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The Crystal Structure of Eosphorite

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The crystal structure of eosphorite, $AlPO_4.(Mn, Fe)(OH)_2.H_2O$, is described with reference to the pseudo-orthorhombic space group *Bbam* with

$$a=10\cdot52,\ b=13\cdot60,\ c=6\cdot97\ \text{Å},\ Z=8\ .$$

The structure was determined by inspection of some Patterson sections, and refined with the aid of three-dimensional differential syntheses. In the structure described there are two parallel sets of infinite chains, one composed of $(Mn, Fe)O_4(OH)_2$ octahedra sharing opposite O–O edges, and the other of $AlO_2(OH)_2(H_2O)_2$ octahedra sharing opposite H_2O corners. These chains alternate, sharing OH corners to form a set of parallel sheets held together by phosphorus ions in tetrahedral coordination of oxygen ions.

Introduction

Crystallographic studies of the childrenite–eosphorite series of minerals ($AlPO_4.(Mn, Fe)(OH)_2.H_2O$) have revealed a contradiction between optical and X-ray diffraction data. Barnes (1949), on the evidence of X-ray diffraction photographs and the report of a small but measurable piezoelectric effect, concluded that childrenite was orthorhombic *Bba*2. However, Hurlbut (1950), on consideration of optical properties, has concluded that these minerals should be classified as monoclinic (pseudo-orthorhombic) with $\beta=90°\ 00'$. Barnes & Shore (1951) have critically re-examined the X-ray diffraction evidence for eosphorite, employing very long X-ray exposures in order to record weak reflections. They have found no evidence of any departure from the space group *Bba*2 (or *Bbam*).

In the present paper a structure will be described which is consistent with the space group *Bbam*. However, certain anomalies of electron density suggest that the structure is only approximate.

Experimental details

The specimen of eosphorite examined was from Newry, Maine. In this specimen the ratio of manganese to iron is about 2 to 1 (Hurlbut, 1950). From single-crystal photographs the crystal appears to be orthorhombic *Bba*2 or *Bbam*, with

$$a=10\cdot52\pm0\cdot04,\ b=13\cdot60\pm0\cdot05,\ c=6\cdot97\pm0\cdot03\ \text{Å}.$$

Also,

D_x (calculated density) $=3\cdot04$ g.cm.$^{-3}$ ($Z=8$)
D_o (measured density) $=3\cdot07$ g.cm.$^{-3}$ (Hurlbut, 1950)
$\mu=33\cdot5$ cm.$^{-1}$ (Mo $K\alpha$) .

The crystal selected for data collection was a rectangular solid $0\cdot17\times0\cdot17\times0\cdot85$ mm., with the long axis parallel to **c**.

Three-dimensional intensity data were recorded on *z*-axis Weissenberg photographs, with molybdenum radiation, for values of *l* up to 12. The equi-inclination setting was used for upper levels, and the correlation of the data was accomplished by means of a double-slit technique. A few reflections on and near the z^*-axis were not recorded by this procedure, and some of these were obtained from precession photographs of the same crystal.

Intensities were estimated visually by comparison with a standard wedge. Corrections were made, where necessary, for distortion of spots on upper-level photographs, and appropriate Lorentz-polarization factors were applied. Absorption corrections were felt to be unnecessary, and were not made.

The number of reflections recorded was 1792. However, 15 of these, having one index greater than 30, could not readily be accommodated in the computational programmes and were not used in the analysis. The number theoretically observable with molybdenum radiation is about 5700. The range of observed amplitudes is about 1 to 70.

Structure determination

The z-axis Patterson projection indicated that the vector density was concentrated on or near the planes $U=0$, $U=\frac{1}{8}$, and $U=\frac{1}{4}$. The three-dimensional Patterson synthesis was therefore computed for these planes only, and a plausible trial structure (with symmetry *Bbam*) was found to be consistent with the vector density distribution. It should be pointed out that the computation of the Patterson synthesis did not require the assumption of orthorhombic symmetry; if $F(hkl)=F(\bar{h}kl)$, as in the present example, the Patterson function is the same for both monoclinic and orthorhombic crystal systems.

Table 1. *Atomic positions*

Atom	Number in cell	x	y	z
(Mn, Fe)	8	0·1323	0·2500	0·2500
P	8	0·3768	0·3334	0·0000
Al	8	0·2500	0·0000	0·2500
$O_1(O^{--})$	8	0·2668 (0·2667)	0·2553 (0·2576)	0·0000 (0·0133)
$O_2(O^{--})$	8	0·0056	0·2195	0·0000
$O_3(H_2O)$	8	0·2528	0·0491	0·0000
$O_4((OH)^-)$	16	0·1103	0·4100	0·1813
$O_5(O^{--})$	16	0·1334	0·6004	0·3202

The trial structure was refined with the aid of three-dimensional differential syntheses (Ahmed & Cruickshank, 1953). For the structure-factor calculations the atoms were assumed to be neutral, and the scattering-factor curves used were as follows: oxygen, McWeeny (1951); aluminium and phosphorus, *Internationale Tabellen* (1935); manganese–iron, weighted mean from Thomas & Umeda (1957). The temperature factor B was assumed to be 0·9 at this stage.

Table 2. *Peak-height and shape characteristics*

Atom	ϱ_o (e/Å^3)	ϱ_o/ϱ_c	α_x	α_y	α_z
Mn	194	0·91	0·93	0·84	0·90
P	123	1·04	1·07	0·98	1·00
Al	104	1·02	1·02	0·93	1·02
O_1	35·2 (37·6)	0·82 (0·91)	0·82 (0·91)	0·92 (0·82)	0·59 (0·81)
O_2	41·7	0·99	1·00	0·95	0·94
O_3	40·5	0·98	0·97	0·89	1·01
O_4	39·8	0·96	0·95	0·86	0·87
O_5	39·8	0·97	0·95	0·89	0·93

α = ratio of observed to calculated curvature.

The final atomic positions, shown in Table 1, were obtained by consideration of the shifts indicated by both F_o and F_c differential syntheses. A summary of peak-height and shape characteristics is given in Table 2. (Since not more than one third of the theoretically observable reflections were used in the analysis the effect of the omitted terms is certain to be appreciable. For this reason it is considered to be more informative to compare the *ratios* of corresponding quantities from the F_o and F_c syntheses.) While most of the atoms appear to be reasonably round, it will be seen that O_1 (which lies on the mirror plane at $z=0$) is considerably elongated in the direction of **c**. A possible explanation is that the thermal motion of this atom is anisotropic, requiring the value $B_z=1{\cdot}6$, compared with the overall value $B=0{\cdot}9$. However, such anisotropy seems unlikely in a structure of this sort. Another possible explanation is that the mirror plane is not a true symmetry element, and that the space group is *Bba*2. This possibility was investigated; a reasonable position for O_1 was assumed, and another cycle of refinement was undertaken. This procedure resulted in some improvement in the shape of O_1, and slightly better agreement between observed and calculated structure amplitudes. (These results could be expected, of course, even if the underlying assumptions were incorrect.) The modified position and the shape characteristics of O_1 are given, in parentheses, in the appropriate tables. No other atom shows any tendency to move from its original position, and the modest improvement in shape and agreement is not convincing proof that O_1 does so. As a matter of convenience, therefore, it seems best to retain the space group *Bbam*.

Reliability of the structure

Fair agreement between observed and calculated peak heights and shapes, and the plausibility of the structure itself, suggest that the analysis is basically sound. The most convincing proof of correctness, however, is the individual agreement between observed and

Table 3. *Agreement summary*

Category			Number of reflections
1. ($\lvert\Delta F\rvert \le \frac{1}{2}F_T$	or	$\lvert\Delta F\rvert \le 0{\cdot}1F_o$	1126
2. ($\lvert\Delta F\rvert \le 1F_T$	or	$\lvert\Delta F\rvert \le 0{\cdot}2F_o$	461
3. ($\lvert\Delta F\rvert \le 1\frac{1}{2}F_T$	or	$\lvert\Delta F\rvert \le 0{\cdot}3F_o$	127
4. ($\lvert\Delta F\rvert \le 2F_T$	or	$\lvert\Delta F\rvert \le 0{\cdot}4F_o$	46
5. ($\lvert\Delta F\rvert \le 2\frac{1}{2}F_T$	or	$\lvert\Delta F\rvert \le 0{\cdot}5F_o$	16
6. (Unspecified)			1

$\Delta F = \lvert F_o\rvert - \lvert F_c\rvert$.

F_T = estimated minimum observable structure amplitude for the indices of the reflection concerned.

Each category includes all reflections which meet the specified conditions, and which have not been previously included. For example, a reflection in category 2 satisfies either (or both) of the conditions $\lvert\Delta F\rvert \le F_T$ and $\lvert\Delta F\rvert \le 0{\cdot}2F_o$, but does not satisfy either of the corresponding conditions for category 1.

calculated structure amplitudes. It seems unnecessary to publish the complete data (although these are available from the author, on request) but a summary is given in Table 3, showing the numbers of reflections corresponding to specified categories of agreement. Structure factors were not calculated for the ultimate atomic positions in Table 1; the summary is therefore based on the penultimate stage of refinement, for which the atomic positions were slightly different. Values of F_o range from 5 to 378; $F_c(000)=907$; unobserved reflections are not considered. The largest discrepancies are found among the weaker reflections; the largest value of F_o found in category 5 is 46. The reflection in category 6 is 406, for which $F_o=27$, and $F_c=10$. The agreement residual

$$(R=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$$

is 0·16, for observed reflections only.

It is considered that the agreement is fair, and that the structure described must be at least approximately correct. Nevertheless the refinement does not appear to be complete, and the anomalous elongation of O_1 emphasizes the dubious aspect of the structure. At this point the significance of the optical behaviour of the crystal becomes apparent. If, as seems to be the case, the crystal is monoclinic with $\beta=90°\,00'$, then the pseudo-orthorhombic structure must be the average (formed by superposition) of the true structure and one related to it by the pseudo-symmetry element. The pseudo-orthorhombic structure may, of course, be based on *Bba*2, rather than *Bbam*; in this case the structure described would be the average of *four* identical, symmetrically-related structures. The agreement summarized above suggests that the structure described is fairly close to the true one, but it is difficult to say *how* close. However, it is hard to see how the true structure could be determined from the existing X-ray data, and it seems best to accept, with due caution, the approximate structure defined in Table 1.

The standard deviations of coordinates were calculated by Cruickshank's method (Lipson & Cochran, 1953). The mean values are, for manganese–iron, 0·0006 Å; for phosphorus 0·0010 Å; for oxygen 0·0035 Å; the aluminium coordinates are fixed by the space group. Unobserved reflections were excluded from the calculations, so that these quantities are probably underestimated. Moreover, the calculations are applicable only to the average, pseudo-orthorhombic structure, and not to the true one. It would be unwise, therefore, to use the values quoted in order to apply significance criteria to any variations or anomalies of interatomic distance.

Discussion of the structure

The structure can be considered formally as a system of linked polyhedra assembled in the following way. $(Mn, Fe)O_4(OH)_2$ octahedra share opposite O–O edges

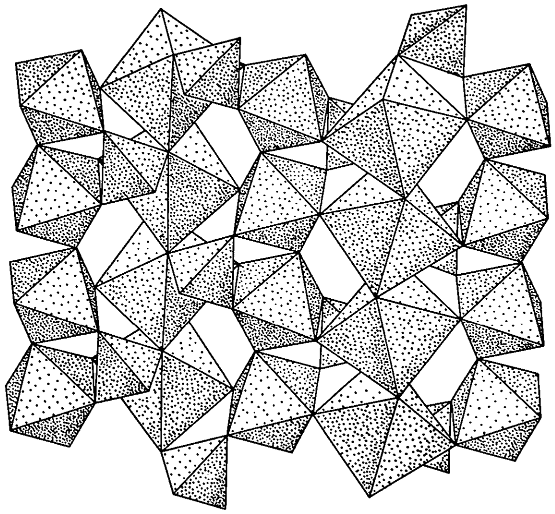

Fig. 1. A portion of the eosphorite structure, showing coordination polyhedra.

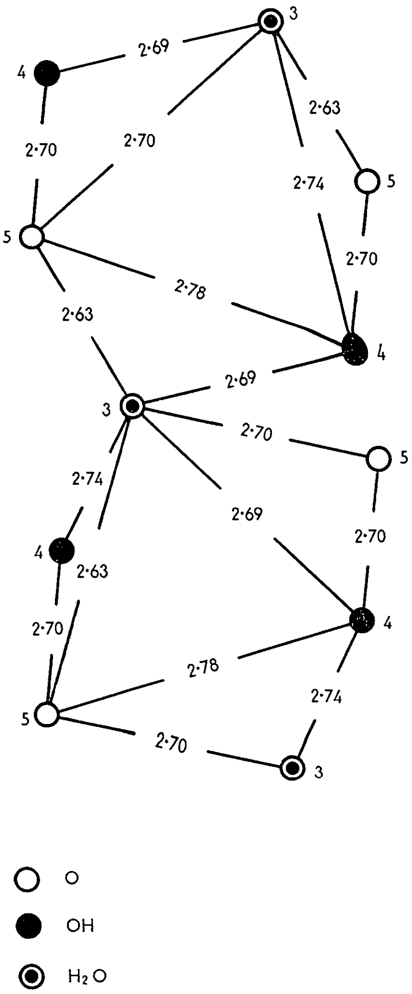

Fig. 2. Two $AlO_2(OH)_2(H_2O)_2$ octahedra, showing arrangement of anions.

to form a set of endless chains, parallel to **c**. $AlO_2(OH)_2(H_2O)_2$ octahedra share opposite H_2O corners to form a parallel set of chains. The two types of chain alternate, sharing OH corners to form infinite sheets. Adjacent sheets are held together by phosphorus cations in tetrahedral coordination of oxygen ions, to form a three-dimensional network. A portion of one sheet and its associated PO_4 tetrahedra is shown in Fig. 1, and appropriate interionic distances are given in Table 4. It is obvious from both figure and table that the (Mn, Fe)$O_4(OH)_2$ octahedra are somewhat distorted. The shared edge is considerably shorter than the others, suggesting repulsion between neighbouring (Mn, Fe) cations. The other polyhedra are more nearly regular. All the cation-anion distances agree well with those found for similar coordination polyhedra in other compounds (Sutton, 1958; Wyckoff, 1948).

Table 4. *Interionic distances*

(Mn,Fe)$O_4(OH)_2$ octahedron	
O_1–O_1	3·49 Å
O_1–O_2	2·79*
O_1–O_4	2·96 3·56
O_2–O_2	3·58
O_2–O_4	3·04 3·09
(Mn, Fe)–O_1	2·25
(Mn, Fe)–O_2	2·23
(Mn, Fe)–O_4	2·24

$AlO_2(OH)_2(H_2O)_2$ octahedron	
O_3–O_4	2·74 Å 2·69
O_3–O_5	2·70 2·63†
O_4–O_5	2·78 2·70
Al–O_3	1·87
Al–O_4	1·97
Al–O_5	1·90

PO_4 tetrahedron	
O_1–O_2	2·54 Å
O_1–O_5	2·55
O_2–O_5	2·52
O_5–O_5	2·51
P–O_1	1·57
P–O_2	1·53
P–O_5	1·55

Cation–Cation distances	
(Mn, Fe)–(Mn, Fe)	3·48 Å
(Mn, Fe)–P	3·32 3·39
(Mn, Fe)–Al	3·62
P–Al	3·16
Al–Al	3·48
P–P	4·16

* Shared edge. † Tentative hydrogen bond.

The identification of OH and H_2O groups, given in Table 1 and implicit in the discussion, depends on the application of Pauling's electrostatic valence rule. The strengths of the cation-anion bonds in the structure are: (Mn, Fe), $\frac{1}{3}$; P, $1\frac{1}{4}$; Al, $\frac{1}{2}$. The sums of the strengths of the bonds terminating in the various anions are shown in Table 5. It seems clear that O_1 and O_2 are saturated oxygen ions, and that O_4 is a nearly-saturated hydroxyl ion. Of the remaining anions, symmetry considerations suggest that O_3 is the H_2O group, and that O_5 is an oxygen ion. This arrangement of anions is shown in Fig. 2. The electrostatic valence rule is satisfied by assuming that O_3 forms hydrogen bonds with two of the four adjacent oxygen ions, the protons being shared between terminal anions. The strength of the O–H bond is taken to be $\frac{1}{2}$, and the amended sums of bond strength are given (in parentheses) in Table 5. The proposed structure is seen to be in fair agreement with the electrostatic valence rule, although the bond strength of $2\frac{1}{4}$ for O_5 is rather high. If the H_2O group has been correctly identified, however, the bonding protons will be closer to O_3 than to the adjacent oxygen anions. The assumption of equal sharing of bond strength between the terminal ions must be modified, and suitable assumptions will slightly reduce the extreme value for O_5.

Table 5. *Bond strengths*

Anion	Coordinated cations	Sum of bond strengths
O_1, O_2	2 (Mn, Fe), 1 P	$1\frac{11}{12}$
O_4	1 (Mn, Fe), 1 Al	$\frac{5}{6}$
O_5	1 P, 1 Al (1 H)	$1\frac{3}{4}$ ($2\frac{1}{4}$)
O_3	2 Al (2 H)	1 (2)

It will have been observed in Fig. 2 that two of the O_3–O_5 bonds terminating in O_3 are much shorter than the other two. It seems reasonable to identify these (somewhat tentatively), as the hydrogen bonds.

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