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Whitmoreite, $Fe^{2+}Fe^{3+}_2(OH)_2(H_2O)_4[PO_4]_2$, A New Species: Its Description and Atomic Arrangement

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Abstract

Whitmoreite, ideally $Fe^{2+}Fe^{3+}_2(OH)_2(H_2O)_4[PO_4]_2$, a 10.00(2) Å, b 9.73(2), c 5.471(8), β 93.8(1)°, $P2_1/c$, $Z = 2$, is a new species derived from the hydrothermal alteration of triphylite from the Big Chief pegmatite, Glendale, South Dakota, and from the Palermo No. 1, North Groton and Fitzgibbon, East Alstead pegmatites, New Hampshire. The mineral occurs as brown to greenish brown acicular crystals elongated parallel to [001] and twinned by reflection parallel to {100}. The observed forms are a{100}, m{110}, s{011}, t{021}, and u{112}. The hardness is 3, the cleavage is fair parallel to {100}, and the specific gravity is 2.87(1). Crystals are biaxial (−), α 1.676(3), β 1.725(4), γ 1.745(4), $b \parallel Y$, $c \parallel Z$, pleochroism X,Y light greenish-brown, Z dark greenish-brown. Electron probe analysis provides Fe 27.8, Mn 3.0, and P 13.0.

The crystal structure analysis [$R(hkl) = 0.14$ by visually inspected films] reveals a new type of Fe^{3+}-O octahedral condensation based on open sheets of composition $[Fe^{3+}_2(OH)_2(O_P)_6]$. These are linked by $[PO_4]$ tetrahedra to form slabs parallel to {100} of composition $[Fe^{3+}_2(OH)_2[PO_4]_2]^{2-}$; the remaining tetrahedral vertices are corner-linked to *trans*-$[Fe^{2+}(O_P)_2(H_2O)_4]$ octahedra. These latter octahedra are (1) partly replaced by Mn^{2+} and (2) partly oxidized, and accommodate the average population, 0.31 Fe^{2+} + 0.27 Mn^{2+} + 0.28 Fe^{3+} + 0.14 Hole.

A network of hydrogen bonds is proposed, which is cut by the {100} plane.

Introduction

Our study is divided into two parts, the first a description of the new species whitmoreite. Owing to crystal-chemical complexities and the frequent multiple roles of water molecules in secondary phosphate crystals, the result of a crystal structure analysis is a necessary part of any adequate description of a new species and the second half of this paper is devoted to that study.

Occurrences and Paragenesis

In 1971, Mr. W. L. Roberts of Rapid City, South Dakota, provided us with specimens of an acicular unknown mineral encrusting siderite in corroded triphylite from the Big Chief pegmatite near Glendale, South Dakota (Middle of E ½, NE ¼, sec. 22, T.2S, R.6E). Almost simultaneously, acicular tan crystals on siderite from the Fitzgibbon pegmatite, East Alstead, New Hampshire (collected by the late Mr. Gunnar Bjareby of Boston) were shown to be the same compound. Finally, in 1973, Mr. Robert Whitmore (an amateur collector of repute) of Weare, New Hampshire, brought to our attention attractive specimens of an acicular radial brown mineral from the Palermo No. 1 pegmatite, N. Groton, New Hampshire, which proved to be the same material. The paragenetic settings at all these localities are practically identical, and the following discussion derived from examination of all samples. The Palermo No. 1 pegmatite is accepted as the type locality owing to the superior quality of the crystals. The diagnostic results derive from a Palermo sample.

Whitmoreite occurs as thin acicular crystals five to ten times as long as they are thick, which range from 0.1 to 2.0 mm in length. Crystals are grouped as fans and sprays but occasionally occur as isolated individuals. A typical appearance involves a small spheroidal core from which radiate small, thin crystals providing the appearance of a burr or a floating naval mine. These crystals are almost invariably perched upon siderite rhombohedra in open cavities. Earlier in the paragenesis are quartz crystals, siderite, and occasional ludlamite and the later species include strunzite, laueite, beraunite, mitridatite, and manganic and ferric oxy-hydroxides. About forty specimens have been examined; although whitmoreite cannot be regarded as an abundant mineral at any of the localities, it appears to be dispersed in small quantity throughout the siderite paragenesis which derived from the alkali-leaching and late stage carbonation of parent triphylite.

Description and Properties

Physical Properties

Whitmoreite is pale tan to deep brown to greenish-brown in color, being not unlike and easily confused with the far more abundant childrenite-eosphorite. The luster is vitreous to subadamantine in the darker colored crystals. The crystals possess a rhomboidal cross-section with a chisel-shaped termination; casual examination suggests a pseudo-orthorhombic development. The hardness is 3 and the cleavage {100} fair. Specific gravity, established by sink-float in methylene iodide-toluene solutions is 2.87 ± 0.01; the computed density accepting the cell contents proposed further on, is 2.85 g cm^{-3}.

Crystal Morphology

Single crystal X-ray study establishes that whitmoreite crystals are usually twinned by reflection parallel to {100}, which imparts an orthorhombic habit to the crystals. Careful search among many specimens failed to reveal a discernible singlet. These crystals almost certainly grew initially as twins but rarely reveal repeated twinning, so that re-entrant angles are infrequently encountered. The crystals are long prismatic to acicular parallel to [001]. Two-circle goniometric study on crystals from the Big Chief and Palermo No. 1 pegmatites revealed the forms *a*{100}, *m*{110}, *s*{011}, *t*{021}, and *u*{112}. Typical developments are presented in Figure 1.

X-ray Crystallography

Powder, single-crystal rotation, and Weissenberg and precession photographs, the data of which were refined by least-squares on the indexed powder lines, provided the following cell criteria: *a* 10.00(2) Å, *b* 9.73(2) Å, *c* 5.471(8) Å, β 93°49(6)′, space group $P2_1/c$, $Z = 2$. In addition, a three-dimensional data set was gathered on Weissenberg photographs. These results were used to index the powder data in Table 1.

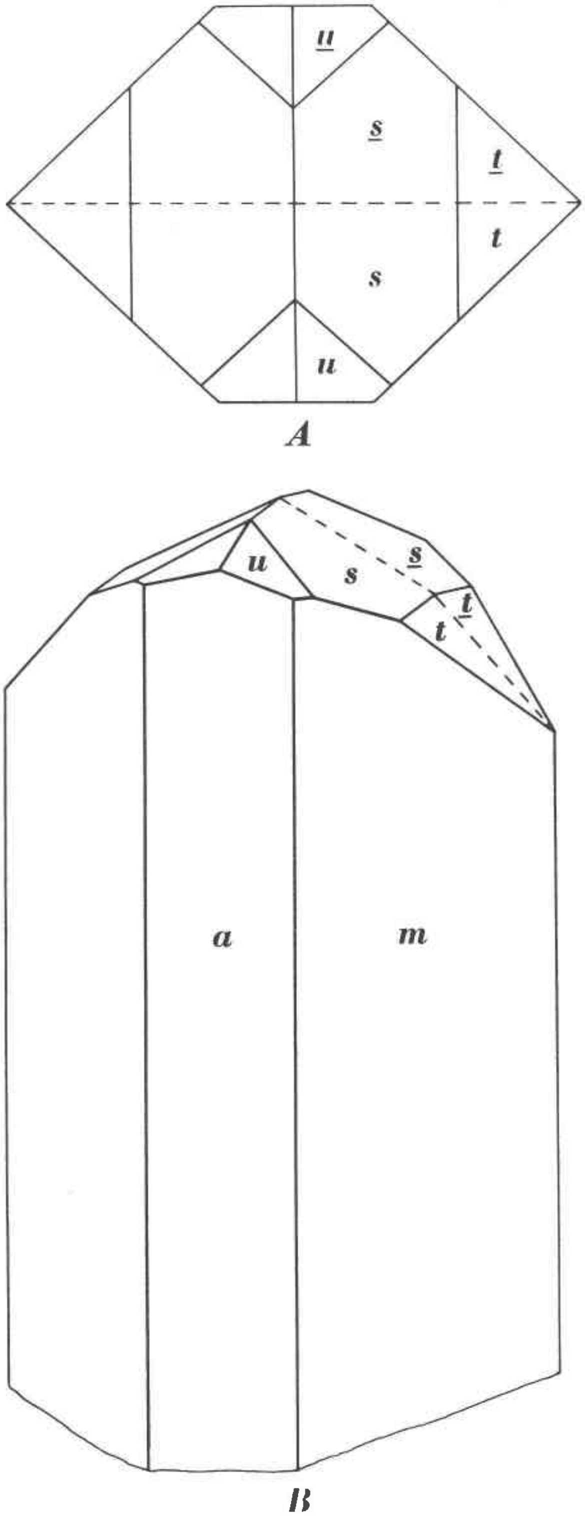

FIG. 1. Typical development of whitmoreite crystals twinned by reflection on {100} showing the forms *a*{100}, *m*{110}, *s*{011}, *t*{021}, and *u*{112}. A. Plan. B. Clinographic projection.

TABLE 1. Whitmoreite. Powder Data†

I/Io	d(obs)	d(calc)	hkl
10	10.05	9.98	100
7	7.01	6.97	110
7	4.98	4.99	200
4	4.81	4.87	020
6	4.42	4.44	210
7	4.21	4.20	111
5	3.476	3.463	$\bar{1}21$
3	3.358	3.366	121
2	3.091	3.085	130
4	3.000	3.000	$\bar{2}21$
5	2.878	2.876	221
7	2.802	2.804	$\bar{3}11$
4	2.726	2.720	230
4	2.585	2.582	$\bar{1}12$
2	2.461	2.464	$\bar{2}02$
3	2.400	2.400	321
2	2.349	2.347	$\bar{1}22$
1	2.264	2.266	212
3	2.222	2.222	041
1	2.173	2.174	$\bar{3}31$
1	2.159	2.158	411
4	2.101	2.101	222
3	2.007		
3	1.982		
3	1.959		
3	1.884		
2	1.837		
2	1.776		
3	1.715		
3	1.681		
3	1.644		
2	1.579		
3	1.555		
2	1.532		
2	1.489		
2	1.461		
2	1.448		

†114.6 mm camera diameter, rolled sphere powder mount. Film corrected for shrinkage and sample corrected for absorption.

The persistent twinning observed for whitmoreite can be explained on the basis of the cell geometry. The addition of a {100} reflection twin plane results in nearly perfect superposition of (*hkl*) and $(\bar{h}kl)$ for $l = 4N$, where N is an integer. Define $2t \approx a^*$. Evidently, $t = 4c^* \sin(\pi/2 - \mu)$. From this equation, $2t = 0.0976$ Å^{-1}, which deviates about 3 percent from $a^* = 0.1002$ Å^{-1}. Alternatively, accepting the values of a^* and c^* from the cell data, $(\pi/2 - \mu) = 3°55'$, a calculated value which differs from the observed $(\pi/2 - \mu) = 3°49'$ by 6′, which is within the limit of experimental error. Thus, it is not possible to separate $(h, k, 4N)$ from $(\bar{h}, k, 4N)$ by any counter diffractometric technique.

Chemical Composition

Owing to the meager quantity of crystals, we despaired of recovering enough material for wet chemical analysis. Accordingly, it was proposed to obtain metals by electron probe microanalysis and derive water content and oxidation grade through crystal structure analysis.

Several small crystals from the Palermo No. 1 pegmatite were submitted for analysis, utilizing wyllieite as a standard. The results are Fe 27.8, Mn 3.0, and P 13.0 percent; no other metals with atomic number greater than oxygen were detected. The proposed formula, discussed further on, provides Fe 31.8, Mn 3.3, and P 13.6 percent with the cumulative analysis low by about 8 percent. This formula, stated as oxides, computes to FeO 4.9, MnO 4.2, Fe_2O_3 40.0, P_2O_5 31.2, and H_2O 19.7 percent.

Optical Properties

Whitmoreite is biaxial (−), α 1.676(3), β 1.725 (4), 1.745(4), $2V$ 60–65°, and reveals near-parallel extinction with $b \parallel Y$ and $c \parallel Z$. The pleochroism is X, Y light greenish-brown, Z dark greenish-brown. Th calculated mean index of refraction, $\langle n \rangle = 1.76$, utilized the tables of oxide specific refractive energies (Larsen and Berman, 1934), and the Gladstone-Dale relationship.

Name

The mineral WHITMOREITE is named in honor of Mr. Robert W. Whitmore of Weare, New Hampshire, devoted collector of pegmatite minerals. Motivated by a keen interest in secondary phosphates, he quite literally overturned the dumps of the abandoned Fletcher pegmatite, bringing to light many fine specimens representing the complex phosphate paragenesis of a now-classic locality.

The species and name were approved by the International Commission on New Minerals and New Mineral Names (IMA). The type specimen has been deposited in the U.S. National Museum.

Whitmoreite: Its Atomic Arrangement

Owing to the persistence of twinning in whitmoreite and the relatively small size of the good crystals, it was not possible to secure a suitable fragment for the three-dimensional data collection by diffractometer.

Crystal structure analysis serves two important purposes in the elucidation of species: the knowledge of the atomic arrangement with the proposition of a precise structural formula; and the determination of bonding properties through interatomic distances and angles. We decided to unravel the whitmoreite structure by visual estimation of photographs on a limited data set, sacrificing the precision usually obtained from the more sophisticated diffractometric techniques. Our results are sufficiently accurate for unambiguous interpretation of the structure, but the errors in bond distances are about ±0.03 Å. Consequently, we shall emphasize only the salient features of the atomic arrangement in this study.

Experimental

A small 0.06 × 0.06 × 0.2 mm twinned crystal was mounted parallel to the *c*-axis and two sets of Weissenberg films of the *hk*0 to *hk*3 levels were collected utilizing unfiltered copper radiation. The films were exposed for 48 hours at 45 kV and 15 mA, the film pairs separated by an attenuating foil of aluminum. Individual intensities were gathered visually with a linear spot scale graded from one to ten. Care was taken to select only those intensities belonging to the same individual. For each reflection, we obtained four readings, including Cu$K\alpha$ and Cu$K\beta$, on the two sets of films. These were scaled and the results averaged. The 402 independent reflections were processed to obtain structure factors after Lorentz and polarization corrections. Since the cross-section of the crystal was only 60 μ × 60 μ and, since the scale factor for each level was varied, we did not correct for absorption.

Solution and Refinement of the Structure

The three-dimensional Patterson synthesis, $P(uvw)$, led to unambiguous interpretation of the two octahedral, Fe(1) and Fe(2), and one tetrahedral P cations. Fourier synthesis with these three atoms as input resolved the positions of all the unique remaining seven non-hydrogen atoms in the structure.

Least squares refinement on the IBM 370 computer proceeded from a local version of the familiar ORFLS program of Busing, Martin, and Levy (1962). Full-matrix scale factors (one for each level); multiplier for Fe(1); and atomic coordinate and isotropic thermal vibration parameters for all non-hydrogen atoms converged to $R(hkl) = [\sum ||F(\text{obs})| - |F(\text{calc})||/\sum |F(\text{obs})|] = 0.14$ for the 402 reflections. We employed the scattering curves for Fe^{2+}, P° and O^{1-} proposed by Cromer and Mann (1968). The results are listed in Table 2, and the structure factors are presented in Table 3. A final difference synthesis failed to reveal any additional atoms in the structure.

Topology and Geometry of the Structure

Whitmoreite possesses a new type of Fe^{3+}-O octahedral condensation, the essential features of which are shown in Figure 2. Each Fe^{3+}-O octa-

TABLE 2. Whitmoreite. Atomic Coordinates and Isotropic Thermal Vibration Parameters†

Atom	x	y	z	B(Å^2)
Fe(1) = 0.58(Fe,Mn)$^{2+}$ + 0.28Fe^{3+}	0.0000	0.0000	0.000	1.9(3)
Fe(2) = 1.0Fe^{3+}	.4603(5)	.1373(5)	.341(1)	2.7(2)
P	.3027(8)	.4256(8)	.325(2)	0.7(2)
O(1)	.393(2)	.477(2)	.124(4)	1.6(5)
O(2)	.359(2)	.481(2)	.579(4)	2.1(5)
O(3)	.158(2)	.482(2)	.275(4)	2.5(5)
O(4)	.304(2)	.262(2)	.317(4)	2.9(5)
OH	.556(2)	.235(2)	.076(4)	1.6(5)
OW(1)	.134(2)	-.102(2)	.298(4)	3.1(6)
OW(2)	.047(2)	.183(2)	.188(4)	3.3(6)

†Estimated standard errors refer to the last digit.

TABLE 3. Whitmoreite. Structure Factors (h, k, F_{obs}, F_{calc})

	L = 0		
0	2	72.9	72.5
0	4	32.2	27.0
0	6	24.6	23.0
0	8	45.1	46.0
1	1	60.8	63.8
1	2	39.6	39.4
1	3	39.5	39.1
1	4	46.5	47.3
1	5	37.9	38.6
1	6	18.3	21.0
1	7	16.7	15.6
1	8	22.2	18.8
1	9	9.3	3.2
2	1	49.0	51.6
2	2	22.8	22.7
2	3	87.3	79.9
2	4	19.1	23.2
2	5	6.8	3.8
2	6	71.2	70.0
2	7	8.5	9.5
2	8	54.1	51.2
2	9	9.3	7.2
3	0	23.6	27.5
3	1	8.4	9.3
3	2	46.2	48.3
3	3	22.6	27.8
3	4	86.2	81.9
3	5	63.8	55.3
3	6	8.0	6.3
3	7	27.7	27.4
3	8	24.5	23.5
3	9	34.7	30.7
4	0	21.7	23.5
4	1	28.6	29.1
4	2	30.2	32.0
4	3	28.4	30.5
4	4	21.3	21.4
4	5	68.4	70.2
4	6	14.6	11.3
4	7	9.0	9.8
4	8	16.1	12.0
4	9	39.6	39.0
5	0	18.4	20.2
5	1	35.0	41.4
5	2	36.3	40.4
5	3	32.5	36.0
5	4	58.8	57.8
5	5	74.9	67.1
5	6	54.9	56.6
5	7	13.1	11.1
5	8	22.7	26.0
5	9	8.7	4.3
6	0	47.0	52.1
6	1	29.0	32.3
6	2	38.6	43.7
6	3	38.7	40.4
6	4	20.7	18.2
6	5	23.6	20.5
6	6	13.0	10.3
6	7	18.6	16.3
6	8	9.0	10.4
7	0	65.5	66.8
7	1	49.5	48.5
7	2	19.1	19.6
7	3	35.1	36.7
7	4	12.8	9.2
7	5	24.5	22.3
7	6	16.1	15.4
8	0	23.9	24.3
8	1	9.0	9.1
8	2	30.3	33.7
8	3	13.1	8.9
8	4	22.9	25.2
8	5	35.9	36.6
8	6	28.4	34.6
9	0	26.4	20.7
9	1	9.3	0.9
9	2	9.3	5.2
9	3	9.2	9.9
9	4	9.1	4.1
10	0	8.9	5.1
	L = 1		
0	1	43.7	38.6
1	1	100.2	93.3
2	1	21.2	20.1
3	1	31.7	29.8
4	1	54.1	56.0
5	1	20.8	22.2
6	1	45.2	42.8
7	1	12.8	9.4
8	1	53.0	46.4
9	1	30.8	25.8
10	1	25.7	22.6
0	2	16.6	18.1
1	2	33.2	40.3
2	2	134.6	122.4
3	2	74.3	73.5
4	2	86.8	93.9
5	2	18.6	19.0
6	2	11.9	3.9
7	2	34.5	31.8
8	2	10.4	17.5
9	2	13.7	0.2
10	2	28.3	22.5
0	3	62.5	64.9
1	3	46.3	43.0
2	3	48.4	46.6
3	3	64.2	62.8
4	3	10.2	4.1
5	3	45.3	40.2
6	3	12.4	6.9
7	3	51.7	45.7
8	3	19.5	10.5
9	3	42.8	36.0
0	4	87.2	86.1
1	4	30.0	26.5
2	4	25.1	22.7
3	4	10.2	5.6
4	4	11.0	6.1
5	4	26.9	24.1
6	4	36.7	32.2
7	4	13.6	7.1
8	4	13.8	16.4
9	4	13.1	1.8
0	5	50.6	50.7
1	5	32.5	26.4
2	5	56.5	59.5
3	5	42.2	36.6
4	5	31.8	28.8
5	5	22.2	19.0
6	5	13.5	8.3
7	5	13.8	5.5
0	6	51.1	46.0
1	6	61.1	57.3
2	6	31.4	25.0
3	6	27.6	21.4
4	6	22.4	15.9
5	6	26.9	22.4
6	6	23.9	19.8
7	6	13.7	6.5
0	7	25.3	19.7
1	7	25.4	20.4
2	7	51.9	47.4
3	7	23.0	21.1
4	7	13.6	5.1
5	7	13.8	4.1
6	7	59.9	56.8
7	7	43.6	36.2
0	8	35.9	29.6
1	8	33.3	22.7
2	8	13.7	5.7
3	8	13.8	4.7
4	8	13.8	11.1
5	8	43.1	29.5
-1	1	20.6	24.1
-2	1	6.4	1.2
-3	1	108.2	129.8
-1	2	63.5	69.5
-2	2	59.8	78.8
-3	2	8.2	9.9
-4	2	9.3	6.8
-5	2	36.3	49.2
-1	3	34.6	43.6
-2	3	30.9	35.7
-3	3	33.9	42.7
-4	3	59.3	73.0
-5	3	19.2	23.9
-6	3	45.6	65.6
-1	4	21.9	15.1
-2	4	13.2	11.0
-3	4	10.0	2.4
-4	4	10.8	4.9
-5	4	20.4	22.0
-6	4	12.7	16.1
-7	4	23.4	38.4
-1	5	17.7	11.0
-2	5	31.7	31.6
-3	5	15.7	18.4
-4	5	59.2	73.0
-5	5	21.8	24.3
-6	5	29.8	33.9
-1	6	34.5	35.0
-2	6	11.7	3.2
-3	6	12.2	12.4
-4	6	18.1	15.8
-5	6	13.3	2.3
-6	6	13.7	8.3
-7	6	27.6	30.8
-1	7	78.3	80.8
-2	7	38.7	37.5
-3	7	29.5	28.2
-4	7	13.5	5.7
-5	7	55.3	57.3
-6	7	33.8	29.7
-7	7	32.6	31.2
-1	8	13.6	6.2
-2	8	13.7	6.3
-3	8	13.8	6.1
-4	8	13.8	11.7
-5	8	13.7	19.7
-6	8	22.8	2.8
	L = 2		
1	0	59.7	68.9
2	0	17.6	14.7
3	0	49.4	46.9
4	0	12.6	13.9
5	0	100.5	105.1
6	0	99.3	100.1
7	0	52.0	50.7
8	0	12.3	18.1
9	0	11.9	11.9
0	1	38.4	38.1
1	1	25.7	24.2
2	1	40.9	33.2
3	1	11.2	5.8
4	1	32.6	30.1
5	1	10.1	2.1
6	1	11.1	7.8
7	1	43.2	37.9
8	1	21.3	17.7
0	2	26.4	19.5
1	2	11.7	8.0
2	2	82.7	92.1
3	2	23.9	22.2
4	2	63.3	57.2
5	2	20.9	19.9
6	2	11.4	7.6
7	2	12.1	5.6
8	2	34.8	32.9
0	3	53.5	45.6
1	3	42.8	38.7
2	3	14.5	11.6
3	3	22.3	25.1
4	3	43.5	37.6
5	3	15.4	18.7
6	3	11.7	8.2
7	3	38.7	31.4
8	3	29.9	27.7
0	4	64.4	59.5
1	4	33.2	30.0
2	4	88.4	88.1
3	4	28.1	23.7
4	4	58.5	51.5
5	4	11.4	2.9
6	4	39.9	30.4
7	4	12.3	3.2
8	4	31.7	25.0
0	5	36.6	34.3
1	5	77.1	74.5
2	5	61.0	60.7
3	5	28.6	24.2
4	5	16.1	13.4
5	5	41.4	32.5
6	5	12.3	1.0
7	5	12.2	9.8
0	6	28.7	27.2
1	6	24.5	18.8
2	6	11.2	11.9
3	6	52.0	51.6
4	6	29.4	21.2
5	6	17.3	8.2
6	6	27.4	26.4
7	6	23.6	15.0
0	7	23.5	22.3
1	7	11.8	12.3
2	7	26.8	21.3
3	7	17.2	14.1
4	7	12.3	0.8
5	7	12.2	5.9
0	8	12.3	17.4
1	8	17.4	11.1
2	8	12.3	10.1
3	8	61.4	57.7
4	8	20.9	15.5
-1	1	77.7	85.3
-2	1	19.3	28.7
-3	1	16.7	23.3
-4	1	19.1	26.9
-1	2	48.7	45.3
-2	2	16.0	18.4
-3	2	78.2	93.4
-4	2	8.9	4.2
-5	2	22.3	29.2
-1	3	45.3	41.8
-2	3	32.4	37.7
-3	3	8.7	1.4
-4	3	31.8	30.9
-5	3	25.7	31.0
-1	4	23.1	18.5
-2	4	24.0	20.5
-3	4	48.2	52.2
-4	4	10.3	1.3
-5	4	24.8	29.1
-6	4	11.8	4.9
-7	4	27.4	31.5
-1	5	36.8	38.5
-2	5	64.0	61.1
-3	5	62.5	65.0
-1	6	59.8	55.8
-2	6	33.3	32.3
-3	6	39.7	40.1
-4	6	45.9	47.9
-1	7	11.8	14.1
-2	7	23.8	26.0
-3	7	24.2	20.9
-4	7	12.2	1.8
-1	8	27.5	24.7
-2	8	12.3	1.2
-3	8	12.3	10.7
-4	8	42.2	44.5
	L = 3		
0	1	38.0	40.6
1	1	25.1	25.1
2	1	79.0	81.4
3	1	24.9	16.8
4	1	18.1	15.4
5	1	51.3	48.4
6	1	12.2	8.2
7	1	12.5	9.7
8	1	32.1	34.4
0	2	21.7	22.6
1	2	36.5	30.2
2	2	29.7	23.9
3	2	32.7	27.2
4	2	64.1	64.0
5	2	35.1	27.6
6	2	12.3	3.6
7	2	21.6	15.9
8	2	33.9	33.2
0	3	15.3	11.4
1	3	50.3	47.4
2	3	13.8	9.8
3	3	57.7	57.4
4	3	11.3	3.4
5	3	52.4	47.3
6	3	12.4	3.3
7	3	12.4	3.7
0	4	10.0	8.6
1	4	17.7	13.6
2	4	10.6	6.8
3	4	15.9	16.8
4	4	16.7	12.3
5	4	12.3	4.7
6	4	48.5	44.3
7	4	21.1	19.4
0	5	11.0	10.7
1	5	11.2	5.1
2	5	20.0	20.4
3	5	50.7	49.3
4	5	12.3	12.7
5	5	28.0	25.3
6	5	12.3	11.3
0	6	11.9	2.9
1	6	20.8	16.6
2	6	12.2	9.4
3	6	12.4	7.5
4	6	12.5	6.1
5	6	30.3	25.1
6	6	35.5	31.6
0	7	68.3	71.1
1	7	33.0	27.4
2	7	25.0	17.9
3	7	12.4	11.5
4	7	44.2	41.0
5	7	11.7	17.2
0	8	12.4	3.9
1	8	24.7	24.7
2	8	27.3	21.4
-1	1	6.6	4.1
-2	1	63.5	74.4
-3	1	27.4	28.7
-4	1	13.8	20.9
-1	2	20.6	13.5
-2	2	22.2	24.3
-3	2	41.3	49.9
-4	2	47.8	62.3
-5	2	35.2	48.0
-1	3	74.8	77.8
-2	3	9.3	10.9
-3	3	54.8	65.0
-4	3	10.7	5.9
-5	3	20.0	23.6
-1	4	43.8	39.8
-2	4	25.3	24.6
-3	4	10.8	8.5
-4	4	11.4	2.5
-5	4	12.0	6.8
-6	4	21.5	30.0
-1	5	24.8	19.2
-2	5	11.3	3.4
-3	5	42.1	44.8
-4	5	17.0	15.4
-5	5	12.4	10.2
-6	5	12.5	16.0
-1	6	16.9	14.7
-2	6	20.2	23.2
-4	6	12.4	10.8
-5	6	25.0	26.2
-6	6	21.2	23.3
-1	7	24.9	19.9
-2	7	25.0	19.3
-3	7	21.7	31.3
-4	7	24.8	21.0
-1	8	21.9	18.5
-2	8	17.4	17.1

hedron has four of its six vertices linked to other equivalent octahedra. One pair of these constitutes a shared edge O(1)-O(1)^{i} and the remaining two corner-link via the (OH)$^-$ ligands. The two (OH)$^-$ ligands occur on adjacent vertices so that they can be regarded in *cis*-configuration with respect to an octahedron. It is noted that the (OH)$^-$ linkages define a step-like corner-chain parallel to [001], which is roughly the distance of two octahedral edges. These chains share O(1)-O(1)^{i} edges with equivalent chains to form an open sheet parallel to {100}. Above and below this sheet, the [PO$_4$] tetrahedra share three of their four vertices with the octahedra to form a slab with formal composition $[Fe^{3+}{}_2(OH)_2[PO_4]_2]^{2-}$. Denoting oxygens associated with the [PO$_4$] tetrahedra as O_P, the octahedral component can be written $[Fe^{3+}{}_2(OH)_2(O_P)_6]$. The slabs are bridged by the Fe(1)-O insular octahedra, ideally written $[Fe^{2+}(O_P)_2(H_2O)_4]$, where O_P are the tetrahedral oxygens not associated with the sheets.

Refinement of the crystal structure showed that the Fe(1) site is only partly occupied. The interatomic distance averages indicate that this partial occupancy results from the presence of some iron in a higher valence state. We propose the distribution Fe(1) = 0.58 (Fe,Mn)$^{2+}$ + 0.28 Fe^{3+} + 0.14 Hole. Noting further that all water molecules are ligands in the structure, the ideal end-member formula for whitmoreite is $Fe^{2+}Fe^{3+}{}_2(OH)_2(H_2O)_4[PO_4]_2$. In real crystals, the Fe(1) site is partly replaced by Mn^{2+} and Fe^{3+}, the latter resulting in disordered vacancies.

Interatomic Distances

Errors in interatomic distances are estimated to be ± 0.03 Å for Me-O bonds and ± 0.04 Å for O-O′ edges. Polyhedral interatomic distances and their averages are listed in Table 4. We note that the Fe(1)-O average, 2.14 Å, is close to the 2.13 Å value calculated for $(Fe^{2+}_{0.31}Mn^{2+}_{0.27}Fe^{3+}_{0.28})$-O using the ionic radii from the tables of Shannon and Prewitt (1969). As expected, the 2.66 Å distance for the shared edge, O(1)-O(1)^{i}, is the shortest for the Fe^{3+}-O octahedron.

Hydrogen Bonds

The $(OH)^-$, OW(1), and OW(2) molecules are potential donors of hydrogen bonds. Since the Fe(1)-O octahedron is insular with respect to other octahedra, it has sufficient geometrical freedom to admit hydrogen bonds.

We propose the hydrogen bonds summarized in Table 4. The corresponding angles are O(3)-OW(1)-O(2), 100°, and OW(2)′-OW(2)-O(4), 93°. The network of OW . . . O bonds connect the $Fe(1)(O_P)_2(H_2O)_4$ octahedron to the octahedral slabs and are cut by the {100} plane. In this model, OW(2) both donates and receives bonds; other possible geometries result either in very long distances—OW(2)^{i}. . . O(3), 3.69 Å—or unreasonable angles—O(3)-OW(2)-O(4), 52°. According to this model, O(1) receives no hydrogen bonds; O(3) and O(4) each receives one bond; and O(2) receives two bonds. This is consistent with the electrostatic valence balance of cations about anions. Only O(1) is oversaturated since it bonds to two Fe^{3+} cations and one P^{5+} cation.

TABLE 4. Whitmoreite. Polyhedral Interatomic Distances†

Fe(1)		Fe(2)	
2 Fe(1)-O(3)^{i}	2.05 Å	Fe(2) -O(4)	1.96
2 " -OW(2)	2.11	" -OH^{i}	1.99
2 " -OW(1)	2.26	" -OH	2.01
		" -O(2)^{i}	2.05
average	2.14	" -O(1)^{i}	2.05
		" -O(1)^{ii}	2.15
2 O(3)^{i}-OW(2)^{iii}	2.85	average	2.04
2 OW(1)-OW(2)	2.95		
2 O(3)^{i}-OW(1)^{iii}	3.02	O(1)^{i} -O(1)^{ii}	2.66*
2 O(3)^{i}-OW(2)	3.05	OH -OH^{i}	2.76
2 O(3)^{i}-OW(1)	3.12	O(2)^{i} -O(4)	2.78
2 OW(2)-OW(1)^{iii}	3.20	O(4) -OH^{i}	2.79
average	3.03	OH -O(2)^{i}	2.88
		O(1)^{ii}-O(2)^{i}	2.88
P		O(1)^{i} -OH^{i}	2.89
		OH -O(4)	2.94
1 P-O(1)	1.53	O(1)^{i} -O(4)	2.96
1 "-O(3)	1.54	O(1)^{i} -O(2)^{i}	2.98
1 "-O(2)	1.56	O(1)^{ii}-OH$_{i}$	3.02
1 "-O(4)	1.61	O(1)^{ii}-OH^{i}	3.07
average	1.56	average	2.88
		Hydrogen Bonds	
1 O(1) -O(3)	2.50		
1 O(2) -O(3)	2.50		
1 O(1) -O(2)	2.51	OW(2) ...OW(2)^{i}	3.03
1 O(1) -O(4)	2.54	OW(2) ...O(4)	2.72
1 O(3) -O(4)	2.61	OH^{ii} ...O(2)	2.76
1 O(2) -O(4)	2.62	OW(1)^{i}...O(3)	2.89
average	2.55	OW(1) ...O(2)	2.91

*Shared edge between Fe^{3+} atoms.

†i = x, 1/2-y, 1/2+z, ii = -x, 1/2+y, 1/2-z, iii = -x, -y, -z referred to coordinates in Table 2.

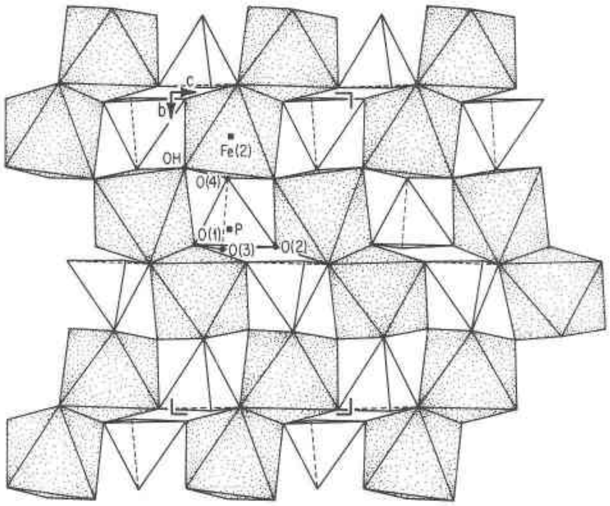

FIG. 2. Polyhedral diagram of the whitmoreite crystal structure down the z^*-axis. The Fe^{3+}–O octahedral sheet is stippled, and the linking $[PO_4]$ tetrahedra above and below the sheet are unshaded. The Fe(1)–O octahedron between the sheets is omitted.

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References

BUSING, W. A., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Nat. Tech. Inform. Serv.* ORNL-TM-**305.**

CROMER, D. T., AND J. B. MANN (1968) X-ray scattering factors computed from numerical Hartree-Fock wavefunctions. *Acta. Crystallogr.* **A24,** 321–324.

LARSEN, E. S., AND H. BERMAN (1934) The microscopic determination of the nonopaque minerals. 2nd ed. *U.S. Geol. Surv. Bull.* **848,** 31.

MOORE, P. B. (1973) Pegmatite phosphates: mineralogy and crystal chemistry. *Mineral. Rec.* **4,** 103–130.

SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B25,** 925–946.

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