

Further consideration of the crystal structure of kaolinite.

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Summary. The layer structure of the kaolin mineral dickite has been shown to differ significantly from the idealized arrangement of regular tetrahedra and octahedra. Since the structure of kaolinite can be studied only by X-ray powder methods, it cannot be refined beyond the idealized arrangement. By applying the dickite type of layer structure to the case of kaolinite, an explanation for the triclinic symmetry of kaolinite has been obtained, and also an improved agreement with the observed X-ray intensities.

A DETAILED structure analysis of kaolinite was first attempted by Gruner (1932), based on X-ray powder diagrams of the mineral. He concluded that the unit cell was monoclinic, with probable space group C_2^4-Cc , and contained two structural layers related by a c -glide plane. However, further examination of powder diagrams of various kaolinites by Brindley and Robinson (1946) revealed that there were reflections that could not be explained in terms of this monoclinic cell, and they put forward a triclinic cell containing only one structural layer. So far, it has been proved that this triclinic cell fits very well with the observed features of the X-ray powder patterns of the mineral as regards both spacings and intensities of reflections.

The structure of the composite layer of Si-O and Al-OH was assumed to have the geometrically idealized arrangement first proposed by Pauling (1930). At that time, there were no means to establish a refined structure for the layer itself in the absence of suitable single crystals. In terms of this idealized layer, it is impossible to account in the actual structure of kaolinite for the α -angle and for a small departure of the β -angle from an idealized displacement of $-a/3$.

Recently, Newnham and Brindley (1956, 1957) have made a detailed analysis of the mineral dickite, a polymorphic form of kaolinite, and have shown that the actual layer structure is distorted to some extent from the idealized arrangement. This has opened the way to an interpretation of the triclinic nature of kaolinite, since there are good reasons for thinking that the structures of the layers in dickite and kaolinite

are very nearly the same. The unit-cell parameters (see table I), X-ray basal reflections, chemical compositions, infra-red spectrograms, and other data for the two minerals are almost identical.

TABLE I. Comparisons of lattice parameters of kaolinite and dickite.

| | <i>Kaolinite</i> | | <i>Dickite</i> | |
|--|----------------------------------|--------------------|---------------------------------------|-----------------------|
| | Brindley and Robinson (1946). | Newnham (1956). | Newnham and Brindley (1956, 1957). | |
| <i>a</i> | 5.15 Å. | 5.139 ± 0.014 Å. | <i>a</i> | 5.149 ± 0.003 Å. |
| <i>b</i> | 8.95 | 8.932 ± 0.016 | <i>b</i> | 8.949 ± 0.005 |
| <i>c</i> | 7.39 | 7.371 ± 0.019 | <i>c</i> | 14.419 ± 0.007 |
| α | 91.8° | 91.6° ± 0.2° | β | 96.80° ± 0.07° |
| β | 104.5-105° | 104.8° ± 0.2° | | |
| γ | 90° | 89.9° ± 0.1° | | |
| $d(001) = c(1 - \cos^2\alpha - \cos^2\beta)^{\frac{1}{2}} = 7.15 \text{ \AA.}$ | | | $d(001)/2 = c(\sin\beta)/2$ | $= 7.16 \text{ \AA.}$ |

The present paper describes further consideration of the triclinic structure of kaolinite based on the layer structure of dickite.

A discussion of the kaolinite structure in relation to the general features of the dickite layer.

The outstanding features of the structure of the dickite layer lie in the rotations of both tetrahedra and octahedra of the composite hexagonal network (Newnham and Brindley, 1956, figs. 3*a*, 3*b*). In an idealized layer of Si-O tetrahedra, if the Si-O and O-O distances are assumed to be 1.62 Å. and 2.65 Å. respectively, the regular tetrahedral network has *a* 5.30 and *b* 9.17 Å. which do not fit with the unit cell dimensions of the kaolin minerals as shown in fig. 1*a*. To fit these dimensions with those of the kaolin minerals, it is necessary to rotate each tetrahedron parallel to the layer in such a manner that the neighbouring tetrahedra rotate in opposite directions, as shown in fig. 1*b*. Such rotations have been found in the actual structure of the dickite layer. The angle of rotation is about 8° in the dickite layer, which agrees fairly well with an idealized rotation of 10° to produce the actual cell dimensions of the kaolin minerals.

So far, a rotation of octahedra in the network of Al-OH has been found in the structure of gibbsite (Megaw, 1934). The polarization of the hydroxyl ions is affected by the high polarizing power of aluminium ions to such an extent as to form hydroxyl bondings between neighbouring hydroxyl ions, resulting in a distortion of the OH-layer from an idealized arrangement. In the dickite structure this sort of distortion has again been found together with a slight expansion of the layer dimensions to fit with those of the Si-O tetrahedral layer. In an actual layer of dickite

the rotation of triangles composed of three hydroxyl ions in the outermost layer is about 3° , while the rotation of these ions in the middle layer is 8° in the opposite direction. These rotations result in a shortening of shared edges of octahedra in accordance with Pauling's rules. Furthermore, as compared with the idealized structural layer, the net result of

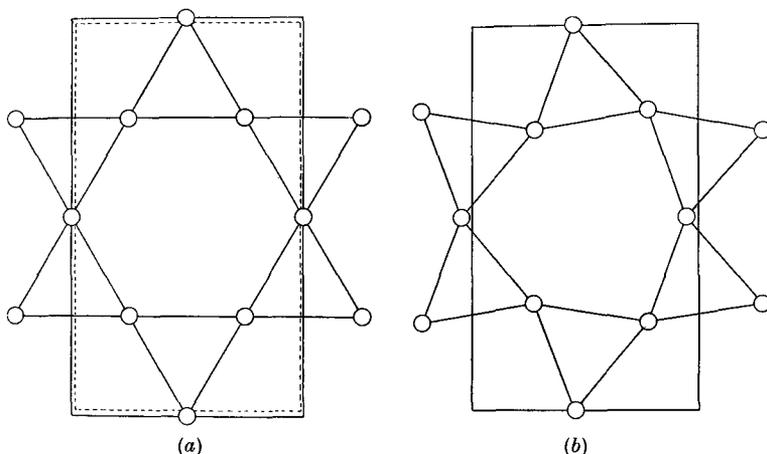


FIG. 1. *a.* Projection on (001) of an idealized silica layer. Dotted lines show the unit-cell dimensions of kaolinite. *b.* Projection on (001) of a silica layer with the tetrahedra rotated to fit the unit-cell dimensions of kaolinite. (Only the oxygen atoms are shown.)

these rotations is a change of the mutual positions of the outermost oxygen and hydroxyl sheets of atoms with regard to the *a*- and *b*-directions.

It can be supposed that the departure of the actual layer from the geometrically idealized arrangement arises from the interactions between ions in side the structural layer, while the stacking of successive layers will be defined mainly by interactions of oxygen ions of one layer with the hydroxyl ions of the adjacent layer which form hydroxyl bondings with each other. If we assume the hydroxyl bonds to be equally distributed, then the distortion of the kaolin layer modifies the displacement of one structural layer with respect to the adjacent layer along both *a*- and *b*-directions. These displacements are shown in figs. 2*a* and 2*b*.

Fig. 2*a* shows the relation between two adjacent kaolinite layers having the idealized structure displaced so that the hydroxyl bonds are all equal. The layer displacement is $-a/3$ and the β angle is 103.5° .

On the other hand, in fig. 2*b* in which a dickite-type layer is used, the equal distribution of OH-O bonds results in the α - and β -angles of kaolinite being 91.4° and 104.1° respectively which are compatible with the observed values, 91.6° for α and 104.8° for β . In the structure of dickite itself, the displacements along *b* are cancelled out throughout the whole crystal, owing to the overall monoclinic symmetry resulting from the two layers in the cell.

It is of interest also to consider the bearing of the dickite-type layer structure on the various layer sequences that have been shown to be possible for the idealized layer (Brindley, 1951). On the basis of equal OH-O bonds between the layers, many stacking sequences appear to be equally probable. The simplest arrangement is an orthogonal one that yields exactly the same distribution of OH-O bonds as is depicted in

TABLE II. Comparisons between calculated and observed X-ray intensities for kaolinite.

| Indices | Calculated | | | Observed | |
|---------|------------|-----|------|----------|-----|
| | I. | II. | III. | IV. | V. |
| (020) | 69 | 75 | 104 | 13 | m- |
| (110) | 200 | 205 | 224 | 27 | m |
| (110) | 20 | 7 | 2 | — | — |
| (111) | 210 | 219 | 213 | 23 | m |
| (111) | 100 | 100 | 100 | 10 | w+ |
| (021) | 163 | 164 | 108 | 9 | w-m |
| (021) | 85 | 50 | 51 | 4 | w |
| (130) | 27 | 32 | 42 | 10 | ms |
| (201) | 26 | 34 | 38 | | |
| (130) | 47 | 34 | 20 | | |
| (131) | 54 | 61 | 59 | 6 | w-m |
| (112) | 41 | 13 | 30 | | |
| (131) | 67 | 73 | 78 | 13 | s |
| (200) | 64 | 84 | 69 | | |
| (112) | 15 | 12 | 14 | | |
| (202) | 187 | 102 | 90 | 20 | vs |
| (131) | 193 | 116 | 85 | | |
| (113) | 28 | 19 | 10 | 11 | s |
| (131) | 190 | 121 | 98 | | |

Cols. I, II, and III give calculated values of $F^2 \Phi(\theta)$, where $\Phi(\theta)$ is the polarization and Lorentz factor. For reflections with $k = 3n$, the line (130), (201), (130) is taken as a standard; with $k \neq 3n$, (111) is taken as a standard.

Col. I is for Brindley and Robinson's structure based on the idealized layer, col. II for the structure based on the dickite-type layer, and col. III for a trial structure based on a somewhat more distorted layer than that in dickite.

Col. IV gives averaged observed X-ray diffractometer data for well-crystallized kaolinites, and col. V gives the qualitative intensities listed by Brindley and Robinson (1946).

fig. 2 *a*. When the dickite-type layer is used the distribution illustrated in fig. 3 is obtained, and it is evident by comparing figs. 2 *b* and 3 that, for a given value of $d(001)$, the arrangement 2 *b* leads to the shorter OH-O bonds. This kind of argument brings one to the point where it is easy to see that different stacking arrangements may lead to secondary variations in the detailed structure of the layers and in the bonding between the layers. In the absence of suitable data for a precision determination of the structure of kaolinite, this line of argument cannot be pursued further for the time being.

In table II, calculations of intensities for kaolinite based on this dickite-type layer are shown along with those for the Brindley-Robinson structure. The agreement with the observed values is somewhat improved as compared with the earlier calculations. A little more improvement may be possible by distorting the layer further (see table II, col. III), but in view of the small number of unique reflections available from X-ray powder diagrams it seems meaningless to attempt further refinement.

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