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Refinement of the crystal structure of parahopeite

By G. Y. Chao

Department of Geology, Carleton University, Ottawa, Canada

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Auszug

Die Kristallstruktur von Parahopeit, $Zn_3(PO_4)_2 \cdot 4H_2O$, wurde auf Grund von *hkl*-Interferenzen verfeinert. Die dabei gefundenen Atomkoordinaten ergeben regelmäßigere Koordinationspolyeder und eine bessere Übereinstimmung der Atomabstände mit solchen, die bei ähnlichen Verbindungen beobachtet wurden.

Abstract

The crystal structure of parahopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, has been refined using three-dimensional intensity data. The refined atomic positions obtained in this paper provided more regular coordination polyhedra with interatomic distances in better agreement with those found in other compounds.

Introduction

Kumbasar and Finney (1968) determined the crystal structure of parahopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, using intensity data collected in the three principal zones. At about the same time the writer collected three-dimensional intensity data and derived the same structure independently. It is felt that the publication of this work provides some more precise structural data which may contribute to the better understanding of the crystal chemistry of the zinc orthophosphates.

X-ray data

Parahopeite is triclinic, space group $P\bar{1}$. Its lattice parameters were determined by Weissenberg and precession methods as well as from powder diffraction data refined by the least-squares method. These are listed in Table 1.

A total of 2097 visually estimated intensities were collected by multiple-film technique, using Cu$K\alpha$ radiation and the Weissenberg

Table 1. *Lattice parameters of parahopeite*

	From single-crystal photographs		From powder photographs
	Kumbasar and Finney	This paper	This paper
a	5.757(5) Å	5.768(5) Å	5.773(6) Å
b	7.534(5)	7.550(5)	7.546(9)
c	5.265(5)	5.276(5)	5.276(5)
α	93°32′	93°25′	93°24′(10)
β	91°18′	91°11′	91° 6′(10)
γ	91°33′	91°22′	91°20′(10)
V	227.89 Å^3	229.30 Å^3	229.36 Å^3

camera. Unobservable reflections were assigned values one-half of the lowest scale on the timed exposure intensity strip. Lorentz and polarization factors were applied. No absorption correction was made because of the small size of the crystal used (approximately a 0.1 mm cube).

Refinement of the structure

The refinement of the structure was carried out by the least-squares method using a full matrix. The scattering curves in the *International tables for crystallography* were used. Individual isotropic temperature factors were first used in the refinement. After eight least-squares cycles the shifts of the parameters became negligible and the R index

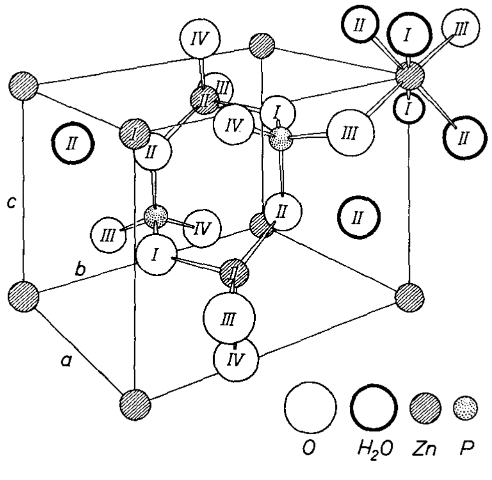

Fig. 1. Perspective projection of the structure of parahopeite. $H_2O(1)$ molecules within the cell are removed to avoid overlapping

Table 2. *Atomic parameters*
(Standard deviations are given in brackets)

	x		y		z		B	
	This paper	K. F.*	This paper	K. F.*	This paper	K. F.*	This paper	K. F.*
Zn(1)	0	0	0	0	0	0	0.613(15)	1.36(9)
Zn(2)	0.2518(1)	0.2521(7)	0.5984(1)	0.5982(5)	0.8166(4)	0.8166(7)	0.501(13)	1.21(7)
P	0.2497(2)	0.2503(15)	0.3621(2)	0.3603(11)	0.2955(4)	0.2932(16)	0.332(18)	1.06(12)
O(1)	0.4675(8)	0.4718(34)	0.2592(6)	0.2640(30)	0.2273(11)	0.2281(41)	0.502(52)	1.27(34)
O(2)	0.2329(6)	0.2307(40)	0.3908(7)	0.3956(30)	0.5863(13)	0.5842(42)	0.794(61)	1.76(40)
O(3)	0.0287(7)	0.0243(39)	0.2522(6)	0.2516(34)	0.1966(11)	0.1963(48)	0.413(48)	1.95(41)
O(4)	0.2505(10)	0.2525(47)	0.5422(6)	0.5263(34)	0.1708(12)	0.1764(52)	0.678(58)	2.79(49)
$H_2O(1)$	0.2297(10)	0.2249(38)	0.8913(7)	0.8886(29)	0.2606(14)	0.2684(47)	1.091(68)	1.52(38)
$H_2O(2)$	0.2655(9)	0.2656(47)	0.0586(7)	0.0617(33)	0.7477(13)	0.7622(55)	0.998(65)	2.59(50)

* KUMBASAR and FINNEY (1968).

Table 3. *Distances and angles for parahopeite*

		PO$_4$ tetrahedron			
P–O(1)	1.530 Å	O(1)–O(2)	2.516 Å	O(1)–P–O(2)	110.0°
P–O(2)	1.542	O(1)–O(3)	2.534	O(1)–P–O(3)	109.8
P–O(3)	1,567	O(1)–O(4)	2.527	O(1)–P–O(4)	110.8
P–O(4)	1.540	O(2)–O(3)	2.510	O(2)–P–O(3)	107.6
		O(2)–O(4)	2.531	O(2)–P–O(4)	110.4
		O(3)–O(4)	2.518	O(3)–P–O(4)	108.2
		ZnO tetrahedron			
Zn(2)–O(1)	1.948 Å	O(1)–O(2)	3.214 Å	O(1)–P–O(2)	112.2°
Zn(2)–O(2)	1.925	O(1)–O(3)	3.248	O(1)–P–O(3)	110.9
Zn(2)–O(3)	1.997	O(1)–O(4)	3.117	O(1)–P–O(4)	106.5
Zn(2)–O(4)	1.943	O(2)–O(3)	3.278	O(2)–P–O(3)	113.4
		O(2)–O(4)	3.224	O(2)–P–O(4)	112.9
		O(3)–O(4)	3.024	O(3)–P–O(4)	100.2
		ZnO octahedron			
Zn(1)–O(3)	2.116 Å (2 ×)	O(3)–H$_2$O(1)	3.015 Å	O(3)–Zn–H$_2$O(1)	91.7°
Zn(1)–H$_2$O(1)	2.101 (2 ×)	O(3)–H$_2$O(1)′	2.946		
Zn(1)–H$_2$O(2)	2.108 (2 ×)	O(3)–H$_2$O(2)	3.072	O(3)–Zn–H$_2$O(2)	93.3
		O(3)–H$_2$O(2)′	2.898		
		H$_2$O(1)–H$_2$O(2)	2.799	H$_2$O(1)–Zn–H$_2$O(2)	93.2
		H$_2$O(1)–H$_2$O(2)′	2.891		

Estimated standard deviations

P–O 0.006 Å; Zn–O 0.006 Å; O–O 0.008 Å; angles 0.2°

was reduced to 0.105 using all reflections. The R index was 0.098 when unobserved reflections were excluded.

Further refinement with anisotropic temperature parameters resulted in a slightly improved R index of 0.097 using all reflections. However, there were no significant changes in the positional parameters.

The final positional parameters and isotropic temperature factors are listed in Table 2 where they are compared to the parameters reported by KUMBASAR and FINNEY. The interatomic distances and bond angles are listed in Table 3. A perspective projection of the structure is shown in Fig. 1.

Discussion

From Table 2 it can be seen that the atomic parameters of KUMBASAR and FINNEY and those of this paper are very similar. However, the latter provided more regular cation-oxygen coordination polyhedra with interatomic distances in better agreement with those found in other compounds. For instance, the P—O(4) distance reported by KUMBASAR and FINNEY was 1.43 Å whereas the distance between the same pair of atoms found in this work is 1.540 Å, a value that falls well within the range of 1.512—1.549 Å for P—O distances in other orthophosphates recorded in the *International tables for crystallography*. KUMBASAR and FINNEY also reported a few short oxygen—oxygen distances such as O(1)—O(4) distance of 2.40 Å, while the shortest oxygen—oxygen distance found in this work is 2.510 Å.

KUMBASAR and FINNEY have shown that the structure of parahopeite is very similar to that of hopeite which is the orthorhombic dimorph of the former. However, the minerals differ in that in hopeite (LIEBAU, 1965) all the oxygen atoms are shared by two coordination polyhedra, one PO_4 tetrahedron and one ZnO_4 tetrahedron or one PO_4 tetrahedron and one $Zn(H_2O)_4O_2$ octahedron, but in parahopeite one of the oxygen atoms, O(3), is shared by three polyhedra, namely a PO_4 tetrahedron, a $Zn(2)O_4$ tetrahedron and a $Zn(1)(H_2O)_4O_2$ octahedron. Consequently, the cation–O(3) distances are considerably longer than the other cation-oxygen distances in each coordination polyhedron. In both structures the octahedral Zn atom is linked to four H_2O molecules and two oxygen atoms. However, in hopeite the oxygen atoms are on two adjacent corners, whereas in parahopeite they are on two opposite corners. In this regard, the structure of parahopeite is similar to that of phosphophyllite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ (KLEBER, LIEBAU and PIATKOWIAK, 1961), in which the two oxygen atoms in the $Fe(H_2O)_4O_2$ octahedron are also on the opposite corners.

Acknowledgements

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