3</td>
<td>3.08</td>
<td>2.02</td>
<td>1.67</td>
<td>1.48</td>
<td>1.45</td>
<td>0.75</td>
<td>0.68</td>
<td>0.68</td>
<td>0.36</td>
</tr>
</tbody>
</table>

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

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 processes 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 Alli (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 characterized more or less 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 dehydra-
tion of a structure often leads directly to recrystal-
lization, with a structural reorganization. Investiga-
tions tend to show that when blocks or units of structure of an old phase can be directly built into a new phase, the transforma-
tion 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 informa-
tion is obtained of the orientation relations of the phas-es (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 dis-
cussed generally a number of transformations of this type.

Dehydration and Recrystallization of Kaolin Minerals. Space does not permit a detailed discussion of recrystal-
lization phenomena generally in layer silicates, but reference may be made to the dehydration and recrystal-
lization of the kaolin structure. The practical importance of the changes in kaolinite has stimulated many investi-
gations (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 asserted, but the details seem to lack precision and different workers have emphatically maintained different points of view as regards the details. Bradly and Hunter (1952) have attempted to obtain further infor-
mation 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 Knorringer, Bradly, 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 prefer-
ential orientation. It still remains to work out the de-
tails 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 ob-
served with an electron microscope and obtained evidence of the development of mullite crystals which have particular orientations with respect to kaolinite crystals.

Oxidation Processes—Chamosite. Oxidation processes have not been studied to any large extent from a struc-
tural 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:

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \]
\[ e^- + (\text{OH})^- \rightarrow O^- + H \]
\[ 2H + O \text{ (atmospheric)} \rightarrow H_2O \]

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:

\[ 4\text{Fe}^{2+} + 4(\text{OH})^- + O_2 \text{ (atmospheric)} \rightarrow 4\text{Fe}^{3+} + 4O^- + 2H_2O \]

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**, 0.83A; Fe***, 0.67A. That atmos-
pheric oxygen plays an important part in the process is proved by the fact that in vacuo or in an inert atmos-
phere 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:

\[ 2(\text{OH})^- = \text{H}_2\text{O} + O^- \]

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\(_4\)) 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 beha-
viour of chamosite with that of kaolinite and to sup-
pose 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\(_4\)) ions as water may be related to their

* Further work by Brindly and Hunter has shown that γ-alumina occurs as a transient phase, and it appears to be orientated 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 such a case, that of 
chlorosilicate, we have clear evidence for such a conclusion.

Dissolution of Chlorites in Acids. Another example of 
chemical reactivity being related to structural en-
vironment has been obtained by Brindley and Youell
(1951) from a study of the acid attack on chlorites. It
was found, that ions such as \( \text{Mg}_2\text{Fe}^{3+} \) occupying octa-
edral positions in the structure, were removed at the same 
rate when the amount dissolved was expressed as a frac-
tion of the total amount of each ion. \( \text{Al} \) was found to be 
removed differently, however, and this was correlated
with the fact that \( \text{Al} \) occupies both tetrahedral and octa-
edral positions in the lattice structure. Octahedral \( \text{Al} \)
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 \( \text{Al} \) were separately deter-
mined by a purely chemical method for the first time.

The results were found to be in agreement with the
allocation of \( \text{Al} \) to the two kinds of lattice positions from
structural considerations and provided an experimental
proof for the customary procedure. What is more im-
portant in the present context is that, here again, there
is evidence for chemical reactivity being related to struc-
tural 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 moder-
ately detailed lines, but it is still growing and is likely
to outgrow any classification which is too rigid in frame-
work. It is hoped that the scheme suggested will be suffi-
ciently 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 \( \text{OH}^- \) ions if one assumes that the excess water is pres-
ent in the form of \( \text{H}_2\text{O}^+ \) 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 \( \text{H}_2\text{O}^+ \) ions,
the analyses can be recalculated to show that there are two interlama-
cular cations per structural unit, in most cases, with \( \text{H}_2\text{O}^+ \) partly
replacing \( \text{K}^+ \).

This suggests that more micas than had been sup-
posed 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 im-
portant.

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 interpreted as arising from "parallel
fundamental fibrils—hexagonally packed in cross section". The
indicated diameters of the fibrils in various samples ranged from
180 to 250 \( \AA \). 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 \( \AA \) from
montmorillonite in certain circumstances. Norrish, working in our
laboratory, has obtained spacings between 35 and 100 \( \AA \).

Stephen and I have obtained a material which we think is a
type of hydrated chlorite and therefore half-way between mont-
morillonite and chlorite. It is a mixture of both swelling and non-
swelling chloritic material. This material gives about 25 \( \AA \) and 22 \( \AA \)
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 \( \AA \) and 24 \( \AA \). The spacings do not
necessarily follow in a rational series.

G. W. Brindley:

I think it is becoming increasingly important to extend measure-
ments into the region of long spacings. In some of the early
chlorite measurements the longest spacing recorded was around
7 \( \AA \) and the 14 \( \AA \) "reflection" was missed, and in some of the
earliest kaolin measurements the 7 \( \AA \) reflection was similarly
looked. Several recent investigations tend to show that spacings
longer than 14 or 18 \( \AA \) do occur in nature. There is the work of
Brindley (1950) on rectorite, which consists of a fairly regular
succession of pyrophyllite and vermiculite layers with a periodicity
of about 25 \( \AA \). There has also been a recent publication (Alexanian
and Wey 1951) in which spacings of the order of 32 \( \AA \) are re-
corded from well-oriented montmorillonites. Long spacings of
the order of 22.5 \( \AA \) have also been recorded from a mica-like min-
eral which has been called allevardite by Calibre 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, 14, and about 14 \( \AA \) do occur, and it becomes increas-
ingly 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 dis-
tribution of intensity in the white radiation that can be very
confusing. We had such an experience in our laboratory. To de-
termine 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
\( \AA \) 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 \( \sin \theta \), then we probably have a disordered or partially dis-
ordered 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 \( \AA \) but also a ring at twice
dimension ranging from 26 to 30 \( \AA \). 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 indi-
cator will show that at a certain temperature there is a pro-
ounced release of atomic oxygen. This release causes a complete
change in the reactivity of the system and explains many of the
phenomena.

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