THE CRYSTAL STRUCTURE OF MITRYAEVAITE, Al5(PO4)2[(P,S)O3(OH,O)]2F2(OH)2(H2O)8{middle dot}6.48H2O, DETERMINED FROM A MICROCRYSTAL USING SYNCHROTRON RADIATION

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THE CRYSTAL STRUCTURE OF MITRYAEVAITE, $Al_5(PO_4)_2[(P,S)O_3(OH,O)]_2F_2(OH)_2(H_2O)_8•6.48H_2O$, DETERMINED FROM A MICROCRYSTAL USING SYNCHROTRON RADIATION

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ABSTRACT

The crystal structure of mitryaevaite, $Al_5(PO_4)_2[(P,S)O_3(OH,O)]_2F_2(OH)_2(H_2O)_8•6.48H_2O$, a secondary mineral from the alteration zone of carbonaceous, vanadium-bearing shales from northwestern Karatau Range and Zhabagly Mountains, southern Kazakhstan, has been determined from a microcrystal ($8 \times 10 \times 65$ µm) using synchrotron X-radiation. The structure was solved by direct methods and refined to $R1 = 0.057$ and $S = 1.020$ using 2111 unique observed reflections ($|F_o| \geq 4\sigma_F$). The structure is triclinic, space group $P\bar{1}$, a 6.918(1), b 10.127(2), c 10.296(2) Å, α 77.036(3), β 73.989(4), γ 76.272(4)°, V 663.8(2) Å^3, $Z = 1$. The structure of mitryaevaite contains five-membered finite chains of corner-sharing ($Al\phi_6$) octahedra. The chains are cross-linked *via* (PO_4) tetrahedra to produce complex slabs that are parallel to the *a* axis, and that are in turn linked through additional (PO_4) tetrahedra to form layers parallel to the (01$\bar{1}$) plane. The heteropolyhedral layers are linked together through hydrogen bonds to H_2O groups located in the interlayer region.

Keywords: mitryaevaite, aluminum phosphate, synchrotron radiation, microcrystallography.

SOMMAIRE

Nous avons déterminé la structure cristalline de la mitryaévaïte, $Al_5(PO_4)_2[(P,S)O_3(OH,O)]_2F_2(OH)_2(H_2O)_8•6.48H_2O$, minéral secondaire provenant d'une zone d'altération de shales carbonacées et vanadifères affleurant dans le nord-ouest de la chaîne de Karatau et des montagnes Zhabagly, dans le sud du Kazakhstan, en utilisant un microcristal ($8 \times 10 \times 65$ µm) étudié avec rayonnement synchrotron. Nous nous sommes servis des méthodes directes pour résoudre la structure, jusqu'à un résidu $R1 = 0.057$ et un indice de concordance $S = 1.020$, avec 2111 réflexions uniques observées ($|F_o| \geq 4\sigma_F$). La structure est triclinique, groupe patial $P\bar{1}$, a 6.918(1), b 10.127(2), c 10.296(2) Å, α 77.036(3), β 73.989(4), γ 76.272(4)°, V 663.8(2) Å^3, $Z = 1$. La structure contient des chaînes finies à cinq membres, qui sont des octaèdres ($Al\phi_6$) partageant des coins. Les chaînes sont liées transversalement par le biais de tétraèdres (PO_4) pour produire des panneaux complexes parallèles à l'axe *a*; ceux-ci sont liés à leur tour par des tétraèdres additionnels pour former des feuillets parallèles au plan (01$\bar{1}$). Les couches hétéropolyédriques sont interconnectées avec des groupes H_2O entre les feuillets par des liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: mitryaévaïte, phosphate d'aluminium, rayonnement synchrotron, microcristallographie.

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Introduction

Of the several hundred known phosphate minerals, most are found in granitic pegmatites, where they form under a wide range of thermodynamic conditions (Hawthorne 1998). The secondary phosphates that occur in the alteration zones of mineral deposits, however, are also of great importance, particularly in their capacity to reduce the mobility of metal ions (such as Pb) (Davis *et al.* 1993, Traina & Leperche 1999). The structures of most are unknown owing to small crystal-size, a feature that has hindered X-ray-diffraction studies. Synchrotron radiation, however, has permitted structure determination of microcrystals of at least 2 μm on edge (Burns *et al.* 2000) or less (Neder *et al.* 1996). In this contribution, the structure of mitryaevaite, a secondary phosphate mineral from Kazakhstan, has been determined from a microcrystal at the GeoSoilEnviro–Consortium for Advanced Radiation Sources (GSECARS) beamline of the Advanced Photon Source (APS) facility at Argonne National Laboratory, Illinois.

Background Information

Mitryaevaite is a hydrated Al fluorophosphate–sulfate mineral from the northwestern Karatau Range of the Zhabagly Mountains in the southern part of Kazakhstan (Ankinovich *et al.* 1997). It was found in the alteration zone of carbonaceous vanadium-bearing shales, in association with minyulite, crandallite, gorceixite, wavellite, variscite, evansite, aluminite, meta-aluminite, kaolinite, fibrous gypsum and hewettite. Ankinovich *et al.* (1997) suggested that mitryaevaite formed by the decomposition of carbonate and sulfide minerals in an environment where weakly acidic solutions mobilized Al from clay minerals in the shale.

Mitryaevaite forms thin white films and streaks of prismatic transparent crystals up to 0.01 mm across and 0.07 mm in maximum length. Trials to obtain diffraction data from single crystals using a sealed-tube X-ray source and a CCD (charge-coupled device) detector failed owing to the small crystal dimensions. Studies of mitryaevaite using electron microscopy were not successful owing to partial dehydration under vacuum and its subsequent amorphization (Bekenova & Shabanova, unpubl. results). The inability of these traditional techniques to provide structural data thus prompted the use of synchrotron radiation.

Experimental

X-ray diffraction

Crystals of mitryaevaite were obtained from the type locality, described by Ankinovich *et al.* (1997). Several crystals with superior optical properties were mounted on a Bruker 1K SMART CCD diffractometer utilizing a sealed-tube Mo$K\alpha$ X-ray source. Exposure times of up to 200 seconds per 0.3° frame-width, however, yielded no useful intensity data. Therefore, a single crystal 8 × 10 × 65 μm^3 was mounted on a tapered glass rod for study at the GSECARS beamline at the Advanced Photon Source. A monochromatic beam (λ = 0.6972 Å) was focused to ~50 μm *via* a cylindrical mirror, with horizontal KB mirrors used to reject high-energy harmonics from the undulator insertion device. Intensity data were collected using a Bruker 2K SMART CCD detector while scanning either the ϕ or ω axes, with 0.3° frame-widths and 5 seconds counting time per frame. A total of 1290 frames (including 40 repeated frames for scaling corrections) were integrated and corrected for Lorentz, polarization, background and synchrotron beam decay using the computer program SAINT (Bruker Analytical X-ray Systems, Madison, Wisconsin), resulting in 5050 reflections [2693 unique; R(int) = 4.23%]. A semi-empirical absorption correction was done on the basis of intensities of equivalent reflections using SADABS (G.M. Sheldrick, unpublished). Data below 10° 2θ (21 reflections, of which three had an intensity greater than $4\sigma_F$) were suppressed owing to high backgrounds and interference from the beamstop created by the intense synchrotron X-ray source. Final unit-cell parameters (Table 1) were calculated by least-squares refinement using 831 strong reflections extracted from the actual dataset. The structure of mitryaevaite was solved *via* direct methods (Sheldrick 1990), and subsequent refinements were carried out with SHELXTL (Bruker Analytical X-ray Systems) and WINGX (Furrugia 1998). A table of structure factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Results

Structure description

There are three symmetrically independent Al positions in mitryaevaite. Each of these is octahedrally coordinated by anions. Al(1) is coordinated by three O atoms, one (OH)$^-$ group and two H$_2$O groups in a *cis* arrangement. Al(2) is coordinated by two *trans* F atoms and four O atoms, whereas Al(3) is coordinated to one F atom, two O atoms, one (OH)$^-$ group and two H$_2$O groups. One of the two P atoms has the usual tetrahedral coordination to O, whereas P(1) is bonded to three O atoms and an (OH)$^-$ group (Table 2).

The structure of mitryaevaite contains layers parallel to the (001) plane consisting of corner-shared (Alϕ_6) octahedra (ϕ = O, OH, H$_2$O or F) and (PO$_4$) tetrahedra (Fig. 1). The main structural element of the aluminophosphate layers is a five-membered finite chain of corner-sharing (Alϕ_6) octahedra that runs parallel to $(4\bar{2}\bar{1})$ (Fig. 2a). Within this chain, adjacent (Alϕ_6) octahedra are joined through bridging (OH)$^-$ or F$^-$ anions. The formula of the chain may thus be written as follows:

TABLE 1. CRYSTALLOGRAPHIC DATA FOR MITRYAEVAITE

a (Å)	6.918(1)	μ (cm^{-1})	48.6
b (Å)	10.127(2)	D_{calc} (g/cm^3)	2.057
c (Å)	10.296(2)	Crystal size (μm)	$8 \times 10 \times 65$
α (°)	77.036(3)	Unique reflections	2693
β (°)	73.989(4)	Unique $F_o = 4\sigma_F$	2135
γ (°)	76.272(4)	Final R $F_o = 4\sigma_F$	0.059
V (Å^3)	663.8(2)	S	1.064
Space group	$P\bar{1}$	$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ^{-3})	−0.90, 0.89

Formula ($Z = 1$): Al$_5$(PO$_4$)$_2$[(P,S)O$_3$(OH,O)]$_2$F$_2$(OH)$_2$(H$_2$O)$_8$•6.48H$_2$O
$R1 = \Sigma F_o − F_c / \Sigma F_o$; $S = [\Sigma w (|F_o| − |F_c|)^2 / (m − n)]^{1/2}$ for m observations and n parameters.

Al(1)O$_3$(H$_2$O)$_2$ − (OH) − Al(3)O$_2$(H$_2$O)$_2$ − F − Al(2)O$_4$ − F − Al(3)O$_2$(H$_2$O)$_2$ − (OH) − Al(1)O$_3$(H$_2$O)$_2$. This chain is surrounded by [P(1)O$_4$] tetrahedra according to isomeric arrangement I, as defined by Moore (1970). The finite chains of octahedra are cross-linked by [P(1)O$_4$] tetrahedra to produce a complex slab parallel to the a axis, which in turn is linked through [P(2)O$_4$] tetrahedra to form layers. The layers are linked by H bonding through H$_2$O groups located in the interlayer space.

TABLE 2. SELECTED INTERATOMIC DISTANCES (Å)
IN THE STRUCTURE OF MITRYAEVAITE

Al(1)	− O(5)	1.854(3)	P(1)	− O(2)	1.534(4)	
	− O(1)	1.867(3)		− O(1)	1.535(2)	
	− OH(9)	1.880(3)		− O(3)	1.539(3)	
	− O(6)	1.887(3)		− OH(4)	1.554(3)	
	− H$_2$O(11)	1.950(3)	<P(1)−φ>		1.54	
	− H$_2$O(12)	1.976(3)				
<Al(1)−φ>		1.90	P(2)	− O(5)b	1.529(2)	
				− O(6)	1.538(3)	
Al(2)	− F(1) 2×	1.834(3)		− O(7)	1.541(2)	
	− O(3) 2×	1.898(3)		− O(8)	1.544(3)	
	− O(7) 2×	1.903(2)	<P(2)−O>		1.54	
<Al(2)−φ>		1.88				
Al(3)	− F(1)	1.845(2)				
	− OH(9)a	1.854(3)	H$_2$O(14)	− H(3)	1.00(5)	
	− O(8)	1.869(3)	H$_2$O(15)	− H(1)	0.85(5)	
	− O(2)a	1.872(3)				
	− H$_2$O(10)	1.935(3)				
	− H$_2$O(13)	1.957(3)				
<Al(3)−φ>		1.89				

a = −x + 1, −y + 1, −z; b = −x, −y + 1, −z

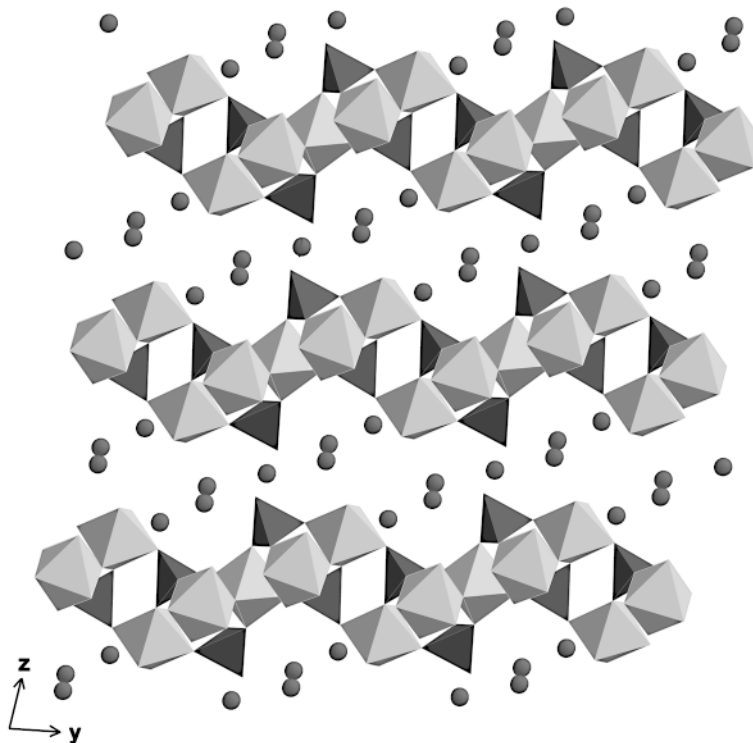

FIG. 1. The crystal structure of mitryaevaite viewed approximately down the a axis. (Alφ$_6$) octahedra and (Pφ$_4$) tetrahedra are shown as dark and light, respectively. Circles designate H$_2$O groups in the interlayer.

TABLE 3. BOND-VALENCE ANALYSIS FOR MITRYAEVAITE*

	Al(1)	Al(2)	Al(3)	P(1)	P(2)	Σ
O(1) *vu*	0.56			1.21		1.77
O(2)			0.55	1.21		1.76
O(3)		0.51$^{2×↓}$		1.19		1.70
OH(4)				1.15		1.15
O(5)	0.58				1.23	1.81
O(6)	0.53				1.20	1.73
O(7)		0.51$^{2×↓}$			1.19	1.70
O(8)			0.56		1.18	1.74
OH(9)	0.54		0.58			1.12
F		0.46$^{2×↓}$	0.44			0.90
H$_2$O(10)			0.46			0.46
H$_2$O(11)	0.45					0.45
H$_2$O(12)	0.42					0.42
H$_2$O(13)			0.44			0.44
H$_2$O(14)						-
H$_2$O(15)						-
H$_2$O(16)						-
H$_2$O(17)						-
Σ	3.08	2.96	3.03	4.76	4.80	

The analysis is based on the bond-valence parameters from Brese & O'Keeffe (1991).

Bond-valence analysis

The calculation of bond-valence sums for atoms in the structure of mitryaevaite was performed using the parameters reported by Brese & O'Keeffe (1991). The results (Table 3) were used to determine the positions of (OH)$^-$ and H$_2$O groups. The bond-valence sums for cations [3.08, 2.96, 3.03, 4.76 and 4.80 *vu* (valence units) for Al(1), Al(2), Al(3), P(1) and P(2), respectively] are in good agreement with their expected formal valences. The distinction between F and O atoms was accomplished on the basis of bond-valence sums and a refinement of site-occupancy factors.

Role of H$_2$O groups and H bonding

The H$_2$O groups in mitryaevaite have two structural roles. The H$_2$O(10), H$_2$O(11), H$_2$O(12) and H$_2$O(13) (Table 4) groups are bonded to Al cations and are thus components of the structural unit. The bond-valence sums incident upon the O atoms (Table 3) for these groups (excluding the O–H bonds) are 0.46, 0.45, 0.42 and 0.44 *vu*, respectively, which are in good agreement with the value of ~0.4 *vu* given by Hawthorne (1992) for this kind of H$_2$O group.
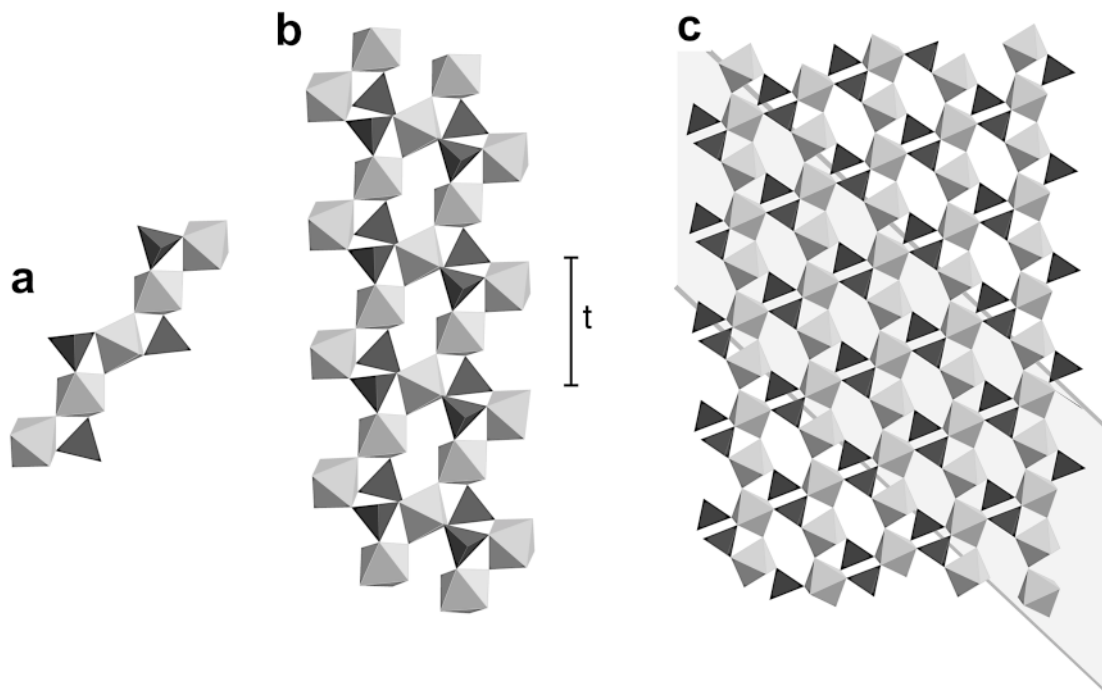

FIG. 2. The main elements of the crystal structure of mitryaevaite: (a) finite chain consisting of five (Alφ$_6$) octahedra with four (Pφ$_4$) tetrahedra; (b) a slab built by condensation of the finite chains, where t is the period of the slab. These slabs can be extracted from structures of minerals of the laueite group; layers of the gordonite structure (c) can be truncated, as shown in gray to produce the mitryaevaite structure.

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) FOR MITRYAEVAITE

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al(1)	0.0218(2)	0.3840(1)	0.2142(1)	0.0010(1)	0.0005(1)	0.0008(1)	0.0018(1)	0.0000(1)	-0.0005(1)	0.0000(1)
Al(2)	0	0	0	0.0009(1)	0.0001(1)	0.0008(1)	0.0018(1)	-0.0001(1)	-0.0004(1)	0.0001(1)
Al(3)	0.4982(2)	0.8020(1)	-0.0738(1)	0.0011(1)	0.0002(1)	0.0009(1)	0.0020(1)	-0.0001(1)	-0.0003(1)	0.0000(1)
P(1)	0.1243(2)	0.0573(1)	0.2564(1)	0.0010(1)	0.0006(1)	0.0008(1)	0.0016(1)	0.0000(1)	-0.0004(1)	0.0000(1)
P(2)	0.1069(2)	0.6704(1)	0.0400(1)	0.0009(1)	0.0002(1)	0.0007(1)	0.0017(1)	0.0000(1)	-0.0004(1)	0.0000(1)
O(1)	-0.0034(5)	0.1999(2)	0.2799(3)	0.0015(1)	0.0009(2)	0.0009(1)	0.0024(1)	-0.0001(1)	-0.0001(1)	0.0001(1)
O(2)	0.3454(5)	0.0664(2)	0.1784(3)	0.0013(1)	0.0002(2)	0.0012(1)	0.0023(1)	0.0000(1)	-0.0001(1)	-0.0003(1)
O(3)	0.0258(5)	-0.0150(2)	0.1817(3)	0.0016(1)	0.0011(2)	0.0017(1)	0.0022(1)	-0.0002(1)	-0.0007(2)	-0.0006(1)
OH(4)	0.1316(5)	-0.0337(3)	0.3988(3)	0.0018(1)	0.0015(2)	0.0018(1)	0.0016(1)	0.0005(1)	-0.0004(2)	0.0001(1)
O(5)	-0.1234(5)	0.3940(2)	0.0844(3)	0.0013(1)	0.0008(2)	0.0014(1)	0.0019(1)	-0.0004(1)	-0.0004(1)	-0.0001(1)
O(6)	0.0238(5)	0.5749(2)	0.1723(3)	0.0012(1)	0.0007(2)	0.0010(1)	0.0017(1)	0.0001(1)	-0.0002(1)	-0.0003(1)
O(7)	-0.0347(5)	0.8131(2)	0.0391(3)	0.0012(1)	0.0001(2)	0.0009(1)	0.0026(1)	-0.0002(1)	-0.0005(1)	-0.0001(1)
O(8)	0.3250(5)	0.6843(2)	0.0387(3)	0.0013(1)	0.0002(2)	0.0013(1)	0.0022(1)	0.0001(1)	-0.0006(1)	-0.0001(1)
OH(9)	0.2793(5)	0.3420(2)	0.0948(3)	0.0013(1)	0.0002(2)	0.0012(1)	0.0022(1)	0.0000(1)	0.0001(1)	0.0000(1)
F	0.2780(4)	0.9466(2)	-0.0573(2)	0.0016(1)	0.0003(2)	0.0011(1)	0.0029(1)	-0.0001(1)	-0.0003(1)	0.0000(1)
H$_2$O(10)	0.5552(5)	0.8235(2)	0.0932(3)	0.0016(1)	0.0012(2)	0.0014(1)	0.0021(1)	-0.0003(1)	-0.0005(1)	-0.0001(1)
H$_2$O(11)	-0.2358(5)	0.4312(3)	0.3462(3)	0.0018(1)	0.0010(2)	0.0017(1)	0.0023(1)	-0.0001(1)	0.0001(1)	0.0000(1)
H$_2$O(12)	0.1615(6)	0.3754(3)	0.3604(3)	0.0023(1)	0.0021(2)	0.0026(1)	0.0026(2)	0.0000(1)	-0.0013(2)	-0.0008(1)
H$_2$O(13)	0.4266(5)	0.7855(3)	-0.2399(3)	0.0020(1)	0.0013(2)	0.0026(1)	0.0025(2)	-0.0005(1)	-0.0006(2)	-0.0006(1)
H$_2$O(14)	0.1449(7)	0.2532(3)	0.6258(4)	0.0034(1)	0.0037(3)	0.0034(2)	0.0026(2)	-0.0006(1)	0.0003(2)	-0.0011(2)
H$_2$O(15)	-0.5917(6)	0.5645(4)	0.2907(4)	0.0032(1)	0.0027(3)	0.0034(2)	0.0037(2)	0.0006(1)	-0.0017(2)	-0.0008(2)
H$_2$O(16)	0.4210(7)	-0.2521(4)	0.4478(4)	0.0048(1)	0.0035(3)	0.0031(2)	0.0049(2)	0.0014(2)	0.0007(2)	0.0008(2)
H$_2$O(17)†	0.5	0	0.5	0.0123(15)	0.0140(30)	0.0093(16)	0.0180(30)	-0.0033(15)	-0.0120(20)	-0.0005(14)
H(1)	-0.5920(90)	0.6340(50)	0.3210(50)	0.0017(12)						
H(2)	0.4820(100)	0.8930(60)	0.1350(60)	0.0035(15)						
H(3)	0.1420(90)	0.3190(50)	0.6850(50)	0.0021(12)						

† site-occupancy factor = 0.48(4).

The H$_2$O(14), H$_2$O(15), H$_2$O(16) and H$_2$O(17) groups are located in the interlayer region and do not bond to any cations other than H. Although some H atoms were located in difference-Fourier maps during the refinement, the positions of others remain unclear. The O···H distances for the observed H atoms are given in Table 2. The H$_2$O(17) position is only partially occupied (site-occupancy factor 0.48), resulting in 6.48 occluded H$_2$O groups in the structural formula.

H-bonding

A bond-valence analysis of the O(4) position (Σ = 1.15 *vu*, Table 3) suggests the presence of a hydroxyl group. Its symmetrically equivalent position, however, is only 2.46 Å away. A Fourier-difference map of this region (Fig. 3) shows a peak of approximately 0.59 e$^-$/Å^3 with a midpoint on the center of symmetry at (0,0,½), 1.23 Å from the O(4) atom center. Two scenarios are suggested to describe this region: first, there may be a symmetrical H bond between equivalent O(4) positions [designated OH(4) hereafter], with the H atom located on the center of symmetry that is at the midpoint be-

tween equivalent OH(4) positions. The H site may not be fully occupied because the extent of symmetrical H-bonding is coupled (for charge-balance reasons) to the degree of S substitution on the P sites (see below). The bond-valence sums on the O atoms of symmetrically bonded (OH)$^-$ groups are typically ~1.5 *vu*, excluding the H-atom contribution (Burns & Hawthorne 1994a, b). For OH(4) in mitryaevaite, this sum is lower (Table 3), yet approaches 1.5 *vu* if one considers that the anion probably accepts a H bond from the neighboring H$_2$O groups.

The second and somewhat favored scenario is that the H atom position is displaced off the center of symmetry. This is suggested by the elongation of the electron density (Fig. 3), which is consistent with H sites [H(4a) and H(4b)] displaced about 0.5 Å from the center of symmetry, as indicated in Figure 3. These sites are approximately 1.0 Å from the O4 centers, a more favorable distance than the 1.23 Å in the symmetrically bonded case. As each of these H sites must be partially occupied, no attempt was made to refine their positions or occupancies.
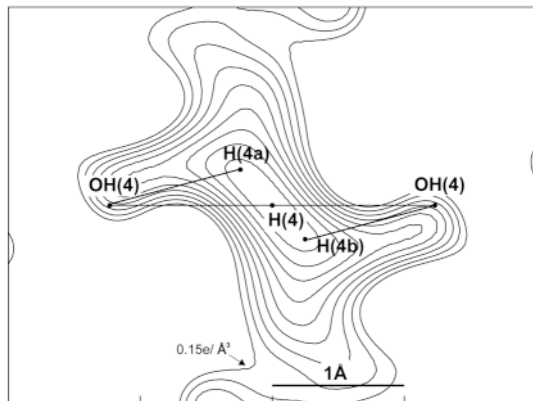
FIG. 3. Fourier-difference map showing an elongated 0.59 e⁻/ Å³ peak (interval = 0.05 e⁻/Å³) at the midpoint $(0,0,\frac{1}{2})$ between two symmetrically equivalent OH(4) atoms. Two possible H-bonding scenarios are shown: H(4) is symmetrically bonded to the OH(4) atoms, and the H atom position is displaced of the symmetry center to partially occupied H(4a) and H(4b) sites.

Mechanism of S ↔ P substitution

The previously published chemical data show that mitryaevaite contains about 5.49 wt.% of SO_3; therefore, substitution of S for P at the tetrahedral sites is proposed (Ankinovich *et al.* 1997). Unfortunately, nei-

ther refinement of site occupancies or examination of temperature factors were able to reveal preferential positions for the S atoms in the structure. We infer, however, that the substitution will be on the P(1) site since this is the site to which the OH(4) group is bound (above). Thus the charge-balance requirements of $S^{6+} \leftrightarrow P^{5+}$ substitution onto the sites are satisfied by the substitution $O^{2-} \leftrightarrow OH^-$ at the OH(4) group.

Structural formula for mitryaevaite

The bond-valence analysis (Table 3) further revealed that a hydroxyl group occupies the OH(9) site (bond-valence sum: 1.12 *vu*) linking the $[Al(1)\phi_6]$ and $[Al(3)\phi_6]$ octahedra. Considering its presence, as well as the symmetrical H-bonding and $S \leftrightarrow P$ substitution mechanism (above), the structural formula of the crystal of mitryaevaite studied should be written as $Al_5(PO_4)_2[(P,S)O_3(OH,O)]_2F_2(OH)_2(H_2O)_8 \cdot 6.48H_2O$. This is a refinement of the formula $Al_{10}[(PO_4)_{8.7}(SO_3OH)_{1.3}]_{\Sigma 10}AlF_3 \cdot 30H_2O$ given for mitryaevaite on the basis of chemical analyses by Ankinovich *et al.* (1997).

Relationships to other mineral structures

The crystal structures of many phosphate and sulfate minerals are based upon infinite chains of corner-sharing $Al\phi_6$ or $Fe^{3+}\phi_6$ octahedra in which octahedra are successively linked through opposing apical $(OH)^-$ or F^- anions. These chains are usually linked to phosphate or sulfate tetrahedra, which may link the chains
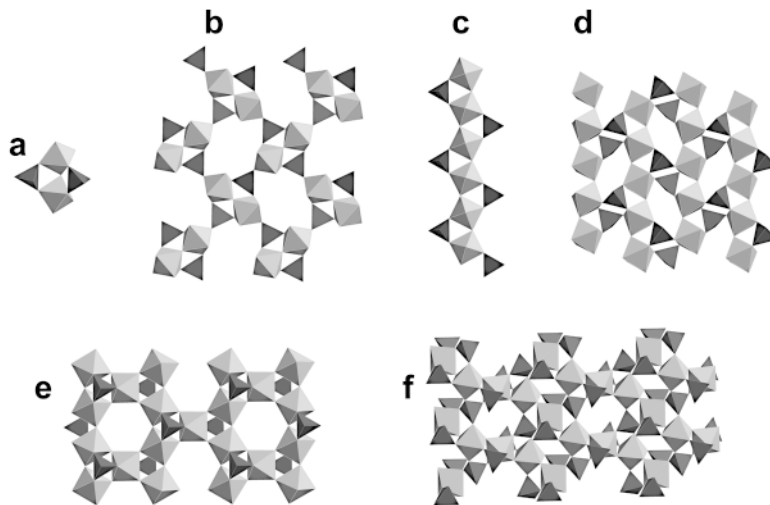

FIG. 4. Finite clusters (a), infinite chains (b), and layers (c,d,e,f) built by corner-sharing of $(Al\phi_6)$ octahedra and $(P\phi_4)$ tetrahedra. Shown are the structural building units or crystal structures of morinite (a), viitaniemiite (b), minyulite (c), metavauxite (d), crandallite (and gorceixite) (e), and montgomeryite (f).

into slabs, sheets or frameworks. The possibility of different arrangements of tetrahedra around the chains of octahedra results in much stereo-isomeric variation. Moore (1970) derived seven possible stereo-isomers for infinite corner-linked chains of octahedra coordinated to adjacent tetrahedra. The linkage of the complex octahedron–tetrahedron chains produces a large number of topologically distinct structural units. As mitryaevaite consists of finite chains, its structure represents a new variation on this theme.

The structure of mitryaevaite is closely related to that of other Al phosphate minerals, which are based on corner-linked octahedra. Morinite, $Ca_2Na[Al_2F_4(OH)(H_2O)_2(PO_4)_2]$ (Hawthorne 1979), is composed of corner-linked octahedra dimers decorated by two (PO_4) tetrahedra (Fig. 4a). The polymerization of such units in two dimensions produces the layers found in minyulite, $K[Al_2F(H_2O)_4(PO_4)_2]$ (Kampf 1977) (Fig. 4c).

The structure of viitaniemiite (Fig. 4b), $Na(Ca_{0.62}Mn_{0.38})[Al(PO_4)F_2(OH)]$ (Pajunen & Lahti 1984) is based on the corner-linked chains of octahedra that are surrounded by (PO_4) tetrahedra. This chain occurs as a backbone for a large number of phosphates and sulfates with octahedrally coordinated cations such as Fe and Al (Moore 1970, Moore & Araki 1974a). Condensation of these chains in two dimensions leads to a variety of stereo-isomeric variations, one of which, arrangement I (Moore 1970), is found in gordonite, $Mg[Al_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_6$ (Leavens & Rheingold 1988), paravauxite, $Fe[Al_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_6$ (Baur 1969), and sigloite, $[Fe((H_2O)_3OH)][Al_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_2$ (Hawthorne 1988). Each of these can be thought of as a parent structure to mitryaevaite, as shown in Figures 2b and 2c. A stereo-isomeric variation of the $[Al_2((PO_4)_2(OH)_2(H_2O)_2]^{2+}$ layer that is not a parent structure to mitryaevaite is metavauxite, $[Fe(H_2O)_6][Al_2(PO_4)_2(OH)_2(H_2O)_2]$ (Baur & Rama Rao 1967) (Fig. 4d).

The polymerization of $(Al\phi_6)$ octahedra in two dimensions by sharing vertices produces the layer shown in Figure 4e. The non-shared vertices of octahedra in such a layer are bonded to (PO_4) tetrahedra. This type of structural unit occurs in crandallite, $Ca[Al_3(OH)_6(PO_3(O_{0.5}(OH)_{0.5}))_2]$ (Blount 1974), and gorceixite, $Ba[Al_3(PO_4)(PO_3(OH))(OH)_6]$ (Radoslovich 1982), two minerals of the alunite group that are associated with mitryaevaite. An example of a chain of octahedra with *cis*- and *trans*-linkage of octahedra is shown in Figure 4f, as observed by Moore & Araki (1974b) in montgomeryite, $Ca_4Mg(H_2O)_{12}[(Al_4(OH)_4(PO_4)_6)]$.

The linkage of chains of octahedra through (PO_4) tetrahedra results in the frameworks shown in Figure 5. In the structure of wavellite, $[Al_3(OH)_3(PO_4)_2](H_2O)_5$ (Araki & Zoltai 1968), the chains of octahedra are parallel to each other (Fig. 5a), whereas in fluellite, $Al_2PO_4F_2(OH)(H_2O)_7$ (Guy & Jeffrey 1966), the chains are opposing and cross-linked by (PO_4) tetrahedra (Fig. 5b).

Al exists as an octahedrally coordinated species in many mineral-forming solutions (Hawthorne 1979, Henry *et al.* 1992). On the basis of the crystal structure of mitryaevaite, we suggest that the polymerization of these species *via* F^- or $(OH)^-$ anions may lead to clusters of corner-sharing $(Al\phi_6)$ octahedra. During crystallization, the mode of their polymerization [*via* $(OH)^-$ or F^- anions (or both) or *via* (PO_4) tetrahedra] may be controlled by pH and the activities of P and F.
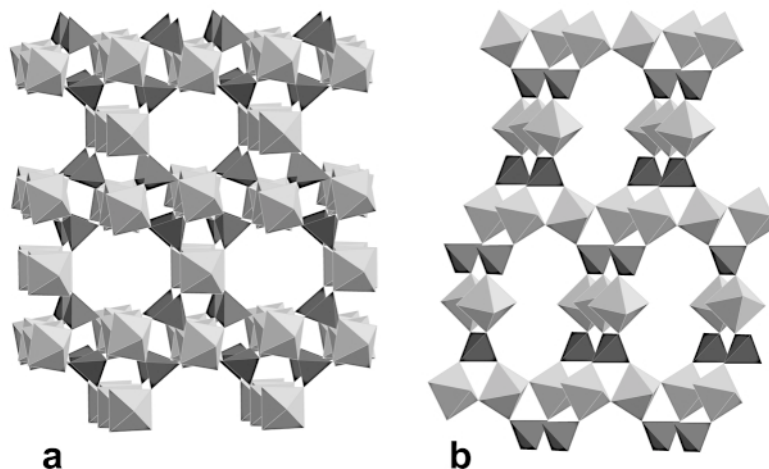

FIG. 5. Frameworks built by corner-sharing of $(Al\phi_6)$ octahedra and (PO_4) tetrahedra in crystal structures of Al phosphate minerals: (a) wavellite and (b) fluellite.

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