

Further Polymorphism in Cronstedtite

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(Received 4 June 1963)

The structures of four polymorphs of cronstedtite, $(\text{Fe}^{\text{II}})_3(\text{Fe}^{\text{III}}\text{Si})\text{O}_4(\text{OH})_5$, with space groups $P6_3$, $P31c$, Cc and Cm have been determined, bringing the total number of known structures of this mineral to eight. Of these four, only the first has been found as isolated crystals. The structure with space group $P31c$ was found twinned with 1-layer cronstedtite of space group $P31m$. The structures with space groups Cc and Cm may be regarded as being formed by the occurrence of regular mistakes in a more common form with space group $P3_1$ with which they were invariably twinned.

Introduction

In a recent paper the present authors (Steadman & Nuttall, 1963) described in detail the structures of four polymorphs of cronstedtite, and mentioned that X-ray evidence had been found for the existence of several others. The structures of the latter were not determined because they were invariably found twinned with one of the other four.

As far as could be ascertained, there were four undetermined structures to be found among the cronstedtite specimens available, and these have now been determined. Three of these have still only been found as twins, and the determinations have been carried out with them in that state; the remaining one has fortunately been found as isolated crystals.

It has not been possible to refine these structures to such a degree as to reveal any distortion within the kaolin-type layer, but the manner of stacking of the layers has been found.

In the case of the twinned crystals, the structure determinations have been described in more detail than usual, in order to show where other interpretations of the photographs are possible.

Cronstedtite structures which are mentioned in this paper but not fully described are discussed in detail in the earlier paper already referred to.

Experimental

Nearly all the necessary information was provided by oscillation photographs taken about an axis perpendicular to the cleavage plane of the crystals with $\text{Co } K\alpha$ radiation. Suitable crystals were readily found in all the specimens.

Structure determination

An assumption made in all the four determinations to be described is that the structures are composed of trioctahedral kaolin-type layers stacked together in the same sense with respect to an axis perpendicular

to the layers. This assumption has, with the extinction symbol, determined the choice of space group in all cases.

The structures will be referred to by their space groups. Previously, each cronstedtite polymorph has been referred to as n -layer, where n is the number of layers in the hexagonal unit cell, but this is ambiguous, now that the new forms have been found. The new method could, of course, lead to the same difficulties if more polymorphs were discovered.

The unit-cell dimensions are summarized in Table 1.

Table 1. *Unit-cell dimensions of cronstedtite polymorphs*

Space group	$P6_3$	$P31c$	Cc	Cm
a (Å)	5.49	5.49	5.49	5.49
b (Å)			9.51	9.51
c (Å)	14.17	14.17	14.29	7.32
β			$82^\circ 38'$	$104^\circ 31'$

Type $P6_3$

Crystals with this structure were most commonly found in specimen BM 31146, from Wheal Maudlin, Cornwall.

Reflexions were indexed in terms of a hexagonal unit cell, and the c dimension showed that the cell contained two cronstedtite layers. The extinction symbol was $P6_3^-$, and the only permissible space group which accommodates the layers is $P6_3$.

With this space group, two possible, enantiomorphous structures may be formed. One is obtained by operating on the layer shown in Fig. 1 with a 6_3 axis passing through P , the origin of the unit cell shown, and the other with it passing through Q .

This structure would give reflexions for the $h, h, 2\bar{h}, l$ zone with the same intensities as those of the structure with space group $P6_3cm$, and a direct comparison of photographs shows this to be the case. No detailed measurements have been made on general reflexions, since no refinement was intended, but sufficient

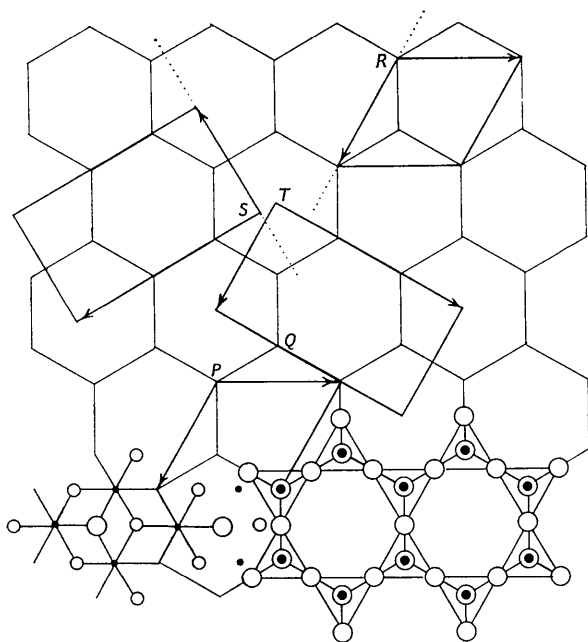


Fig. 1. The cronstedtite layer. For clarity, the tetrahedral part of the layer is shown only in the lower right corner, and the octahedral part which surmounts it in the lower left. The hexagonal pattern represents the rest of the layer. In the tetrahedra the solid circles are $\frac{1}{2}(\text{Fe} + \text{Si})$, and the circles concentric with them are OH ions at the apex above each of them. In the octahedra the black dots are Fe ions and the small open circles are OH. All other circles are oxygen atoms.

The origins of the unit cells of the four polymorphs are P ($P6_3$), R ($P31c$), S (Cc) and T (Cm). The a axes are the shorter ones in the non-hexagonal cells. The origin S is at a distance $b/12$ from T , the centre of the hexagon.

The dotted lines show the positions of one of the c -glide planes in structures with space groups $P31c$ and Cc .

checks have been made to confirm that the structure is essentially correct.

Type $P31c$

Only one crystal has been found which contains a region with this structure, and by far the greater part of the crystal was of 1-layer cronstedtite of space group $P31m$. The new structure was revealed on a rotation photograph, and unfortunately the crystal was heated for the purpose of investigating thermal transformations before the significance of certain extra reflexions was apparent.

The evidence for its existence was the presence of reflexions with $h-k \neq 3n$ which showed a 2-layer spacing in the c direction. Since the twins were perfectly aligned, it had to be assumed, to begin with, that the new structure gave all the reflexions given by $P31m$ and the extra ones in addition. The extinction symbol was then $P-c$, and the only space group corresponding to this which can accommodate two cronstedtite layers is $P31c$.

An investigation was made of the possibility that

the new structure may not in fact give all the reflexions of $P31m$, and also that the reflexions which it does give may show a higher Laue symmetry than those of $P31m$. Fortunately, even accepting these possibilities, the space group remains unambiguously $P31c$.

The only way in which the layers can be accommodated is by operating on the layer in Fig. 1 with the c -glide plane which is shown containing the a axis.

Type Cc

This structure and that of type Cm were revealed by faint reflexions on c -axis oscillation photographs of 3-layer cronstedtite of space group $P3_1$, taken from specimen BM 51868, from Wheal Jane, Cornwall. They did not occur twinned with any other form.

Faint extra reflexions were found on hkl rows with $h-k \neq 3n$, and certain reflexions from the $P3_1$ structure on these rows were unusually intense. It was assumed that a structure was present which, for this class of reflexion, gave only these extra reflexions and the enhanced ones, but not the rest of the reflexions from $P3_1$. It was also assumed that the rest of its reflexions coincided with those of the $P3_1$ structure for which $h-k=3n$ and were similar to them in intensity, since the spots on the photographs appeared to have the intensities to be expected from $P3_1$ alone.

The whole pattern produced by the new structure possessed Laue symmetry $2/m$, with the diad parallel to the cronstedtite layer. All reflexions were indexed in terms of a monoclinic cell (2nd setting) with the axes shown in Fig. 1, and an acute angle β equal to $\arccos a/3c$, the c axis extending through two layers. The extinction symbol was $C-c$, and the only possible space group is Cc .

The only way of forming the structure is by operating on the layer in Fig. 1 with the c -glide plane which is shown containing the a axis of the unit cell. This means that the layer to be placed above that in Fig. 1 is its reflexion across that plane, and is shifted relative to it a distance $+a/6$.

The structure gives reflexions in the positions expected. In particular, the reflexions which coincide with those of $P3_1$ for which $h-k=3n$ do have intensities which are either similar or identical with them. The reason for the similarity is that the atoms in the octahedral part of each layer, which form the greater part of the layer, have x and y coordinates which are simple fractions of the unit cell dimensions, and the difference between the $P3_1$ structure and the new one consists of displacements between the layers which are multiples of these fractions.

Type Cm

Some photographs of the $P3_1$ structure showed no extra spots on rows for which $h-k \neq 3n$, but did show systematic enhancements among these reflexions, and the pattern of enhancements was quite

different from the pattern of reflexions given by the Cc structure. It was assumed that a new structure was present which, for this class of reflexion, gave only those which were found to be enhanced, and, for the remainder, gave reflexions coinciding with the reflexions of $P3_1$ for which $h-k=3n$, and similar to them in intensity.

The reflexions showed monoclinic symmetry. The a and b axes (2nd setting) are shown in Fig. 1, and the obtuse angle β is equal to $\arccos(-a/3c)$, where the c axis extends through one layer only. The extinction symbol was $C---$, and the space group is therefore Cm .

To form the structure, each layer keeps the same orientation as the one below it, and is displaced with respect to it a distance $-a/3$, the axes of Fig. 1 being used.

The structure gives the expected reflexions, and, as in the case of the Cc structure, those which coincide with the reflexions of the $P3_1$ structure for which $h-k=3n$ have intensities which are either equal to them or nearly equal.

Discussion

The structures can most easily be described, and the relations between them appreciated, in terms of the displacements and rotations which occur between successive layers. The displacements are shown in Fig. 2, which has the same orientation as Fig. 1. The distinction between the displacements A and B has been made because they produce different relationships between adjacent layers. The difference lies in the relative positions of the basal oxygen atoms of one layer and the octahedral iron atoms of the layer beneath, and is described in detail in the earlier paper (Steadman & Nuttall, 1963).

The most interesting structures are Cc and Cm , since these can be regarded as mistakes in the 3-layer $P3_1$ structure. The $P3_1$ was formed by the repeated operation of the sequence of displacements A_1, A_2, A_3 . The structure Cc , though described earlier in terms of the operation of a glide plane, can be formed,

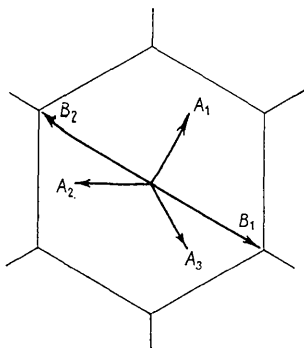


Fig. 2. Displacements between successive layers. The A displacements are of magnitude $a/3$, and the B of $b/3$, where a and b are the dimensions of the unit cells shown in Fig. 1.

starting with the layer in Fig. 1, by the sequence of displacements $A_2, A_1, A_2, A_1, \dots$. The Cm structure is even further from the 'correct' structure, in that all layers suffer the same displacement, and the sequence for Fig. 1 is A_1, A_1, A_1, \dots .

Support for the view that these are mistakes is provided by the fact that they have never been found as isolated crystals, but always as regions of a crystal with the $P3_1$ structure. The close relationship between these new structures and that of the polymorph with which they always occur is one reason for confidence in the correctness of the structures.

It would be interesting to know the exact situation of the mistake regions in the crystal, because this would throw light on the question of the growth mechanism of this and other kaolin-type silicates. It might be possible to postulate a dislocation mechanism for the generation of mistake structures within a crystal, but, until more is known, this could be misleading. There would certainly be no grounds for assuming, without further evidence, that the perfect structure and its mistakes are twinned on the cleavage plane.

The $P3_1c$ structure is formed by the alternating sequence $B_1, B_2, B_1, B_2, \dots$.

The structure $P6_3$ is formed by the repetition of the displacement B_1 , with respect to the layer immediately below, but always accompanied by a rotation of the layer by 60° (or 180°) about the centre of one of the hexagons in Fig. 1. Since this has been found in isolated crystals, it cannot be regarded as a mistake structure, although many crystals of 6-layer cronstedtite of space group $R3$ have been found which give reflexions which show the presence of two regions of structure $R3$, with different orientations, and a region of structure $P6_3$. Again, the precise relation between the twins is not known.

Now that so many polymorphs of this mineral are known, an attempt is being made to show how the structures which have been found to exist are related to the larger number of structures which it would be possible to form with trioctahedral silicate layers. One determination of the possible structures and their space groups has been made by Zvyagin (1962), but the results do not seem to be entirely satisfactory, because the space groups of five forms of cronstedtite ($P3_1m, P3_1c, P6_3, P6_3cm$ and $R3$) do not appear in the list.

We should like to thank Mr P. G. Embrey, of the British Museum, who has kindly provided us with samples of cronstedtite from every specimen which the museum possesses.

References

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