

The Crystal Structure of Astrophyllite

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The mineral astrophyllite, $(K, Na)_3(Fe, Mn)_7Ti_2Si_8(O, OH)_{31}$, is triclinic. The *A*-face-centred unit cell chosen has parameters $a = 5.36$, $b = 11.76$, $c = 21.08$ Å, $\alpha = 85^\circ 08'$, $\beta = 90^\circ 00'$, $\gamma = 103^\circ 13'$ and contains two formula units. The projection of the structure along the *x* axis has been determined from *OkI* data. The structure is closely related to that of biotite mica but contains octahedrally coordinated titanium in the 'tetrahedral' layer.

Introduction

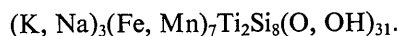
Astrophyllite is one of a large group of silicate minerals which occur as accessory or pegmatite minerals in alkaline igneous rocks. These minerals (for example ramsayite, lãvenite, narsarsukite) are characterized chemically by the presence of large amounts of sodium, titanium or zirconium and often manganese and the almost complete absence of aluminum and magnesium. They show a wide variety of crystal structures of types not found in the more common rock-forming minerals.

An independent determination of the structure of astrophyllite has been made by Пэн & Ма (1963) and shows the same basic units as found in this determination. A slight difference in chemical composition, however, has produced a different stacking arrangement and symmetry.

Experimental

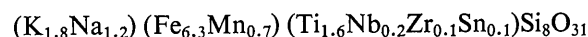
The specimen used for the structure determination came from El Paso County, Colorado, U.S.A. (Cambridge University collection no. TW 4085). Astrophyllite is triclinic, but in order to emphasize similarities with biotite and other layered silicates an *A*-face-centred cell was used instead of a primitive cell. The parameters of the face-centred cell, determined from Weissenberg photographs, are given in Table 1. A body-centred cell can also be chosen which has the parameters *a*, *c* and β in common with the *A*-face-centred cell and very similar values for *b* and γ .

Examination of sixteen published chemical analyses of astrophyllite indicated that the general formula is:



The face-centred cell contains two formula units. Some analyses showed partial replacement of titanium by zirconium, niobium, aluminum and iron. A continuous range of iron/(iron+manganese) ratios from 0.90 to 0.16 (koupleskite) was found. For the initial stages of the structure determination the formula was taken as: $K_3Fe_7Ti_2Si_8O_{31}$.

At a late stage in the refinement the specimen was analysed by chemical and X-ray fluorescence methods and gave the formula:



The contents of the titanium and potassium atom sites were adjusted accordingly before the final cycles of refinement.

Owing to the perfect (001) cleavage considerable difficulty was experienced in finding single crystals suitable for the collection of intensities with a Weissenberg camera. Good results were obtained for zero-layer photographs when crystals were rotated about the *x* axis (along which the crystals are usually elongated) but higher layers were less satisfactory. The reflexions were elongated along the festoons to form streaks, in reciprocal space, parallel to the b^* axis, indicative of structural disorder. However, as the repeat distance along the *x* axis is short (5.36 Å), it was decided to obtain the main features of the structure from a projection along this axis. Multiple-film technique was used with molybdenum $K\alpha$ radiation and intensities were measured by visual comparison with a fifteen-point scale. 241 *OkI* reflexions were recorded. In general, each reflexion occurred at a measurable intensity on three or four films and was measured twice on each half of the Weissenberg photograph.

When the intensities had been converted to structure amplitudes two statistical tests for centrosymmetry (Wilson, 1949; Howells, Phillips & Rogers, 1950) were made. These both indicated that the projection of the structure along the *x* axis was centrosymmetric.

Determination of the structure

The starting point for the postulation of a structure for astrophyllite was the close resemblance to biotite as shown in Table 1. Fig. 1 shows the projection along the *x* axis of the structure of biotite (*C2/c* polymorph). The atoms are arranged in layers parallel to the perfect (001) cleavage. The iron and magnesium atoms are in octahedral coordination with oxygen atoms and the octahedra share edges to form continuous sheets, to either side of which SiO_4 tetrahedra are attached. These tetrahedra share corners to form continuous sheets of

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six-membered rings. The slabs formed by the combination of one 'octahedral' and two 'tetrahedral' sheets are separated by layers of potassium atoms.

Table 1. Comparison of *astrophyllite* and *biotite*

Unit cell	Astrophyllite	Biotite
<i>a</i>	5.36 Å	5.3 Å
<i>b</i>	11.76	9.2
<i>c</i>	21.08	20.2
α	85°08'	90°
β	90 00	95
γ	103 13	90
Space group	$A\bar{1}$	$C2/c$
Cleavage	(001) perfect	(001) perfect
Unit-cell contents	$K_6Fe_{14}Ti_4Si_{16}O_{62}H_8$	$K_4Fe_{12}Si_{16}O_{48}H_8$

The perfect (001) cleavage suggested a layer structure for *astrophyllite*. The similarity of the chemical formula and the value of *c* to those of *biotite* indicated that the layers might closely resemble the *biotite* layers in composition and position (*i.e.* *z* coordinate). A one-dimensional Fourier synthesis of the electron density projected onto the *z* axis supported this view and implied that the titanium atoms were present in approximately the same (001) layers as the silicon atoms.

The *astrophyllite* and *biotite* cells show most differences in the parameters *b* and γ . The greater extension, parallel to the *y* axis, of the *astrophyllite* cell is matched by increased numbers of iron and potassium atoms in the cell and it was assumed that the sheets of these atoms were continuous. There are however the same number of silicon atoms per cell in both minerals and therefore continuous sheets of SiO_4 tetrahedra are not possible in *astrophyllite*. Investigation of the possible arrangements of the iron atoms showed that the cell dimensions *a*, *b* and γ fitted a (001) layer of atoms in the same configuration as in *biotite* but spaced further apart. The relations of the two unit cells to a layer of iron atoms are shown in Fig. 2, the cells being drawn to different scales. The greater spacing of the atoms in *astrophyllite* is in agreement with the fact that whereas in *biotite* the iron may be replaced by magnesium (radius 0.65 Å) in *astrophyllite* it is replaced by manganese (radius 0.80 Å).

The odd number of iron atoms in each sheet implied that one of them must lie on a centre of symmetry. The Patterson function $P(yz)$ was calculated and showed clearly the iron atoms in the positions postulated. It also indicated that most of the other atoms lay on lines joining the iron atoms and perpendicular to the (001) plane.

A cell parameter of approximately 5.3 Å occurs in many silicate minerals, related to the repeat distance of a pyroxene-type chain of SiO_4 tetrahedra. The *a* dimension of *astrophyllite* therefore suggested the presence of chains parallel to the *x* axis, as did the moderate ($0kl$) cleavage.

Examination of the $0kl$ structure amplitudes indicated pseudosymmetry in *astrophyllite*. The weighted

reciprocal lattice [Fig. 3(a)] has mirror lines parallel and perpendicular to the z^* axis. The apparent symmetry cannot be completely confirmed as the angle α^* is not 90° and, apart from the $07l$ points, the reciprocal lattice points are not in equivalent positions on either side of the mirror lines. However, the amplitudes of equivalent $07l$ and $0,14,l$ reflexions show close agreement. The corresponding symmetry in direct space is shown in Fig. 3(b). Although the mirror lines parallel to the trace of the *y* axis in the projection run continuously through the lattice, those perpendicular to it are continuous only within the primitive unit cell. This pseudosymmetry was of great value in further limiting the possible arrangements of the atoms.

By restricting attention to thirteen low angle reflexions and calculating structure factors for SiO_4 tetrahedra and titanium atoms in all reasonable positions, the structure shown in Fig. 4 was arrived at. Fig. 5 shows the configuration of SiO_4 tetrahedra and TiO_6 octahedra in this structure.

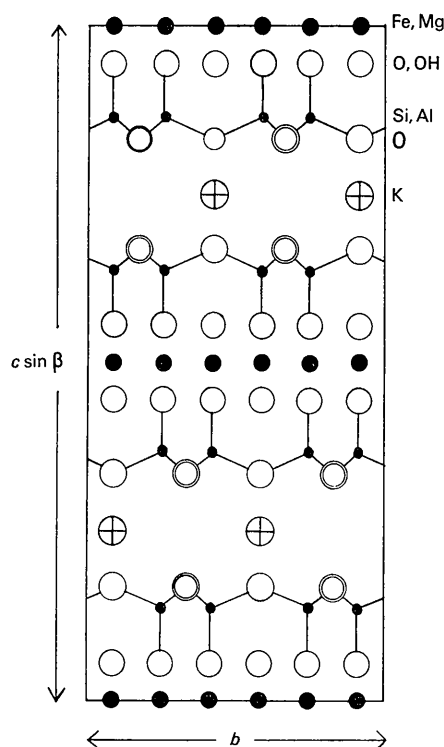


Fig. 1. Biotite. Projection along the *x* axis.

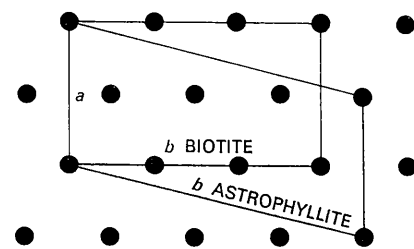


Fig. 2. Relation of unit cells to iron atoms.

The refinement

The initial structure gave a residual factor $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ of 0.55. The structure could be separated into two sections, the iron atoms and the rest of the structure. The strength of the 07l reflexions and the evidence of the Patterson function indicated that the iron atoms were probably equally spaced along the lines $z = 0.25$ and $z = 0.75$. In these 'ideal' positions they make no contribution to the 0kl reflexions with $k \neq 7n$. The rest of the structure gave good agreement for all reflexions except those with $k = 1, 6$ and 8. These reflexions gave very poor agreement between $|F_o|$ and $|F_c|$ and in most cases $|F_c|$ was too small. As it was not

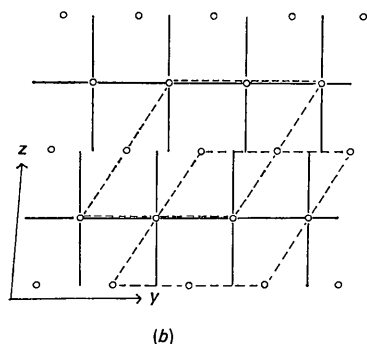
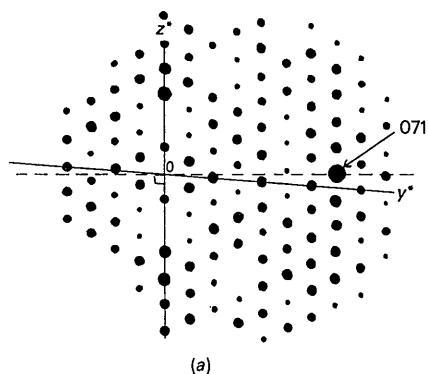


Fig. 3. Pseudosymmetry. (a) Weighted reciprocal lattice; mirror line dashed. (b) Direct lattice; centres of symmetry marked by circles, mirror lines by full lines and possible primitive unit cells by dashed lines.

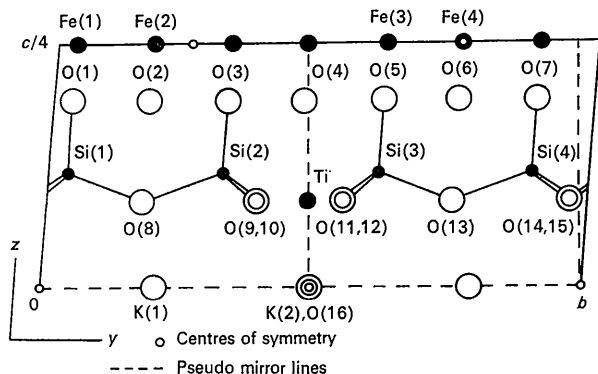


Fig. 4. Initial structure showing labelling of atoms.

possible to increase sufficiently the values of $|F_c|$ for these reflexions by adjusting the non-iron atoms within the general configuration of the postulated structure, it was evident that the iron atoms must make a contribution to the structure factors of those reflexions which showed discrepancies. This was supported by the fact that a slight shift of the iron atoms from the 'ideal' positions could be made to yield a large contribution to the reflexions 01l, 06l and 08l without affecting very much the other reflexions.

With the iron atoms assumed to be moved slightly from the 'ideal' positions the 0kl reflexions can be divided into three groups, according to the value of the index k .

Group A, $k = 7n$: - For these reflexions the iron atoms make a very large contribution to the structure factors and in most cases fix the signs. Slight movement of the atoms does not alter their contribution sufficiently to change the signs.

Group B, $k = 7n \pm 1$: - The iron contribution to these structure factors is large and its phase depends on the positions of the atoms relative to the 'ideal' positions in which the contribution is zero. For these reflexions incorrect movement of the iron atoms will give the wrong sign to many structure factors and thus direct the refinement away from the true path.

Group C, $k = 7n \pm x$ where $x > 1$: - For these reflexions the iron contribution is negligible unless the atoms are moved well away from the 'ideal' positions. The signs of the structure factors are determined by the rest of the structure.

Refinement was carried out with a least-squares program designed specifically for two-dimensional projec-

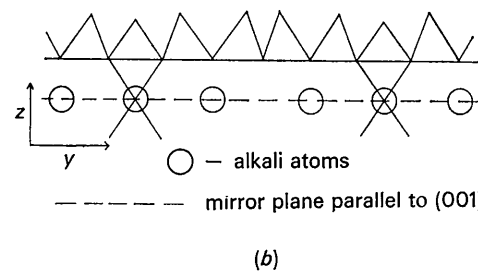
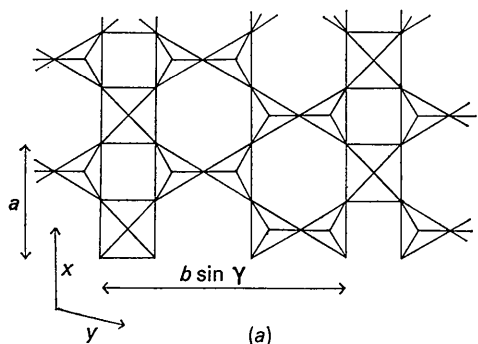


Fig. 5. Initial structure. (a) Arrangement of a sheet of SiO_4 tetrahedra and TiO_6 octahedra. (b) Relation of adjacent sheets. The mirror plane is only approximate.

dium. The major difference between the formula assumed at the start of the investigation and that found by analysis was in the contents of the titanium site. In order to correct for this the atomic scattering factors were calculated for a composite atom of 0.8 Ti, 0.1 Nb, 0.05 Zr, 0.05 Sn. These were close to those for iron by which the titanium factors were therefore replaced. These changes raised the residual to 0.14. The temperature factors and then the positions of the oxygen atoms were again refined and reduced R to 0.10. No further refinement was attempted as the atom coordinates were now steady, and in view of the complicated chemistry of the specimen the temperature factors were of limited significance.

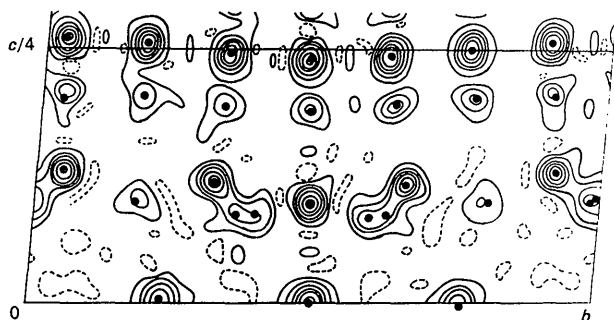


Fig. 6. Final structure. Electron density projected along the x axis and atom positions from least-squares refinement. The contours are drawn at equal intervals on an arbitrary scale with the zero contour broken. For labelling of atoms see Fig. 4.

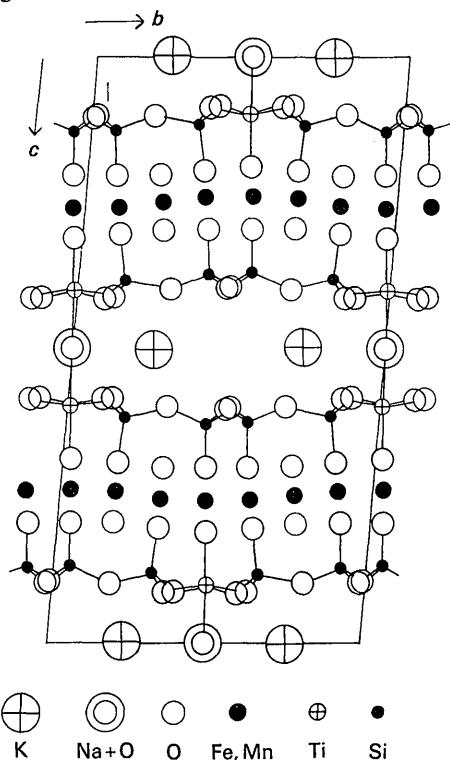


Fig. 7. Final structure. Projection along the x axis of the atomic arrangement of the full A -face-centred cell. Ti-O and Si-O bonds indicated.

Discussion

The electron density distribution calculated from the final structure is shown in Fig. 6. Fig. 7 shows the projection of the full A -face-centred cell. The short x axis repeat distance allows the basic features of the structure in three dimensions to be determined and approximate x coordinates to be calculated by making use of the known dimensions of the SiO_4 tetrahedron. The arrangement found is shown in Fig. 8.

The structure of astrophyllite is seen to have close affinities with the trioctahedral micas and can best be described in terms of its departures from the structure of biotite (Fig. 1). The biotite layer of SiO_4 tetrahedra is replaced by a layer of TiO_6 octahedra and SiO_4 tetrahedra in the ratio 1:4, arranged ideally as in Fig. 5. The true arrangement is in fact slightly distorted by rotation of the TiO_6 octahedron about an axis perpendicular to (001) and corresponding movement of the attached tetrahedra. The SiO_4 tetrahedra form infinite chains $(\text{Si}_4\text{O}_{12})_n$, parallel to the x axis, of a type so far not found in any other silicates. In order to fit to the octahedral layer, the tetrahedral layers of biotite are contracted by rotation of the tetrahedra (Radoslovich, 1960; Steinfink, 1962). The $(\text{Fe}, \text{Mn})\text{O}_6$ octahedra of astrophyllite are larger than the $(\text{Fe}, \text{Mg})\text{O}_6$ octahedra of biotite and the repeat distances of the octahedral layer will be greater than those of the $(\text{Si}_4\text{O}_{12})_n$ chains. In the direction of the x axis the two units fit apparently by shrinking of the octahedra in this direction. In the direction perpendicular to the x axis the matching is achieved by corrugating the octahedral layer and attaching the chains to the concave surfaces. A somewhat similar configuration is found in the structure of antigorite (Zussman, 1954). By slight rotation the TiO_6 octahedra joining the chains are made to fit the convex surfaces. The lengths, in the x axis projection, of the bonds Ti-O(4) and Ti-O(16) are of approximately the

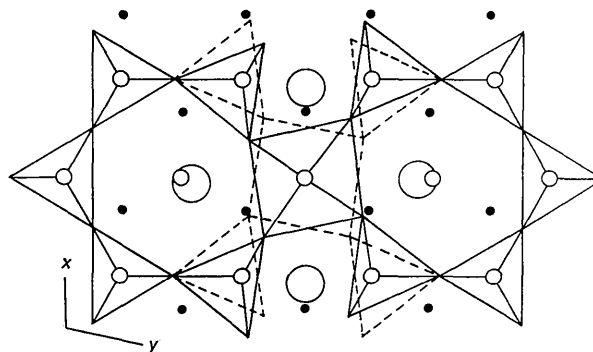


Fig. 8. Projection along [001] of one layer ($z=0$ to $z=c/4$) of the structure showing the probable arrangement in three dimensions deduced from the x -axis projection. Black dots: iron atoms at approximately $z=c/4$; large circles: alkali atoms at $z=0$; small circles: oxygen atoms shared by 'octahedral' and 'tetrahedral' layers. Edges of tetrahedra and TiO_6 octahedron outlined. Dashed lines indicate an alternative arrangement.

correct value for a titanium–oxygen bond, and the bonds must therefore lie close to the plane of projection, perpendicular to (001). As the atom O(16) is shared by TiO_6 octahedra on either side of the sheet of alkali atoms the tetrahedral layers are related by an approximate mirror plane parallel to (001). The potassium atoms, site K(1), are therefore each bonded to two rings of six oxygen atoms, as in the micas, and also to O(16) in the plane of the alkali atoms. The sodium atoms are in tenfold coordination, bonded to four atoms on each side of the alkali atom plane and two atoms, O(16) in the plane.

There are a number of possible variations in the structure:

(a) *Rotation of the TiO_6 octahedron.* In any layer of the structure there are two possible arrangements, as shown in Fig. 8. The differences between these are small and probably restricted to the atoms Si(2,3) and O(9,10,11,12).

(b) The relative rotation of the TiO_6 octahedra in adjacent layers could make the structure centrosymmetric or asymmetric. These variations would have small differences in the arrangement of the oxygen atoms around the alkali atoms.

(c) In this specimen the corrugation of the octahedral layer limits the number of polymorphs produced by the relative positions of the tetrahedral layers on either side to two, the atoms differing in x coordinates only. These can be distinguished by the value of the angle β (90° or 101°).

(d) The possible occurrence of many more varieties of astrophyllite is suggested by the specimen studied by Пэн & Ма (1963). This has the formula $(\text{K}_2\text{Na}_2)(\text{Fe}_5\text{Mg}_2)\text{Ti}_2\text{Si}_8(\text{O},\text{OH})_{31}$. The structure consists of the same ‘octahedral’, ‘tetrahedral’ and alkali atom layers but the presence of magnesium in the octahedral layer has produced a more symmetrical stacking of the units.

In this specimen the octahedral layer is flat and the positions of attachment of the titanium and silicon chains of the tetrahedral layer are apparently associated with the different sizes of the MgO_6 and FeO_6 octahedra and not with alterations in size produced by curvature. As a result the TiO_6 octahedra on either side are attached to the same octahedron of the Fe, Mg layer. The mirror lines perpendicular to (001) shown in Fig. 3(b) become in this specimen mirror planes running continuously through the now monoclinic lattice. The extra sodium atoms in this specimen are accommodated by replacing the atom in site K(2) by an atom on either side of this position, spaced at right-angles to the x axis.

The fact that the variations in ‘repeat distance’ of a composite TiO_6 – SiO_4 layer can be matched to a flat octahedral layer by the replacement of iron by magnesium suggests that with appropriate compositions of the octahedral layer continuous ‘tetrahedral’ layers with other ratios of titanium to silicon may be possible. The ratio 1:2 has already been found in bafertisite and some other minerals.

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The Crystal and Molecular Structure of Dimethylphosphinic Acid

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The crystal structure of dimethylphosphinic acid, $(\text{CH}_3)_2\text{PO}(\text{OH})$, has been determined from three-dimensional X-ray data. Crystals of this compound are monoclinic, space group $C2/c$, with 8 molecules in the unit cell. Cell dimensions are $a = 15.78$, $b = 6.76$, $c = 10.94$ Å; $\beta = 125^\circ 40'$. The structure has been refined by the method of least squares. The final R index for 852 observed reflexions is 0.078. The phosphorus atom has the expected tetrahedral configuration. The P–C bond lengths are equal within experimental error, with a mean value of 1.78 Å. The two P–O bond lengths are 1.50 and 1.56 Å. Strong O–H \cdots O hydrogen bonds, 2.48 Å in length and arranged around twofold screw axes, hold the molecules together to form chains along the b axis.

As a part of a series of investigations of Zn(II) and Co(II) di- n -alkylphosphinate polymers, which were found to be chains of tetrahedral metal atoms bonded with phosphinate bridges both in non-coordinating

solvents and in the solid state (Crescenzi, Giancotti & Ripamonti, 1965; Rose & Block, 1965; Giancotti & Ripamonti, 1966), the structure of dimethylphosphinic acid, $(\text{CH}_3)_2\text{PO}(\text{OH})$, was determined by a single-