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The crystal structure of parahopeite

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Summary. Parahopeite, $Zn_3(PO_4)_2.4H_2O$, is the triclinic dimorph of hopeite. The crystal structure of parahopeite has been determined to be similar to phosphophyllite, $Zn_2Fe(PO_4)_2.4H_2O$ and to hopeite in that one of the two zinc atoms is six-coordinated and the other is four-coordinated. Parahopeite differs from the other two minerals though because one of the P–O tetrahedral oxygen atoms is bonded to both the six- and the four-coordinated cations. That is, all four tetrahedral oxygen atoms are bonded to the four-coordinated zinc in parahopeite, whereas in phosphophyllite and hopeite only three of these oxygen atoms are so bonded.

WOLFE (1940) classified minerals of the type $A_3(XO_4).nH_2O$; for the type $A_3(XO_4)_2.4H_2O$ he included the minerals anapaite, $Ca_2Fe(PO_4)_2.4H_2O$, phosphophyllite, $Zn_2Fe(PO_4)_2.4H_2O$, and hopeite and parahopeite, both $Zn_3(PO_4)_2.4H_2O$. Anapaite appears to belong to this classification only by virtue of its formula. The remaining three minerals are characterized by the presence of a four-coordinated cation whereas the cations of anapaite and ludlamite, $Fe_3(PO_4)_2.4H_2O$ (not included in Wolfe's classification) are all six-coordinated and appear to bear no structural relationship to the zinc phosphate hydrates.

The structure of phosphophyllite was determined by Kleber *et al.* (1961). Correct structure determinations of hopeite were made by Gamidov *et al.* (1963) and by Liebau (1965), following the incorrect determination by Mamedov *et al.* (1961). In both phosphophyllite and hopeite there are two crystallographic zinc positions; one has six-fold coordination, the other four-fold. Both are layer structures and both

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have a negative optic sign with the fast ray vibrating perpendicular to the layer (see Wolfe, 1940). Parahopeite, however, has a positive optic sign and the refractive indices do not suggest a layer structure. It is therefore of interest to determine the structure of parahopeite in order to compare the four-coordinated zinc to the P–O tetrahedron and six-coordinated zinc in the other two minerals.

Crystal data and structure determination

Parahopeite is triclinic $P\bar{1}$. The reciprocal and direct unit cell dimensions derived from precession film measurements are: a 5·757, b 7·534, c 5·625 Å, all ±0·005 Å, α 93° 32′, β 91° 18′, γ 91° 33′, all ±5′, V 227·89 Å^3; a^* 0·17377, b^* 0·13301, c^* 0·19030 Å^{-1}, α^* 86° 26′, β^* 88° 36′, γ^* 88° 22′, V^* $4{\cdot}388\times10^{-3}$ Å^{-3}. Data were collected for the zero levels about the a-, b-, and c-axes by means of Weissenberg normal-beam films utilizing Mo-$K\alpha$ radiation. Intensities were measured visually.

TABLE I. Positional parameters for parahopeite. Standard deviations are given in parentheses.

Atom	x	y	z	B
Zn(1)	0	0	0	1·36(9)
Zn(2)	0·2521(7)	0·5982(5)	0·8166(7)	1·21(7)
P	0·2503(15)	0·3603(11)	0·2932(16)	1·06(12)
O(1)	0·4718(34)	0·2640(30)	0·2281(41)	1·27(34)
O(2)	0·2307(40)	0·3956(30)	0·5842(42)	1·76(40)
O(3)	0·0243(39)	0·2516(34)	0·1963(48)	1·95(41)
O(4)	0·2525(47)	0·5263(34)	0·1764(52)	2·79(49)
$H_2O(1)$	0·2249(38)	0·8886(29)	0·2684(47)	1·52(38)
$H_2O(2)$	0·2656(47)	0·0617(33)	0·7622(55)	2·59(50)

The structure of parahopeite was determined by examination of Patterson projections to find the positions of Zn(2) and P, Zn(1) being restricted to the origin by symmetry. F_{obs} Fourier projections were calculated to determine the positions of the oxygen atoms and water molecules.

Refinement has been accomplished by means of full-matrix least-squares using 287 observed reflections. The 61 non-observed reflections were not used in the refinement process. The R-factor based on the observed reflections only has been reduced in the refinement from an initial value of 0·290 to 0·094. Positional parameters and isotropic temperature factors are listed in table I; bond distances and angles appear in table II.

TABLE II. Bond distances and angles for parahopeite. Only distances less than 3·20 Å are listed.

Zn(1)–O(3) = 2·10 (2×)
Zn(1)–H_2O(1) = 2·12 (2×)
Zn(1)–H_2O(2) = 2·06 (2×)

O(3)–Zn(1)–H_2O(1) = 92·0°
O(3)–Zn(1)–H_2O(2) = 92·5°
H_2O(1)–Zn(1)–H_2O(2) = 93·6°

Zn(2)–O(1) = 1·90
Zn(2)–O(2) = 1·90
Zn(2)–O(3) = 1·98
Zn(2)–O(4) = 2·00

O(1)–Zn(2)–O(2) = 111·5°
O(1)–Zn(2)–O(3) = 110·6°
O(1)–Zn(2)–O(4) = 108·0°
O(2)–Zn(2)–O(3) = 113·0°
O(2)–Zn(2)–O(4) = 110·8°
O(3)–Zn(2)–O(4) = 102·1°

P–O(1) = 1·52
P–O(2) = 1·55
P–O(3) = 1·58
P–O(4) = 1·43

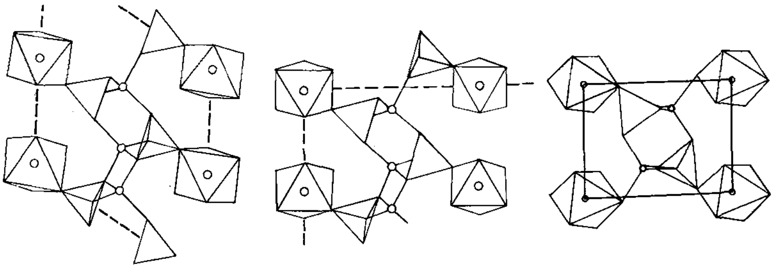
O(1)–P–O(2) = 111·0°
O(1)–P–O(3) = 112·6°
O(1)–P–O(4) = 109·0°
O(2)–P–O(3) = 107·0°
O(2)–P–O(4) = 109·0°
O(3)–P–O(4) = 108·0°

O(1)–O(2) = 2·53, 3·14
O(1)–O(3) = 2·58, 3·19
O(1)–O(4) = 2·40, 3·16
O(1)–H_2O(1) = 3·15
O(1)–H_2O(2) = 2·92, 3·00

O(3)–O(4) = 2·43, 3·10
O(3)–H_2O(1) = 2·93, 3·03
O(3)–H_2O(2) = 2·87, 3·00
O(4)–H_2O(1) = 2·75
H_2O(1)–H_2O(2) = 2·84, 2·86, 2·95, 3·05

O(2)–O(3) = 2·51
O(2)–O(4) = 2·42
O(2)–H_2O(2) = 2·75

σ(Zn–O) = 0·02 Å
σ(P–O) = 0·02 Å
σ(O–O) = 0·03 Å



FIGS. 1 to 3: FIG. 1 (left). A portion of the crystal structure of phosphophyllite projected on to (010). Scale of figure is relative for comparison with fig. 3, *c*-axis is horizontal. (After Liebau, 1965.) FIG. 2 (middle). A portion of the crystal structure of hopeite projected on to (001). Scale of figure is relative and the origin has been shifted for comparison with fig. 3, *a*-axis is horizontal. (After Liebau, 1965.) FIG. 3 (right). The crystal structure of parahopeite projected on to (001). *a*-axis is horizontal.

Discussion

Unfortunately bond lengths for the three mineral structures cannot be compared directly. The structures of hopeite and phosphophyllite have been extrapolated in the third dimension and no accurate atomic positions are available for this third direction. The structures are, however, very similar. In all three structures there are two crystallographic 'zinc' atoms (one iron and one zinc in phosphophyllite), one being six-coordinated by oxygen and water the other four-coordinated by oxygen. In both phosphophyllite and hopeite (fig. 1 and 2) the P–O tetrahedron shares one oxygen with six-coordinated zinc (Zn^{vi}) and three with four-coordinated zinc (Zn^{iv}). The P–O tetrahedron in parahopeite (fig. 3) shares one oxygen not only with Zn(1) but also with Zn(2), a situation not observed in the other two structures. But, as in hopeite and phosphophyllite, the four oxygen atoms to (Zn^{iv}) belong to four different tetrahedra.

The perfect {010} cleavage discussed by Ledoux *et al.* (1919) is accounted for by considering that only one bond between Zn^{vi} and oxygen need be broken. This is similar to the situation found in phosphophyllite and hopeite where Zn^{vi}–O bonds are broken to produce the cleavage.

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