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The Structures of Trioctahedral Kaolin-Type Silicates

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From an examination of the known, fully ordered structures of trioctahedral, kaolin-type silicates,
four rules are obtained which govern the way in which the layers forming the structures are stacked
together. All the possible structures which may be formed in conformity with these rules are then
derived. A consideration of the nature of the rules shows that the polymorphism in these silicates
is unlikely to be caused by random slip occurring during the early stages of crystal formation,
followed by growth around a screw dislocation.

Recent work on cronstedtite by Steadman & Nuttall (1963, 1964) has revealed eight structures of this mineral which differ from each other principally in the way in which the trioctahedral kaolin-type layers are stacked together. Polymorphism of this kind had been known previously in other minerals of this class, such as amesite and chrysotile, but these did not show such an extent of structural variety.

The present work was undertaken as an attempt to discover general principles underlying all these ordered structures, in the hope that knowledge of this kind would assist in the discovery of further structures, and, more important, would lead to an understanding of the way in which the minerals are

Fig. 1. The trioctahedral kaolin-type layer. The unit of structure referred to in the text is shown bounded by *a* and *b* axes, of which the *a* axis is the shorter. The smaller open circles are hydroxyl groups. The larger ones at the base of the layer are oxygen atoms, and those within the layer may be oxygen or hydroxyl.

formed. The first purpose has already been fulfilled, and details are given in an appendix.

The trioctahedral layer

The ideal structure of this layer is shown in Fig. 1. No attempt has been made to show there the departures from regularity which real layers invariably possess, since these vary from one polymorph to another. This paper will not be concerned with detailed variations of the composition or geometry of the layer, but it may be that such details do influence the structures decisively; Newnham (1961), for example, has shown how the structures of the dioctahedral minerals kaolinite and dickite appear to be determined very largely by the distortion of the layers.

The octahedral part of each layer will be referred to as being above the tetrahedral part.

Interlayer relationships

In all known structures, the layers fit together in such a manner that the oxygen atoms of one layer and the hydroxyl groups of the layer below are related in ways similar to those shown in Fig. 2(*a*) and (*b*). These again are ideal positions. The distinction is made there between the structures in which oxygen atoms fall (*a*) in triangles of hydroxyl groups which have no cation beneath them and (*b*) in triangles which do have cations beneath them. The relationships of (*a*) and (*b*) (Fig. 2) will be referred to as α and β respectively.

In the derivation of the possible structures which may exist, the structures will be regarded as being formed by stacking layers together, each layer suffer-
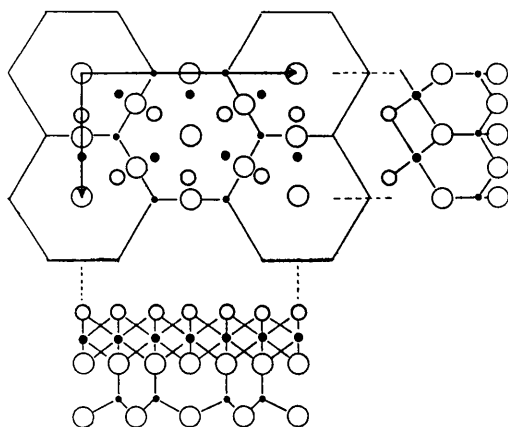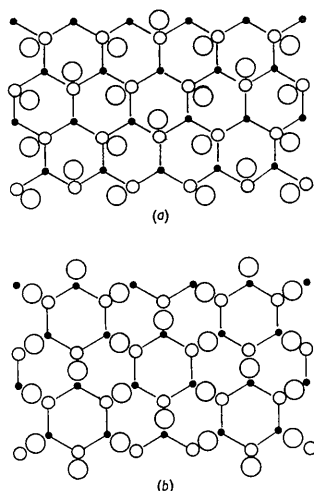
(a)

(b)

Fig. 2. Interlayer O–OH relationships. The smaller open circles are hydroxyl groups of the lower layer, and the solid circles are cations lying below them at the centres of the octahedra of which they form part. The larger circles are the basal oxygen atoms of the upper layer. The hexagonal net of octahedral bonds which is shown in this diagram is not to be confused with the net of tetrahedral bonds in Fig. 1.

Fig. 3. The displacements which may occur between successive layers.

ing a displacement or rotation (either of which may be zero) with respect to the layer beneath it. The stacking vectors which describe the permissible displacements are

$$\mathbf{s}_{\alpha 1} = -\tfrac{1}{3}\mathbf{a} \qquad\quad +\mathbf{e}$$
$$\mathbf{s}_{\alpha 2} = \tfrac{1}{6}\mathbf{a} - \tfrac{1}{6}\mathbf{b} + \mathbf{e}$$
$$\mathbf{s}_{\alpha 3} = \tfrac{1}{6}\mathbf{a} + \tfrac{1}{6}\mathbf{b} + \mathbf{e}$$
$$\mathbf{s}_{\beta 0} = \qquad\qquad\quad \mathbf{e}$$
$$\mathbf{s}_{\beta 1} = \qquad\quad \tfrac{1}{3}\mathbf{b} + \mathbf{e}$$
$$\mathbf{s}_{\beta 2} = \qquad -\tfrac{1}{3}\mathbf{b} + \mathbf{e} \,,$$

where $\mathbf{a}$ and $\mathbf{b}$ are the translations of the axes shown in Fig. 1, and $\mathbf{e}$ is a vector perpendicular to the layer and of magnitude equal to the thickness of it. The notation used here is that developed by Dornberger-Schiff (1956). The subscript letters α and β are intended to show whether the α or β relationship between oxygen atoms and hydroxyl groups is produced as a result of the displacement. Fig. 3, which has the same orientation as Fig. 1, shows the projection of these displacements (with the exception of $\mathbf{s}_{\beta 0}$) in the ab plane. The directions of these displacements are fixed in relation to the layer of Fig. 1, and if this layer, in being placed in position, is rotated, they rotate with it. The displacements of any layer are considered in relation to the layer on which it is being placed, and not to directions which are fixed by the lowest layer of the structure.

The only rotation, apart from zero, which it is necessary to consider is one of 180° (or 60°) about the centre of one of the hexagons in Fig. 1.

It is possible for other rotations about other centres to take place and still maintain the correct interlayer relationship, but they are all equivalent to some
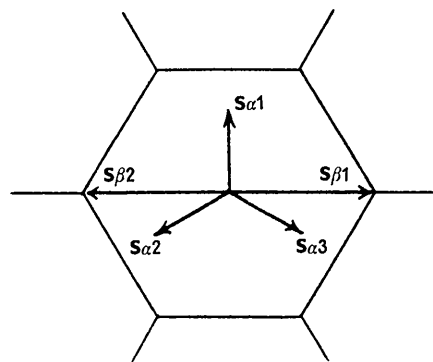
combination of the displacements and the rotation already described. Similarly, other displacements, in addition to those of Fig. 3, are possible, but they are equivalent to the ones shown.

A distinction has been made between displacements $\mathbf{s}_{\beta 1}$ and $\mathbf{s}_{\beta 2}$ because, though they produce the same relationship between the oxygens of one layer and the octahedra of the layer beneath, they produce different relationships between other parts of the layers. In fact, two layers related by a displacement of $\mathbf{s}_{\beta 1}$ form the mirror image of a pair related by $\mathbf{s}_{\beta 2}$.

The necessity for the three displacements $\mathbf{s}_{\alpha 1}$, $\mathbf{s}_{\alpha 2}$ and $\mathbf{s}_{\alpha 3}$ arises for a different reason. If one layer is laid down, and a second is placed on it with one of the $\mathbf{s}_\alpha$ displacements, it is immaterial which displacement is chosen, since, unlike the $\mathbf{s}_\beta$ displacements, the three produce the same interlayer relationship, with only a difference of orientation. But when a third layer is placed on the second, again with an $\mathbf{s}_\alpha$ displacement, the relation between third and first layers does depend on the choice of $\mathbf{s}_{\alpha 1}$, $\mathbf{s}_{\alpha 2}$ or $\mathbf{s}_{\alpha 3}$; two of them will produce enantiomorphous structures, and the other will produce a completely different structure. This complication, in which displacements are equivalent when considered with respect to the previous layer, but not to the last but one, does not arise with $\mathbf{s}_\beta$ displacements.

Structure formation

If no restrictions govern the relationships between successive layers in a structure, the number of structures which may be formed is infinite. There is at present no *a priori* justification for supposing that restrictions apply, but it may be suspected that they do, since only eight or nine structures have been found in about 200 crystals of cronstedtite from nine localities.

Zvyagin (1962), in considering the dioctahedral kaolin-type silicates, assumed that 'the relative positions of every pair of layers will be identical throughout the structure, and that a transition from the first to the second layer will be equivalent to that from the second to the third'. This condition

does not apply to at least one cronstedtite structure, though this may depend upon the interpretation of it, and will not be applied here. The work of Oughton (1957) on amesite was less general, and applied only to structures which had a two-layer repeat and in which every layer was rotated with respect to its neighbours. Newnham (1961), too, only considered two-layer structures.

The four conditions to be applied in the present work, in the derivation of the possible structures, have been obtained by the empirical method of examining the known polymorphs and finding generalizations which can be made concerning their structures. These will be stated now, and the structures from which they were obtained will be given later.

Rule 1

If a certain operation P, which relates one layer to the next, is followed by an operation Q at the next boundary, then whenever P occurs, Q follows. (P and Q are combinations of displacement and rotation).

Rule 2

Displacements of types s_α and s_β never occur together in the same structure.

Rule 3

Displacements of type s_α are never accompanied by rotation.

Rule 4

Rotation occurs either at all interlayer boundaries or at none.

Table 1. *Permissible sequences of operations*

Structure number	Sequence of operations	Space group
1	$s_{\beta 0}$	$P31m$
2	$s_{\beta 1}$	$R3$
3	$s_{\beta 2}$	$R3$
4	$s_{\beta 0}s_{\beta 1}$	$R3$
5	$s_{\beta 0}s_{\beta 2}$	$R3$
6	$s_{\beta 0}s_{\beta 1}s_{\beta 2}$	$P3$
7	$s_{\beta 0}s_{\beta 2}s_{\beta 1}$	$P3$
8	$s_{\beta 1}s_{\beta 2}$	$P31c$
9	$s_{\beta 0}(R)$	$P6_3cm$
10	$s_{\beta 1}(R)$	$P6_3$
11	$s_{\beta 2}(R)$	$P6_3$
12	$s_{\beta 0}(R)s_{\beta 1}(R)$	$R3$
13	$s_{\beta 0}(R)s_{\beta 2}(R)$	$R3$
14	$s_{\beta 0}(R)s_{\beta 1}(R)s_{\beta 2}(R)$	$P6_3$
15	$s_{\beta 0}(R)s_{\beta 2}(R)s_{\beta 1}(R)$	$P6_3$
16	$s_{\beta 1}(R)s_{\beta 2}(R)$	$R3c$
17	$s_{\alpha 1}$	Cm
18	$s_{\alpha 1}s_{\alpha 2}$	Cc
19	$s_{\alpha 1}s_{\alpha 2}s_{\alpha 3}$	$P3_1$
20	$s_{\alpha 1}s_{\alpha 3}s_{\alpha 2}$	$P3_2$

The sequences of operations which can be carried out without breaking these rules are given in Table 1. The symbols have the meaning given earlier and in Fig. 3. The letter R in parenthesis means that a rotation accompanies the displacement just preceding the R. Pairs of sequences which form enantiomorphous structures are bracketed together.

The structures are shown diagrammatically in Fig. 4. For this purpose, a unit of the layer has been chosen with the axes shown in Fig. 1, and the structures 1–16 are shown projected along the a direction. It is convenient to use this unit even though the layer and most of the structures have trigonal or hexagonal
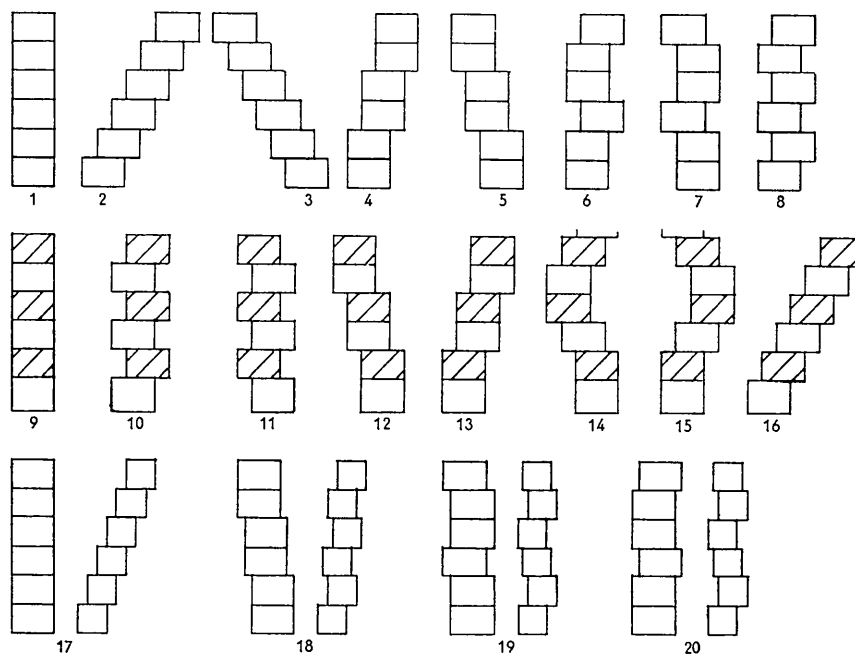

Fig. 4. The possible structures. Structures 1–16 are shown in projection along the a axis of Fig. 1, with the b axis pointing to the right. All shifts are of $\pm b/3$. For structures 17–20, the left-hand diagram is the projection along the a axis, and the other is the projection along the b axis with the a axis pointing to the left. In projection, the shifts are $\pm b/6$, $-a/3$ and $+a/6$.

symmetry. The units shown shaded in structures 9–16 have been rotated 180°. Each of the structures 17–20, in which s_α-displacements occur, is shown in projection along a and b, the former being on the left in all cases.

Discussion

The structures found in cronstedtite as isolated crystals are 1, 9, (10, 11), (12, 13), (19, 20), and those found only in component parts of a composite crystal, related as if by a twin law to components with one of the structures of the first-named set, are

8	with	1
(14, 15)	with	(10, 11)
17 and 18	with	(19, 20)

Also, 10 is frequently found in a similar relationship with (12, 13).

Amesite possesses the structures 9, (10, 11) and (12, 13).

The various forms of chrysotile cannot usefully be considered, because of their high degree of disorder, but clino-chrysotile can be regarded as structure 1, and ortho-chrysotile as 9, both with complete randomness introduced in the b direction.

The structures can be grouped in three categories, 1 to 8, 9 to 16 and 17 to 20, not only according to structure, but to diffraction effects, since all the members of each group give certain intense reflexions which are identical or almost identical. (For the hexagonal structures they are those with $h-k=3n$.) In the third group, all members have been found (making no distinction between members of an enantiomorphous pair), but only 19 as isolated crystals. In the second group, all but 16 have been found, much the commonest being 9 and 10. However, members of the first group are scarce; 1 itself is quite common, but 8 has been seen once only.

One cronstedtite structure found by Frondel (1962) does not appear in the list of possible structures given here. It is reported as being rhombohedral, with nine layers in the unit cell. The structure has not been determined.

The fact that the known structures obey the four rules, in particular rule 1, carries an important implication. This is that the position and orientation of a layer on its neighbour depends upon the next-nearest neighbour. This would not be physically reasonable if the variety of polymorphs had been created by random slip occurring during the early stages of growth, with the consequent creation of screw dislocations, as has been suggested for the polymorphs of cadmium iodide.

The rules formulated above are relevant to the problem of the disorder which is commonly present in crystals of this class of mineral. The presence of disorder appears to show that a layer may be placed indifferently in one of several positions on its neighbour, yet if this were the case, it would not be expected that the polymorphism would obey the rather stringent rules. More remarkable is the fact that the disorder itself obeys rule 2. If this rule were to be relaxed, and displacements of $s_{\beta 0}$ and s_α-type were found randomly in a structure, all reflexions would suffer the kind of streaking which is in practice always confined to a certain class.

APPENDIX

Many crystals of cronstedtite have been found which give reflexions that can be indexed on a hexagonal unit cell containing six layers. Reflexions with $h-k \neq 3n$ are present for all values of l, but it is clear that several composite crystals, each giving reflexions with a limited sequence of l-values, are responsible for the complete series. It has been assumed previously (Steadman & Nuttall, 1963) that the reflexions could be accounted for by two crystals of structure 12 and one of 10.

However, the structure 14 would give reflexions of series hkl with $h-k=3n$ and $l \neq 3n$, and this, together with one crystal of structure 10, would give a complete series. Examination of the $10l$ series for many crystals has revealed one which, because of very slight misalignment of the components, shows the reflexions which structure 14 would give, separated from the rest. No measurement of intensities could be made. It is almost certain that structure 14 is present in this case, but the earlier explanation may apply to most crystals of this type.

The reflexions of structure 14 could not have been picked out from the confusion of other reflexions without knowing the possible structures and making a search for the expected series.

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