

REFINEMENT OF THE CRYSTAL STRUCTURE OF USHKOVITE FROM NEVADOS DE PALERMO, REPÚBLICA ARGENTINA

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ABSTRACT

The crystal structure of ushkovite, triclinic, a 5.3468(4), b 10.592(1), c 7.2251(7) Å, α 108.278(7), β 111.739(7), γ 71.626(7)°, V 351.55(6) Å³, $Z = 2$, space group $P\bar{1}$, has been refined to an R index of 2.3% for 1781 observed reflections measured with MoK α X-radiation. The crystal used to collect the X-ray-diffraction data was subsequently analyzed with an electron microprobe, to give the formula (Mg_{0.97} Mn²⁺_{0.01}) (H₂O)₄ [(Fe³⁺_{1.99} Al_{0.03}) (PO₄) (OH) (H₂O)₂]₂ (H₂O)₂, with the (OH) and (H₂O) groups assigned from bond-valence analysis of the refined structure. Ushkovite is isostructural with laueite. Chains of corner-sharing {Fe³⁺ O₂ (OH)₂ (H₂O)₂} octahedra extend along the c axis and are decorated by (PO₄) tetrahedra to form [Fe³⁺₂ O₄ (PO₄)₂ (OH)₂ (H₂O)₂] chains. These chains link *via* sharing between octahedron and tetrahedron corners to form slabs of composition [Fe³⁺₂ (PO₄)₂ (OH)₂ (H₂O)₂] that are linked by {Mg O₂ (H₂O)₄} octahedra.

Keywords: ushkovite, crystal-structure refinement, electron-microprobe analysis.

SOMMAIRE

Nous avons affiné la structure cristalline de l'ushkovite, triclinique, a 5.3468(4), b 10.592(1), c 7.2251(7) Å, α 108.278(7), β 111.739(7), γ 71.626(7)°, V 351.55(6) Å³, $Z = 2$, groupe spatial $P\bar{1}$, jusqu'à un résidu R de 2.3% en utilisant 1781 réflexions observées mesurées avec rayonnement MoK α . Le même cristal a par la suite été analysé avec une microsonde électronique pour établir la formule chimique, (Mg_{0.97} Mn²⁺_{0.01}) (H₂O)₄ [(Fe³⁺_{1.99} Al_{0.03}) (PO₄) (OH) (H₂O)₂]₂ (H₂O)₂, les groupes (OH) et (H₂O) étant assignés selon une analyse des valences de liaison à partir de la structure affinée. L'ushkovite possède la même structure que la laueite. Des chaînes d'octaèdres {Fe³⁺ O₂ (OH)₂ (H₂O)₂} liés par partage de coins sont parallèles à l'axe c et sont décorées avec des tétraèdres (PO₄) pour former des chaînes de stoechiométrie [Fe³⁺₂ O₄ (PO₄)₂ (OH)₂ (H₂O)₂]. Ces chaînes sont liées entre elles par partage de coins d'octaèdres et de tétraèdres pour former des panneaux de composition [Fe³⁺₂ (PO₄)₂ (OH)₂ (H₂O)₂]; à leur tour, ceux-ci sont liés par des octaèdres {Mg O₂ (H₂O)₄}.

(Traduit par la Rédaction)

Mots-clés: ushkovite, affinement de la structure cristalline, analyse à la microsonde électronique.

INTRODUCTION

Ushkovite, ideally Mg (H₂O)₄ [Fe³⁺₂ (PO₄)₂ (OH)₂ (H₂O)₂] (H₂O)₂, is a transition-metal phosphate mineral first described by Chesnokov *et al.* (1983) from a granitic pegmatite in the Il'men Mountains, Urals, Russia. It was described as a product of supergene weathering of triplite, and is associated with carbonate-fluorapatite, beraunite, mitridatite and hydrous Mn-oxides. The cell dimensions, symmetry and chemical formula (Chesnokov *et al.* 1983) indicate that ushkovite is

isostructural with laueite (Baur 1969a). We have long been interested in the crystal chemistry of hydroxy-hydrated oxysalt-minerals, particularly the role of H in their structures (Hawthorne 1992, 1997), and here we report a crystal-structure refinement of ushkovite, focusing in particular on the hydrogen-bond arrangement and the different roles of H₂O in the structure. As shown by Hawthorne (1994, 1997) and Schindler & Hawthorne (2001a, b, c), hydrogen bonds play a major role in controlling the chemical composition and stability of hydroxy-hydrated oxysalt minerals.

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OCCURRENCE

Ushkovite occurs in the El Peñón granitic pegmatite, located at 24°50'S, 66°19'39"W, 3920 m above sea level in the El Quemado pegmatite field, Nevados de Palermo, Salta Province, República Argentina. El Peñón is a rare-element pegmatite of the beryl type, beryl – columbite – phosphate subtype (Černý 1991); it is discordantly emplaced in mottled cordierite-bearing mica schists. It is 60 m long by 4 to 10 m wide, approximately tabular, and has an N40–45°W strike and 65° southwest dip. The pegmatite body is zoned, and consists of border, wall and intermediate zones, a core zone and transitional units close to the border between the intermediate zone and the core (Galliski 1983). The border zone is 0.05 m wide, with fine-grained quartz, plagioclase (An_{14–18}) and muscovite as the main minerals, and apatite and schorl as accessory phases. The wall zone is medium grained, with quartz, plagioclase (An_{8–10}), K-feldspar and muscovite as essential minerals. It passes with an increasing grain-size to the intermediate zone, which contains the same mineral assemblage. The core is composed of massive milky quartz. The pegmatite was mined for tantalite in 1943–45, first in the alluvium, and then in two small quarries opened at each end of the pegmatite. The principal accessory minerals are concentrated at the outer margin of the core and in the transitional units (which do not represent more than 1–2% by volume of the pegmatite). They include white to yellowish beryl, tourmaline, fine-grained muscovite,

bismuthinite, columbite, tantalite, uraninite, Mn-oxides, microlite, tapiolite, triphylite–lithiophilite, eosphorite, brazilianite, arrojadite–dickinsonite, bederite (Galliski *et al.* 1999), fairfieldite, phosphosiderite and ushkovite. Samples of secondary phosphates are common in the dumps. Ushkovite, originally identified as laueite (Galliski 1983), usually occurs as ≤0.6 mm idiomorphic crystals (Fig. 1), light orange to dark honey yellow in color (Fig. 2), that normally form clusters on the surface of millimeter-sized cavities in quartz or albite. These cavities in some cases contain ushkovite and manganese oxides that replace some dark, altered and unknown phosphate, of which relics persist.

EXPERIMENTAL

The crystal selected for collection of X-ray intensity data was mounted on a Siemens P4 automated four-circle diffractometer. Thirty reflections were aligned using MoK α X-radiation; the cell dimensions were determined by least-squares refinement of the setting angles, and the values are given in Table 1. A total of 2172 intensities was collected over one asymmetric unit with the index ranges $7 \leq h \leq 7$, $0 \leq k \leq 14$, $10 \leq l \leq 9$ at a fixed scan-speed of 1.5°/min. Other conditions were as described by Hawthorne & Groat (1985). A psi-scan absorption correction reduced $R(\text{azimuthal})$ from 2.2 to 0.9°, with the crystal modeled as a triaxial ellipsoid; application of this absorption correction to the intensity data and making the usual geometrical corrections re-

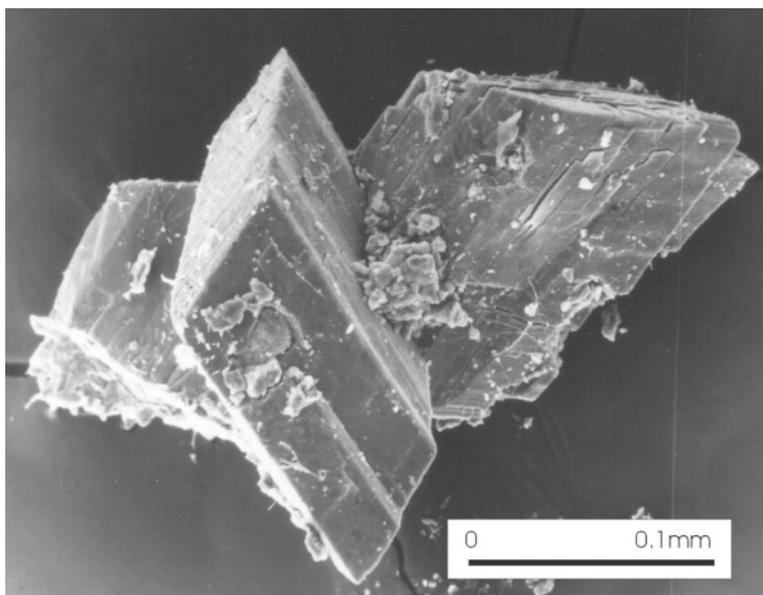


FIG. 1. SEM image of crystals of ushkovite.



FIG. 2. An aggregate of pale yellow crystals of ushkovite.

sulted in 2067 unique reflections, of which 1781 were considered as observed (greater than 5σ above background).

All calculations were done with the SHELXTL PC(PLUS) system of programs; R indices are of the form given in Table 1. Using the atom parameters of gordonite (Leavens & Rheingold 1988), the structure of ushkovite was refined to convergence and all H posi-

tions were then found on difference-Fourier maps. All non-H atoms were represented with anisotropic displacements, the isotropic displacements for the H atoms were fixed (Table 2), and the structure was refined to convergence at an R -index of 2.3% with soft constraints (Rollet 1970) ($O-H \approx 0.98 \text{ \AA}$) on all H atoms. Final positions and displacement parameters are listed in Table 2, selected interatomic distances are given in Table 3, and a bond-valence table is given as Table 4. Structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Subsequent to the collection of the X-ray intensity data, the crystal was embedded in epoxy preparatory to analysis with an electron microprobe. However, during this procedure, the crystal dehydrated and was no longer suitable for electron-microprobe analysis. Another crystal was selected and was attached to the surface of a clear plastic disk with a crystal face horizontal. The disk was carbon-coated, and the crystal was analyzed with a Cameca SX-50 instrument operating in wavelength-dis-

TABLE 1. USHKOVITE: CRYSTAL DATA AND REFINEMENT INFORMATION

a (Å)	5.3468(4)	Crystal size (mm)	0.04 x 0.08 x 0.10
b	10.592(1)	Radiation	MoK α
c	7.2251(7)	Total unique $ F_o $	2067
α (°)	108.278(7)	No. $ F_o > 5\sigma$	1781
β	111.739(7)	$R(\text{obs})$ %	2.3
γ	71.626(7)	$wR(\text{obs})$ %	2.3
V (Å ³)	351.55(6)		
Sp. Gr.	$P\bar{1}$		

Unit cell contents: $2\{(Mg_{0.97}Mn^{2+}_{0.01})(H_2O)_4[(Fe^{3+}_{1.99}Al_{0.01})(PO_4)_2(OH)_2(H_2O)_2](H_2O)_2\}$
 $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$
 $wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma F_o^2]^{1/2}$, $w = 1/\sigma^2 F \cdot [1 - \exp(-1.5(\sin\theta/\lambda)^2)]$

TABLE 2. ATOM COORDINATES AND DISPLACEMENT FACTORS FOR USHKOVITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{eq}
<i>M</i> (1)	0	0	0	0.0088(4)	0.0087(4)	0.0170(4)	0.0034(4)	0.0042(3)	-0.0012(3)	0.0114(3)
<i>M</i> (2)	0	1/2	0	0.0076(2)	0.0098(2)	0.0064(2)	0.0023(1)	0.0020(1)	-0.0023(1)	0.0077(1)
<i>M</i> (3)	0	1/2	1/2	0.0091(2)	0.0113(2)	0.0066(2)	0.0020(1)	0.0018(1)	-0.0033(1)	0.0089(1)
<i>P</i>	0.34610(9)	0.67354(5)	0.93022(7)	0.0064(2)	0.0078(2)	0.0079(2)	0.0022(2)	0.0018(2)	-0.0016(2)	0.0074(2)
O(1)	0.1722(3)	0.6547(1)	0.0437(2)	0.0110(6)	0.0110(6)	0.0123(6)	0.0022(5)	0.0057(5)	-0.0036(5)	0.0106(5)
O(2)	0.3029(3)	0.5785(2)	0.7154(2)	0.0107(6)	0.0147(6)	0.0082(6)	0.0000(5)	0.0020(5)	-0.0050(5)	0.0116(5)
O(3)	0.2670(3)	0.8221(1)	0.9125(2)	0.0120(6)	0.0090(6)	0.0190(7)	0.0055(5)	0.0058(5)	0.0000(5)	0.0130(5)
O(4)	0.3433(3)	0.3623(1)	0.9488(2)	0.0062(5)	0.0127(6)	0.0094(6)	0.0023(5)	0.0011(5)	-0.0010(5)	0.0101(5)
O(5) = (OH)	0.1575(3)	0.5047(2)	0.2979(2)	0.0085(6)	0.0225(7)	0.0076(6)	0.0052(5)	0.0017(5)	-0.0040(5)	0.0125(5)
O(6) = (H ₂ O)	0.2396(3)	0.3058(2)	0.5443(3)	0.0149(7)	0.0161(7)	0.0122(6)	0.0034(5)	0.0028(5)	-0.0008(5)	0.0154(5)
O(7) = (H ₂ O)	0.2326(4)	0.0053(2)	0.3102(3)	0.0280(9)	0.0282(9)	0.0204(8)	0.0064(7)	0.0014(7)	-0.0047(7)	0.0275(7)
O(8) = (H ₂ O)	0.2274(4)	0.1104(2)	0.9685(3)	0.0155(8)	0.0160(8)	0.0678(14)	0.0160(8)	0.0176(8)	-0.0007(6)	0.0307(8)
O(9) = (H ₂ O)	0.2634(4)	0.8043(2)	0.5093(3)	0.0267(9)	0.0326(10)	0.0253(9)	0.0103(7)	0.0107(7)	-0.0065(7)	0.0264(7)
H(1)	0.3590(9)	0.480(4)	0.329(6)							0.0500*
H(2)	0.295(8)	0.318(4)	0.6930(8)							0.0500*
H(3)	0.416(4)	0.271(4)	0.514(6)							0.0500*
H(4)	0.231(8)	0.096(2)	0.402(5)							0.0500*
H(5)	0.209(8)	-0.053(3)	0.381(5)							0.0500*
H(6)	0.128(7)	0.205(1)	0.966(6)							0.0500*
H(7)	0.423(2)	0.111(4)	0.008(6)							0.0500*
H(8)	0.253(8)	0.818(4)	0.647(2)							0.0500*
H(9)	0.160(7)	0.735(3)	0.416(5)							0.0500*

* fixed during refinement

persion mode at 15 kV and 10 nA and with a 25 µm beam using the following standards: mariçite (P, Fe), andalusite (Al), spessartine (Mn), and forsterite (Mg). The chemical composition of ushkovite is given in Table 5; it was normalized to eighteen O atoms per formula unit (*pfu*), with OH = 2 *pfu* and H₂O = 8 *pfu*. The calculated amount of H₂O (as determined from the crystal structure) is 37.43 wt.%. Ushkovite degraded rapidly under the electron beam in the electron microprobe; the anomalously high oxide total when the known amount of H₂O is included, 116.36 wt.%, is in accord with dehydration of the crystal during analysis.

DISCUSSION

Cation coordination

There is one unique *P* site completely occupied by P that is coordinated by four O atoms in a tetrahedral arrangement; the <P–O> distance of 1.539 Å is close to the grand <P–O> distance of 1.537 Å reported by Baur (1974). There are three *M* sites, each coordinated by six anions in an octahedral arrangement. From the site-scattering values, the *M*(1) site is occupied by species with a *Z* (mean atomic number) value of ~12. Thus the unit formula (Table 5) calculated from the chemical composition indicates that *M*(1) is occupied dominantly by Mg, and the <*M*(1)–O> distance of 2.069 Å (Table 3) and incident bond-valence of 2.12 valence units (*vu*)

(Table 4) are in accord with this assignment. The site-scattering at the *M*(2) and *M*(3) sites and the unit formula (Table 5) indicate that these sites are occupied predominantly by Fe. The <*M*(2)–O> and <*M*(3)–O> distances of ~2.01 Å (Table 3) and the incident bond-valence sums of ~3.01 *vu* (Table 4) indicate that the Fe is in the trivalent state.

Structure topology

The *M*(2)φ₆ (φ: unspecified anion) and *M*(3)φ₆ octahedra link through *trans* vertices to form an [*M*φ₅] chain extending in the *c* direction; individual *M*φ₆ octahedra link through (OH) groups [the O(5) anion, Table 4]. The [*M*φ₅] chain is decorated by (PO₄) tetrahedra that share corners with adjacent octahedra and assume a staggered configuration along the length of the chain; the resulting [*M*₂ (PO₄)₂ (OH)₂ O₂ (H₂O)₂] chain ([*M*₂ (TO₄)₂ φ₆] is shown in Figure 3. Adjacent chains link directly by sharing octahedron and tetrahedron corners to form a slab of composition [*M*₂ (PO₄)₂ (OH)₂ (H₂O)₂] in the (010) plane (Fig. 4). Note that this slab can also be considered as [*M* (PO₄)₂ φ₂] chains (designated as the kröhnkite-like chain by Hawthorne 1985, 1997), extending in the *a* direction and linked by {MO₄(H₂O)₂} octahedra. Note that the *c* and *a* unit-cell dimensions are defined by repeat distances of the [*M*₂ (TO₄)₂ φ₆] chain (~ 7 Å) and the [*M* (TO₄)₂ φ₂] chain (~ 5.4 Å). These slabs are linked into a three-

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN USHKOVITE

$M(1)-O(3)_{a,h}$	2.053(1)	$M(2)-O(1)_{,b}$	2.011(2)
$M(1)-O(7)_{,c}$	2.115(2)	$M(2)-O(4)_{d,h}$	2.028(1)
$M(1)-O(8)_{d,e}$	<u>2.040(3)</u>	$M(2)-O(5)_{,b}$	<u>1.990(1)</u>
$\langle M(1)-O \rangle$	2.069	$\langle M(2)-O \rangle$	2.010
$P-O(1)_{,f}$	1.536(2)	$M(3)-O(2)_{,h}$	1.976(1)
$P-O(2)$	1.542(1)	$M(3)-O(5)_{,h}$	1.956(2)
$P-O(3)$	1.528(2)	$M(3)-O(6)_{,h}$	<u>2.103(1)</u>
$P-O(4)_{,g}$	<u>1.550(1)</u>	$\langle M(3)-O \rangle$	2.012
$\langle P-O \rangle$	1.539		
$O(5)-H(1)$	0.980(7)	$H(1)-O(2)_{,i}$	1.83(2)
$O(6)-H(2)$	0.98(1)	$H(2)-O(4)$	1.70(1)
$O(6)-H(3)$	0.98(3)	$H(3)-O(9)_{,j}$	1.69(3)
$H(2)-H(3)$	1.54(5)	$H(2)-O(6)-H(3)$	103(3)
$O(7)-H(4)$	0.98(2)	$H(4)-O(6)$	2.15(2)
$O(7)-H(5)$	0.98(5)	$H(5)-O(9)_{,j}$	1.90(4)
$H(4)-H(5)$	1.58(5)	$H(4)-O(7)-H(5)$	107(3)
$O(8)-H(6)$	0.98(2)	$H(6)-O(1)_{,h}$	1.81(3)
$O(8)-H(7)_{,f}$	0.98(2)	$H(7)_{,f}-O(3)_{,g}$	1.83(3)
$H(6)-H(7)_{,f}$	1.56(4)	$H(6)-O(8)-H(7)_{,f}$	105(3)
$O(9)-H(8)$	0.98(3)	$H(8)-O(3)$	1.88(3)
$O(9)-H(9)$	0.98(3)	$H(9)-O(5)$	2.32(3)
$H(8)-H(9)$	1.59(4)	$H(8)-O(9)-H(9)$	109(4)
$O(5)-H(1)-O(2)$	159(4)		
$O(6)-H(2)-O(4)$	170(3)	$O(8)-H(6)-O(1)_{,h}$	154(4)
$O(6)-H(3)-O(9)_{,j}$	170(4)	$O(8)-H(7)_{,f}-O(3)_{,g}$	159(4)
$O(7)-H(4)-O(6)$	166(4)	$O(9)-H(8)-O(3)$	173(3)
$O(7)-H(5)-O(9)_{,j}$	164(3)	$O(9)-H(9)-O(5)$	147(2)

a: $x, -1+y, -1+z$; b: $-x, 1-y, -z$; c: $-x, -y, -z$; d: $x, y, -1+z$;
e: $-x, -y, 1-z$; f: $x, y, 1+z$; g: $1-x, 1-y, 2-z$; h: $-x, 1-y, 1-z$;
i: $1-x, 1-y, 1-z$; j: $x, -1+y, z$.

dimensional structure by $\{M O_2 (H_2O)_4\}$ octahedra ($M = Mg$) (Fig. 5); two vertices of each octahedron are shared with (PO_4) tetrahedra of adjacent $[M_2 (PO_4)_2 (OH)_2 (H_2O)_2]$ slabs, and the remaining vertices of the octahedra are (H_2O) groups.

Hydrogen bonding

All H atoms in ushkovite were located during refinement, and a stereochemically reasonable hydrogen-bonding scheme results, with all $H \cdots O$ bonds in the range 1.69–2.32 Å and $O-H \cdots O$ angles in the range 147–173°; in addition, the $H-O-H$ angles of the (H_2O) groups are in the range 103–109° (*i.e.*, not differing significantly from the ideal $H-O-H$ angle of $\sim 105^\circ$).

The $O(5)$ anion is an (OH) group, and the $O(6)-O(9)$ anions are (H_2O) groups (Table 4). The $H(1)$ atom that is part of the (OH) group at $O(5)$ hydrogen bonds to an $O(2)$ anion in an adjacent chain in the same slab. The (H_2O) groups involving the $O(6)$, $O(7)$ and $O(8)$ atoms are bonded to octahedrally coordinated cations: Mg at $M(1)$ for $O(7)$ and $O(8)$, and Fe^{3+} at $M(3)$ for $O(6)$; note the long $M(3)-O(6)$ bonds (Tables 3, 4). The $O(6)$ atom links to $H(2)$ and $H(3)$, which hydrogen bond to $O(4)$ and $O(9)$, respectively. The $O(4)$ anion is only [2]-coordinated (ignoring any hydrogen bonds), and its incident bond-valence from $M(2)$ and P are the lowest values

TABLE 5. CHEMICAL COMPOSITION (wt. %) AND UNIT FORMULA (*apfu*)* OF USHKOVITE

P_2O_5	32.70	P	2.00
Al_2O_3	0.36		
Fe_2O_3	36.61	Al	0.03
FeO	0.29	Fe^{3+}	<u>1.99</u>
MnO	0.21	Σ	2.02
MgO	<u>9.05</u>		
Σ	78.93	Mg	0.97
		Mn	<u>0.01</u>
		Σ	0.98

* calculated on the basis of 18 anions with $OH = 2$ and $H_2O = 8$ *apfu*

TABLE 4. BOND-VALENCE TABLE (*vu*) FOR USHKOVITE*

	$M(1)$	$M(2)$	$M(3)$	P	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	Σ
O(1)		0.499 ^{x2} ↓		1.263						0.20				1.962
O(2)			0.551 ^{x2} ↓	1.242	0.20									1.993
O(3)	0.364 ^{x2} ↓			1.292							0.20	0.20		2.056
O(4)		0.475 ^{x2} ↓		1.215		0.30								1.970
O(5)		0.530 ^{x2} ↓	0.584 ^{x2} ↓		0.80								0.10	2.014
O(6)			0.387 ^{x2} ↓			0.70	0.80	0.10						1.987
O(7)	0.320 ^{x2} ↓							0.90	0.80					2.020
O(8)	0.374 ^{x2} ↓									0.80	0.80			1.974
O(9)							0.20		0.20			0.80	0.90	2.100
Σ	2.116	3.008	3.044	5.012	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

* curves from Brown (1981)

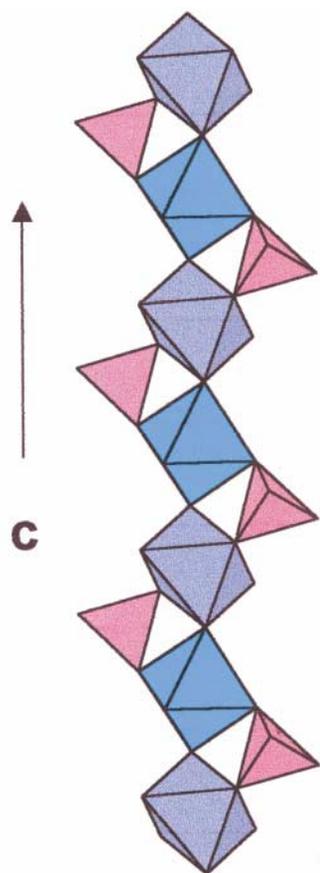


FIG. 3. The $[M_2(T\phi_4)_2\phi_6]$ chain in ushkovite; $M(2)$ and $M(3)$ octahedra are blue and mauve, respectively, (PO_4) tetrahedra are shown in pink.

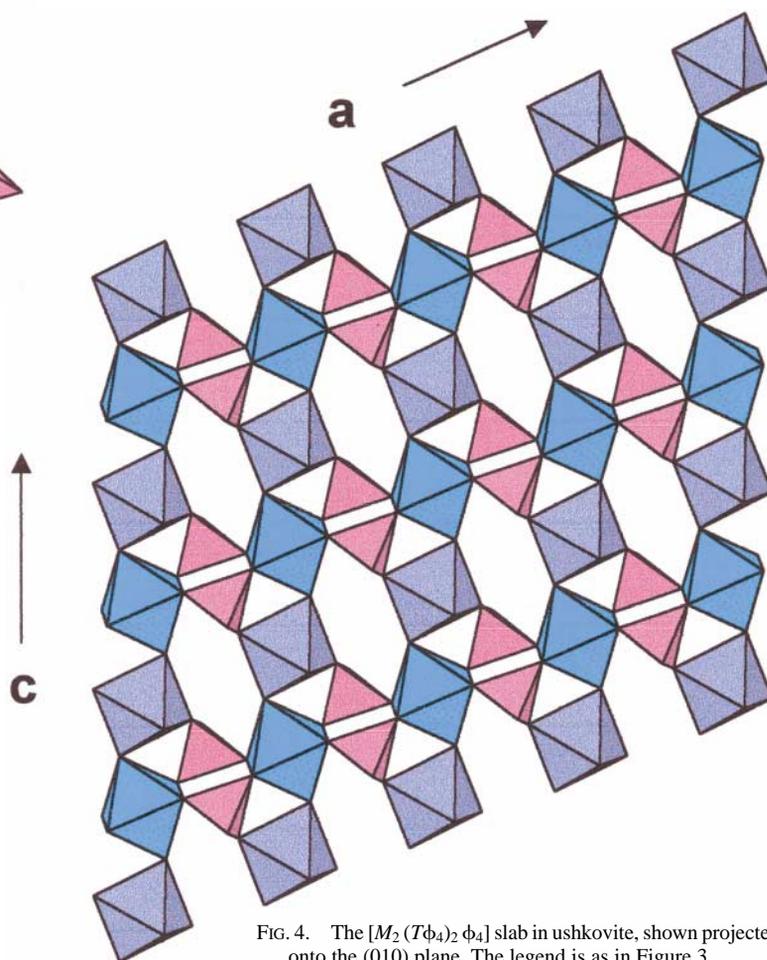


FIG. 4. The $[M_2(T\phi_4)_2\phi_4]$ slab in ushkovite, shown projected onto the (010) plane. The legend is as in Figure 3.

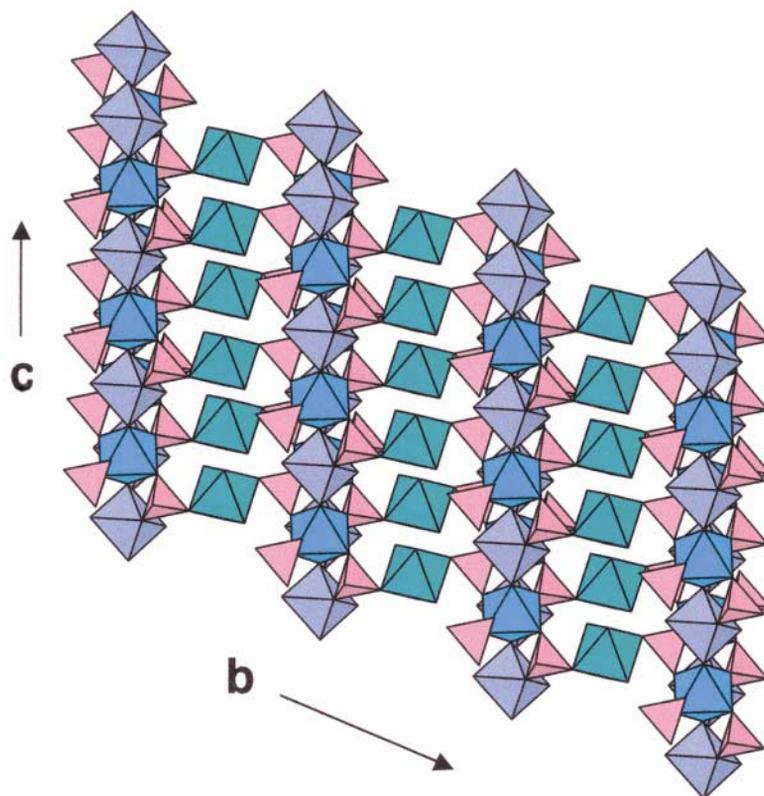


FIG. 5. The crystal structure of ushkovite projected onto (100). The legend is as in Figure 3, with $M(1)$ octahedra shown in green.

from these cations to any anion. Thus, O(4) requires a fairly strong hydrogen bond (0.30 vu , 1.70 Å) to satisfy its incident bond-valence requirements.

The O(7) atom links to H(4) and H(5) which hydrogen bond to O(6) and O(9), respectively. Thus the O(6) atom is [4]-coordinated by Fe^{3+} , H(2), H(3) and H(4), the bonds involving H(2) and H(3) being donor–H bonds and the bond involving H(4) being a H–acceptor (hydrogen) bond. The O(8) atom links to H(6) and H(7) that hydrogen bond to O(1) and O(3), respectively. Note that O(3) is the only anion bonded to a metal cation that accepts two hydrogen bonds (and hence is [4]-coordinated). The (H₂O) group at O(9) involves the H(8) and H(9) atoms that hydrogen bond to O(3) and O(5), respectively. The O(9) atom also accepts two hydrogen bonds [from H(3) and H(5), Table 4] and hence is [4]-coordinated, as is commonly the case for (H₂O) groups held in a structure solely by hydrogen bonding.

Relation to other minerals

The satisfactory nature of the structure refinement confirms that ushkovite is a member of the laueite group. Details of the minerals of the laueite and related groups are given in Table 6. In a paper of fundamental importance, Moore (1970) examined the topological aspects of $[^{6}M\phi_5]$ chains decorated by (TO_4) tetrahedra. He showed that there are seven distinct types of such chains with a repeat unit of two octahedra; these chains have a repeat distance of ~ 7 Å along their length, and were designated as 7 Å chains. As noted above, the structures of the laueite-group minerals, together with their related groups (Moore 1975, Hawthorne 1988, 1990, 1997) (Table 6), are based on the type-I 7 Å chain shown in Figure 3. A range of relative sizes of tetrahedra and octahedra can be accommodated in a chain of this topology by flexure and extension along the length of the chain. Indeed, those minerals with $M = Al$ and Fe^{3+} have repeat distances along the chain of 6.98 and 7.25 Å, respectively.

TABLE 6. MINERALS OF THE LAUEITE AND RELATED GROUPS

Mineral	Formula	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Sp. Gr.	Ref.
<i>Laueite group</i>									
gordonite	Mg(H ₂ O) ₄ [Al ₂ (PO ₄) ₂ (OH) ₂ (H ₂ O) ₂](H ₂ O) ₂	5.24	10.49	6.96	107.4	111.1	72.4	P1	(1)
mangangordonite	Mn ²⁺ (H ₂ O) ₄ [Al ₂ (PO ₄) ₂ (OH) ₂ (H ₂ O) ₂](H ₂ O) ₂	5.257	10.363	7.040	105.44	113.07	78.69	P1	(1)
laueite	Mn ²⁺ (H ₂ O) ₄ [Fe ³⁺ ₂ (PO ₄) ₂ (OH) ₂ (H ₂ O) ₂](H ₂ O) ₂	5.28	10.66	7.14	107.9	111	71.1	P1	(2)
paravauxite	Fe ²⁺ (H ₂ O) ₄ [Al ₂ (PO ₄) ₂ (OH) ₂ (H ₂ O) ₂](H ₂ O) ₂	5.233	10.541	6.962	106.9	110.8	72.1	P1	(3)
sigloite	(Fe ³⁺ , Fe ²⁺)(H ₂ O, OH) ₄ [Al ₂ (PO ₄) ₂ (OH) ₂ (H ₂ O) ₂](H ₂ O) ₂	5.26	10.52	7.06	106.97	111.5	69.5	P1	(4)
ushkovite	Mg(H ₂ O) ₄ [Fe ³⁺ ₂ (PO ₄) ₂ (OH) ₂ (H ₂ O) ₂](H ₂ O) ₂	5.347	10.592	7.225	108.28	111.74	71.63	P1	(5)
<i>Stewartite group</i>									
stewartite	Mn ²⁺ (H ₂ O) ₄ [Fe ³⁺ ₂ (PO ₄) ₂ (OH) ₂ (H ₂ O) ₂](H ₂ O) ₂	10.398	10.672	7.223	90.10	109.1	71.83	P1	(6)
<i>Pseudolaueite group</i>									
pseudolaueite	Mn ²⁺ (H ₂ O) ₄ [Fe ³⁺ (PO ₄)(OH)(H ₂ O)] ₂ (H ₂ O) ₂	9.647	7.428	10.194	—	104.63	—	P2 ₁ /a	(7)
<i>Metavauxite group</i>									
metavauxite	Fe ²⁺ (H ₂ O) ₄ [Al(PO ₄)(OH)(H ₂ O)] ₂	10.22	9.56	6.94	—	97.9	—	P2 ₁ /c	(8)
<i>Strunzite group</i>									
strunzite	Mn ²⁺ (H ₂ O) ₄ [Fe ³⁺ (PO ₄)(OH)(H ₂ O)] ₂	10.228	9.837	7.284	90.17	98.44	117.44	P1	(9)
ferrostrunzite	Fe ²⁺ (H ₂ O) ₄ [Fe ³⁺ (PO ₄)(OH)(H ₂ O)] ₂	10.23	9.77	7.37	89.28	98.3	117.3	P1	—

References: (1) Leavens & Rheingold (1988); (2) Moore (1965); (3) Baur (1969a); (4) Hawthorne (1988); (5) this study; (6) Moore & Araki (1974); (7) Baur (1969b); (8) Baur & Rama Rao (1967); (9) Fanfani *et al.* (1978).

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