

# Ferribushmakinite, $\text{Pb}_2\text{Fe}^{3+}(\text{PO}_4)(\text{VO}_4)(\text{OH})$ , the $\text{Fe}^{3+}$ analogue of bushmakinite from the Silver Coin mine, Valmy, Nevada

A. R. KAMPF<sup>1,\*</sup>, P. M. ADAMS<sup>2</sup>, B. P. NASH<sup>3</sup> AND J. MARTY<sup>4</sup>

<sup>1</sup> Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA

<sup>2</sup> 126 South Helberta Avenue #2, Redondo Beach, California 90277, USA

<sup>3</sup> Department of Geology and Geophysics, University of Utah, Salt Lake City, UT 84112, USA

<sup>4</sup> 5199 East Silver Oak Road, Salt Lake City, UT 84108, USA

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## ABSTRACT

Ferribushmakinite (IMA2014-055),  $\text{Pb}_2\text{Fe}^{3+}(\text{PO}_4)(\text{VO}_4)(\text{OH})$ , the  $\text{Fe}^{3+}$  analogue of bushmakinite, is a new mineral from the Silver Coin mine, Valmy, Iron Point district, Humboldt County, Nevada, USA, where it occurs as a low-temperature secondary mineral in association with plumbogummite, mottramite, Br-rich chlorargyrite and baryte on massive quartz. Ferribushmakinite forms yellow slightly flattened prisms up to 0.2 mm long growing in X and sixling twins. The streak is pale yellow. Crystals are translucent and have adamantine lustre. The Mohs hardness is ~2, the tenacity is brittle, the fracture is irregular to splintery and crystals exhibit one or two fair cleavages in the [010] zone. The calculated density is 6.154 g/cm<sup>3</sup>. Electron microprobe analyses provided: PbO 63.69, CaO 0.07, CuO 1.11, Fe<sub>2</sub>O<sub>3</sub> 7.63, Al<sub>2</sub>O<sub>3</sub> 1.63, V<sub>2</sub>O<sub>5</sub> 12.65, As<sub>2</sub>O<sub>5</sub> 3.09, P<sub>2</sub>O<sub>5</sub> 8.63, H<sub>2</sub>O 1.50 (structure), total 100.00 wt.% (normalized). The empirical formula (based on nine O a.p.f.u.) is:  $(\text{Pb}_{1.99}\text{Ca}_{0.01})_{\Sigma 2.00}(\text{Fe}_{0.66}\text{Al}_{0.22}\text{Cu}_{0.10})_{\Sigma 0.98}(\text{V}_{0.97}\text{P}_{0.85}\text{As}_{0.19})_{\Sigma 2.01}\text{O}_{7.84}(\text{OH})_{1.16}$ . Ferribushmakinite is monoclinic,  $P2_1/m$ ,  $a = 7.7719(10)$ ,  $b = 5.9060(7)$ ,  $c = 8.7929(12)$  Å,  $\beta = 111.604(8)^\circ$ ,  $V = 375.24(9)$  Å<sup>3</sup> and  $Z = 2$ . The eight strongest lines in the powder X-ray diffraction pattern are [ $d_{\text{obs}}$  in Å ( $I(hkl)$ ): 4.794(46)(011); 3.245(84)( $\bar{2}11$ ); 2.947(100)(020, $\bar{2}12$ , $\bar{1}03$ ); 2.743(49)(112); 2.288(30)(220); 1.8532(27)( $\bar{3}14$ , $\bar{4}03$ ); 1.8084(27)(multiple); and 1.7204(28)(312,114,321)]. Ferribushmakinite is a member of the brackebuschite supergroup. Its structure ( $R_1 = 3.83\%$  for 577  $F_o > 4\sigma F$ ) differs from that of bushmakinite only in the dominance of  $\text{Fe}^{3+}$  over Al in the octahedral site.

**KEYWORDS:** ferribushmakinite, new mineral, crystal structure, brackebuschite supergroup, Silver Coin mine, Valmy, Nevada.

## Introduction

THE Silver Coin mine is a small base-metal deposit in north-central Nevada that was operated principally for silver. The last ore production from the mine was in 1929, but since the late 1980s, the mine has been a popular collecting site. To date,

five new mineral species have been described from the Silver Coin mine: zinclipcombite (Chukanov *et al.*, 2006), meurigite-Na (Kampf *et al.*, 2009), iangreyite (Mills *et al.*, 2011), krásnoite (Mills *et al.*, 2012) and fluorowardite (Kampf *et al.*, 2014).

In May of 1991, Richard W. Thomssen of Carson City, Nevada, collected specimens containing yellow crystals in attractive sixling twins. Based upon powder X-ray diffraction

\* E-mail: akampf@nhm.org

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(XRD), the mineral was originally identified as heyite. Recent detailed examination of this material, including crystal structure determination and electron microprobe analysis (EMPA), has shown it to be a new mineral species.

The mineral is named ferribushmakinite, based upon it being the  $\text{Fe}^{3+}$  analogue of bushmakinite (Yakubovich *et al.*, 2002), with  $\text{Fe}^{3+}$  replacing Al. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2014-055). The holotype specimen is housed in the collections of the Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue number 64512.

### Occurrence and paragenesis

Ferribushmakinite occurs in the phosphate stope at the Silver Coin mine, Valmy, Iron Point district, Humboldt County, Nevada, USA (40°55'44"N 117°19'26"W). The mineral is a low-temperature secondary mineral associated with plumbogummite, mottramite, Br-rich chlorargyrite and baryte on massive quartz. More than 130 mineral species have been reported from the Silver Coin mine. The vast majority of these are found in the phosphate stope. A partial list was provided by Thomssen and Wise (2004).

At the Silver Coin mine, quartz veins containing argentiferous galena, sphalerite and pyrite were emplaced, in part, along faults and fractures in phosphatic argillites. When exposed to vadose water, the pyrite and other sulfides were oxidized, producing acidic fluids that leached  $\text{PO}_4$  and Al from the argillite wall rocks. The prolific secondary assemblage then precipitated along fractures and bedding planes.

### Physical and optical properties

Ferribushmakinite occurs as yellow, slightly flattened prisms, elongated on [010] and exhibiting the crystal forms  $\{001\}$ ,  $\{10\bar{1}\}$  and  $\{1\bar{1}0\}$ . Individual crystals are up to 0.2 mm long. Crystals are ubiquitously twinned, typically forming interpenetrant X and sixling twins (Figs 1 and 2). An analysis of single-crystal XRD data using the *TwinSolve* program in the *CrystalClear* software package (Rigaku Corp.), determined the twinning to be by rotation of  $180^\circ$  on  $[111]$ . The program *Geminography* (Nespolo and Ferraris, 2006) confirmed the likelihood of



FIG. 1. Ferribushmakinite on plumbogummite (1.6 mm field of view).

this twin operation, yielding an obliquity of 0.22 and the twin plane (223). It is a hybrid twin by monoclinic pseudoholohedry. A single twin operation yields an X twin and combining it with the same operation on  $[1\bar{1}1]$  yields a sixling twin (Fig. 3).

The mineral has a pale yellow streak. Crystals are translucent and have adamantine lustre. Ferribushmakinite does not fluoresce in longwave or shortwave ultraviolet light. The Mohs hardness is  $\sim 2$ , the tenacity is brittle, the fracture is irregular to splintery and crystals exhibit one or two fair cleavages in the [010] zone. The density could not be measured because it is greater than those of available high-density liquids and there is

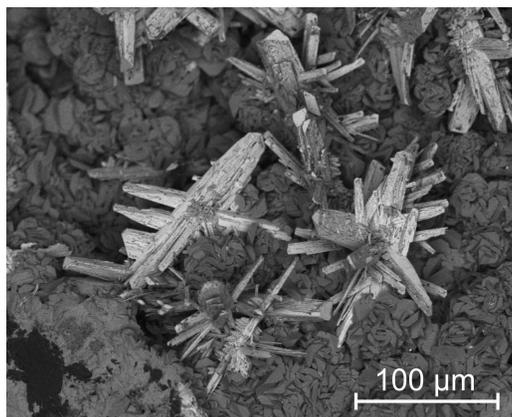


FIG. 2. Backscatter electron image of ferribushmakinite on plumbogummite.

FERRIBUSHMAKINITE, A NEW MINERAL FROM THE SILVER COIN MINE, NEVADA

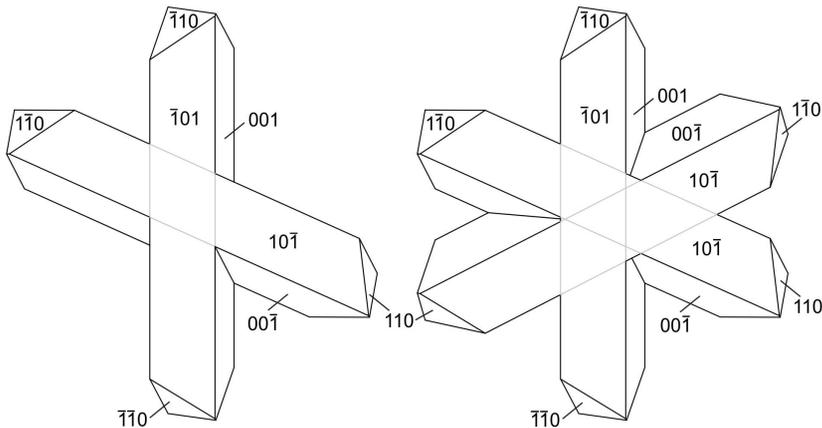


Fig. 3. Crystal drawings of ferribushmakinite X twin (left) and sixling twin (right), clinographic projections.

insufficient material for physical measurement. The calculated density based on the empirical formula and the unit cell refined from the single-crystal data is 6.154 g/cm<sup>3</sup>. Ferribushmakinite is easily soluble in room-temperature dilute HCl.

The indices of refraction could not be measured because they are higher than available index liquids. The Gladstone-Dale relationship (Mandarino, 1981) predicts an average index of refraction of 2.127. The translucency of crystals further interfered with the optical study. Retardation observations along the thin edges of crystals indicated the prisms to be both length fast and length slow, depending on their orientations. Because the prisms are elongated on [010], the optical orientation can be partially provided as  $Y = b$ .

**Chemical composition**

Quantitative analyses (4) were performed at the University of Utah using a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers (WDS). Analytical conditions were 15 kV accelerating voltage, 10 nA beam current and a beam diameter of 10 μm. No other elements were detected by energy dispersive spectroscopy. Other probable elements were sought by WDS-EMPA. Raw X-ray intensities were corrected for matrix effects with a  $\phi(\rho z)$  algorithm (Pouchou and Pichoir, 1991). Ferribushmakinite crystals fragment very easily; consequently, we were unable to obtain an adequate polish for the analyses. The rough surfaces yielded significantly low analytical totals. Analytical data are given in Table 1. We have also provided analytical values normalized to 100% for

TABLE 1. Electron microprobe data for ferribushmakinite.

Constituent	Wt.%	Min.	Max.	SD	Probe standard	Normalized
PbO	56.47	55.14	58.45	1.49	crocoite	63.69
CaO	0.06	0.05	0.07	0.01	diopside	0.07
CuO	0.98	0.80	1.15	0.16	Cu metal	1.11
Fe <sub>2</sub> O <sub>3</sub>	6.77	6.51	7.12	0.27	hematite	7.63
Al <sub>2</sub> O <sub>3</sub>	1.45	0.96	1.71	0.34	YAG	1.63
V <sub>2</sub> O <sub>5</sub>	11.22	10.61	11.54	0.42	Y vanadate (syn)	12.65
As <sub>2</sub> O <sub>5</sub>	2.74	2.29	3.16	0.36	GaAs (syn)	3.09
P <sub>2</sub> O <sub>5</sub>	7.65	7.23	8.28	0.46	apatite	8.63
H <sub>2</sub> O*	1.33					1.50
Total	88.67					100.00

\* Based on the structure

comparison. The empirical formula (based on nine O a.p.f.u.) is  $(\text{Pb}_{1.99}\text{Ca}_{0.01})_{\Sigma 2.00}(\text{Fe}_{0.66}\text{Al}_{0.22}\text{Cu}_{0.10})_{\Sigma 0.98}(\text{V}_{0.97}\text{P}_{0.85}\text{As}_{0.19})_{\Sigma 2.01}\text{O}_{7.84}(\text{OH})_{1.16}$ . The ideal formula is  $\text{Pb}_2\text{Fe}^{3+}(\text{PO}_4)(\text{VO}_4)(\text{OH})$ , which requires PbO 64.03,  $\text{Fe}_2\text{O}_3$  11.45,  $\text{P}_2\text{O}_5$  10.18,  $\text{V}_2\text{O}_5$  13.04,  $\text{H}_2\text{O}$  1.29, total 100 wt%.

### X-ray crystallography and structure refinement

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II

curved imaging plate microdiffractometer, with monochromatized  $\text{MoK}\alpha$  radiation. For the powder-diffraction study, a Gandolfi-like motion on the  $\varphi$  and  $\omega$  axes was used to randomize the sample and observed  $d$  spacings and intensities were derived by profile fitting using *JADE 2010* software (Materials Data, Inc.). The powder data are presented in Table 2. Unit-cell parameters refined from the powder data using *JADE 2010* with whole pattern fitting are:  $a = 7.776(2)$ ,  $b = 5.914(2)$ ,  $c = 8.797(2)$  Å,  $\beta = 111.582(8)^\circ$  and  $V = 376.19(18)$  Å<sup>3</sup>.

TABLE 2. Powder XRD data for ferribushmakinite. Calculated lines with intensities <2 are not shown.

$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{calc}}$	$hkl$
20	8.20	8.1752	18	0 0 1	4	1.9013	1.9140	4	0 3 1
3	7.12	7.2259	2	1 0 0			1.8665	2	3 2 0
46	4.794	4.7874	38	0 1 1			1.8542	12	$\bar{3}$ 1 4
9	4.603	{ 4.6334	6	1 0 1	27	1.8532	{ 1.8521	6	$\bar{4}$ 0 3
		{ 4.5729	2	1 1 0			{ 1.8404	3	$\bar{4}$ 1 2
7	4.447	4.4580	5	$\bar{1}$ 1 1			1.8251	5	$\bar{4}$ 1 1
7	4.122	4.0876	5	0 0 2			1.8119	2	1 3 1
7	3.884	3.8738	9	$\bar{2}$ 0 1			1.8081	8	1 2 3
23	3.644	3.6454	19	1 1 1	27	1.8084	{ 1.8065	4	4 0 0
		3.6130	6	2 0 0			{ 1.8007	2	1 0 4
5	3.479	3.4765	5	$\bar{1}$ 1 2			1.7975	4	$\bar{3}$ 2 3
		3.3982	5	$\bar{2}$ 0 2			1.7737	3	0 3 2
19	3.381	{ 3.3611	19	0 1 2	21	1.7601	{ 1.7585	4	$\bar{1}$ 2 4
84	3.245	3.2392	84	$\bar{2}$ 1 1			1.7550	10	$\bar{2}$ 3 1
2	3.106	3.1019	6	1 0 2			1.7260	4	3 1 2
		2.9530	32	0 2 0	28	1.7204	{ 1.7224	6	1 1 4
100	2.947	{ 2.9455	25	$\bar{2}$ 1 2			{ 1.7165	10	3 2 1
		2.9308	42	$\bar{1}$ 0 3			1.7035	4	$\bar{2}$ 3 2
22	2.768	2.7774	11	0 2 1			1.6677	5	$\bar{1}$ 1 5
49	2.743	2.7462	48	1 1 2	18	1.6668	{ 1.6622	9	1 3 2
		2.7335	5	1 2 0			1.6340	2	2 3 1
		2.7251	3	0 0 3	9	1.6292	{ 1.6329	2	$\bar{4}$ 1 4
		2.7084	7	$\bar{1}$ 2 1			1.6196	6	$\bar{4}$ 2 2
12	2.629	2.6246	14	2 1 1	8	1.6091	1.6052	5	$\bar{3}$ 1 5
5	2.471	2.4607	3	$\bar{2}$ 1 3			1.5758	2	0 1 5
		2.4343	3	$\bar{1}$ 2 2	6	1.5731	{ 1.5691	3	$\bar{4}$ 2 3
9	2.410	2.4086	6	3 0 0			1.5445	3	3 0 3
		2.3937	2	0 2 2	6	1.5449	{ 1.5399	2	3 2 2
		2.3662	2	$\bar{3}$ 1 1	6	1.4962	1.4981	4	$\bar{1}$ 2 5
37	2.288	2.2864	30	2 2 0			1.4765	6	0 4 0
		2.2655	3	$\bar{3}$ 0 3	12	1.4735	{ 1.4743	4	$\bar{5}$ 1 1
5	2.229	2.2290	3	$\bar{2}$ 2 2			1.4654	2	$\bar{2}$ 0 6
2	2.151	2.1502	2	$\bar{2}$ 0 4			1.4638	2	$\bar{1}$ 3 4
7	2.105	2.1095	5	3 0 1	3	1.4392	1.4393	2	3 3 1
23	2.080	2.0802	22	$\bar{1}$ 2 3	6	1.3866	1.3865	4	$\bar{3}$ 3 4
8	2.052	2.0526	9	$\bar{1}$ 1 4			1.3742	2	$\bar{4}$ 3 1
		1.9954	8	$\bar{2}$ 2 3	8	1.3708	{ 1.3731	3	2 2 4
13	1.9962	{ 1.9866	4	3 1 1			{ 1.3686	3	3 2 3
10	1.9355	1.9369	6	$\bar{4}$ 0 2					

The complex multiple twinning and relatively poor quality of ferribushmakinite crystals made the selection of a single crystal for structure-data collection very challenging. The small crystal fragment chosen only provided usable data to 25° $\theta$ . The Rigaku *CrystalClear* software package was used for processing the structure data, including the application of an empirical multi-scan absorption correction using *ABSCOR* (Higashi, 2001). The structure was solved by direct methods using *SIR2004* (Burla *et al.*, 2005). *SHELXL-2013* software (Sheldrick, 2008) was used for the refinement of the structure. A difference Fourier synthesis located the H7 atom position, which was refined with a soft constraint on the OH7–H7 distance of 0.9(3) Å. The isotropic displacement parameter of H7 was set to 1.2  $\times$  that of the OH7 atom. There remain four residual electron density maxima >1.5 e, all of which are within 1.2 Å of Pb1 or Pb2. Details of the data collection and structure refinement are

provided in Table 3. Fractional coordinates and displacement parameters are provided in Table 4, selected interatomic distances in Table 5 and bond valences in Table 6.

## Discussion

The structure of ferribushmakinite (Fig. 4) contains edge-sharing chains of Fe<sup>3+</sup>O<sub>6</sub> octahedra along [010]. The chains are decorated with PO<sub>4</sub> and VO<sub>4</sub> tetrahedra yielding Fe<sup>3+</sup>(PO<sub>4</sub>)(VO<sub>4</sub>)(OH) structural units (Fig. 5), which are linked together *via* bonds to two different Pb atoms. Pb1 and Pb2 are both bonded to 12 O atoms in off-centre coordinations, typical of Pb<sup>2+</sup> with stereoactive lone-pair electrons. Ferribushmakinite is isostructural with other members of the brackebuschite supergroup (c.f. Cámara *et al.*, 2014) and is most similar to bushmakinite (Yakovovich *et al.*, 2002), differing only in the dominance of Fe<sup>3+</sup> over Al in the octahedral site.

TABLE 3. Data-collection and structure-refinement details for ferribushmakinite.

Diffractionmeter	Rigaku R-Axis Rapid II
X-ray radiation / power	MoK $\alpha$ ( $\lambda = 0.71075$ Å) / 50 kV, 40 mA
Temperature	298(2) K
Structural formula	Pb <sub>2</sub> (Fe <sub>0.81</sub> Al <sub>0.19</sub> )(P <sub>0.80</sub> As <sub>0.20</sub> )(V <sub>0.82</sub> As <sub>0.18</sub> )O <sub>9</sub> (OH)
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>
Unit-cell dimensions	<i>a</i> = 7.7719(10) Å <i>b</i> = 5.9060(7) Å <i>c</i> = 8.7929(12) Å $\beta$ = 111.604(8)°
<i>V</i>	375.24(9) Å <sup>3</sup>
<i>Z</i>	2
Density (for above formula)	6.236 g cm <sup>-3</sup>
Absorption coefficient	49.136 mm <sup>-1</sup>
<i>F</i> (000)	607.8
Crystal size	50 $\times$ 10 $\times$ 2 $\mu$ m
$\theta$ range	3.00 to 25.02°
Index ranges	$-8 \leq h \leq 9$ , $-6 \leq k \leq 7$ , $-10 \leq l \leq 10$
Reflections collected / unique	3209 / 729 [ <i>R</i> <sub>int</sub> = 0.077]
Reflections with <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> )	577
Completeness to $\theta = 25.02^\circ$	99.6%
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Parameters refined	85
Goof	1.067
Final <i>R</i> indices [ <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> )	<i>R</i> <sub>1</sub> = 0.0383, <i>wR</i> <sub>2</sub> = 0.0799
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0535, <i>wR</i> <sub>2</sub> = 0.0856
Extinction coefficient	0.0010(5)
Largest diff. peak / hole	+2.18 / -1.80 e/Å <sup>3</sup>

$R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$ . Goof =  $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ .  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  
 $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  where *a* is 0.0237, *b* is 4.6913 and *P* is  $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$ .

TABLE 4. Atom coordinates and displacement parameters ( $\text{\AA}^2$ ) for ferribushmakinite.

	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Pb1	0.69645(12)	0.25	0.59365(10)	0.0380(4)	0.0307(6)	0.0505(7)	0.0344(6)	0.000	0.0138(4)	0
Pb2	0.27478(12)	0.25	0.73570(10)	0.0380(4)	0.0302(6)	0.0546(7)	0.0332(6)	0.000	0.0163(4)	0
Fe*	0	0	0	0.0230(12)	0.0211(19)	0.029(2)	0.0181(18)	0.0005(13)	0.0066(14)	-0.0012(14)
P*	0.0298(6)	0.25	0.3337(5)	0.0247(17)	0.027(3)	0.029(3)	0.020(2)	0	0.0105(18)	0
V*	0.4348(4)	0.25	0.1726(3)	0.0231(14)	0.019(2)	0.030(2)	0.0193(19)	0	0.0066(13)	0
O1	0.900(2)	0.25	0.4257(17)	0.045(4)	0.053(11)	0.050(11)	0.032(9)	0	0.017(8)	0
O2	0.233(2)	0.25	0.4516(17)	0.044(4)	0.048(11)	0.063(11)	0.021(8)	0	0.013(7)	0
O3	0.9963(14)	0.0296(17)	0.2252(11)	0.032(3)	0.037(6)	0.041(6)	0.015(5)	0.001(4)	0.005(4)	-0.004(5)
O4	0.548(2)	0.25	0.0465(18)	0.040(4)	0.035(9)	0.061(11)	0.040(9)	0	0.031(7)	0
O5	0.4955(13)	0.4827(17)	0.2946(11)	0.029(2)	0.028(6)	0.037(6)	0.027(5)	-0.005(4)	0.015(4)	-0.007(5)
O6	0.1929(18)	0.25	0.0493(15)	0.028(3)	0.020(8)	0.043(9)	0.022(7)	0	0.008(6)	0
OH7	0.8286(18)	0.25	0.9194(16)	0.026(3)	0.014(7)	0.032(9)	0.025(8)	0	-0.002(6)	0
H7	0.75(2)	0.25	0.98(2)	0.032						

\* Refined site occupancies: Fe: Fe<sub>0.8(2)</sub>Al<sub>0.19(2)</sub>; P: P<sub>0.80(2)</sub>As<sub>0.20(2)</sub>; V: V<sub>0.83(3)</sub>As<sub>0.18(3)</sub>.

TABLE 5. Selected bond distances (Å) and angles (°) in ferribushmakinite.

Pb1-O1	2.528(17)	Pb2-O2	2.398(14)	Fe-OH7( $\times 2$ )	1.939(8)	V-O4	1.650(14)	P-O1	1.510(17)
Pb1-O5( $\times 2$ )	2.600(10)	Pb2-O5( $\times 2$ )	2.470(10)	Fe-O3( $\times 2$ )	1.998(9)	V-O5( $\times 2$ )	1.700(9)	P-O2	1.538(16)
Pb1-OH7	2.663(13)	Pb2-O4	2.776(15)	Fe-O6( $\times 2$ )	2.034(9)	V-O6	1.791(13)	P-O3( $\times 2$ )	1.578(10)
Pb1-O3( $\times 2$ )	2.858(10)	Pb2-O3( $\times 2$ )	2.796(10)	<Fe-O>	1.993	<V-O>	1.710	<P-O>	1.535
Pb1-O5( $\times 2$ )	2.867(9)	Pb2-O6	3.050(14)	Hydrogen bond (D = donor, A = acceptor)					
Pb1-O2( $\times 2$ )	3.056(4)	Pb2-O1	3.175(15)	D-H	$d(D-H)$	$d(H...A)$	<DHA	$d(D...A)$	A
Pb1-O2	3.349(17)	Pb2-O1( $\times 2$ )	3.340(7)	OH7-H7	0.90(3)	1.91(6)	167(19)	2.79(2)	O4
<Pb1-O>	2.846	Pb2-O4( $\times 2$ )	3.513(8)	<Pb2-O>	2.920				

TABLE 6. Bond-valence analysis for ferribushmakinite.\* Values are expressed in valence units.

	O1	O2	O3	O4	O5	O6	OH7	$\Sigma$
Pb1	0.32	$0.11 \times 2 \downarrow \rightarrow$ 0.06	$0.16 \times 2 \rightarrow$		$0.27 \times 2 \rightarrow$ $0.16 \times 2 \rightarrow$		0.24	2.02
Pb2	0.08	0.41	$0.18 \times 2 \rightarrow$	0.19	$0.36 \times 2 \rightarrow$	0.11		2.03
Fe	$0.06 \times 2 \downarrow \rightarrow$		$0.50 \times 2 \rightarrow$	$0.04 \times 2 \downarrow$		$0.45 \times 2 \downarrow \rightarrow$	$0.59 \times \downarrow \rightarrow$	3.08
P	1.43	1.33	$1.19 \times \rightarrow$	1.49	$1.30 \times 2 \rightarrow$	1.02		5.14
V				0.18			0.82	5.11
H7				1.94	2.09	2.03	2.24	1.00
$\Sigma$	1.95	2.02	2.04					

\* Multiplicity is indicated by  $\times \downarrow \rightarrow$ . Bond strengths are based on refined site occupancies;  $Pb^{2+}$ -O bond-valence parameters from Krivovichev and Brown (2001);  $P^{5+}$ -O and  $Al$ -O from Brese and O'Keeffe (1991);  $Fe^{3+}$ -O,  $V^{5+}$ -O and  $As^{5+}$ -O from Brown and Altermatt (1985); hydrogen-bond strengths based on O...O bond lengths, also from Brown and Altermatt (1985).

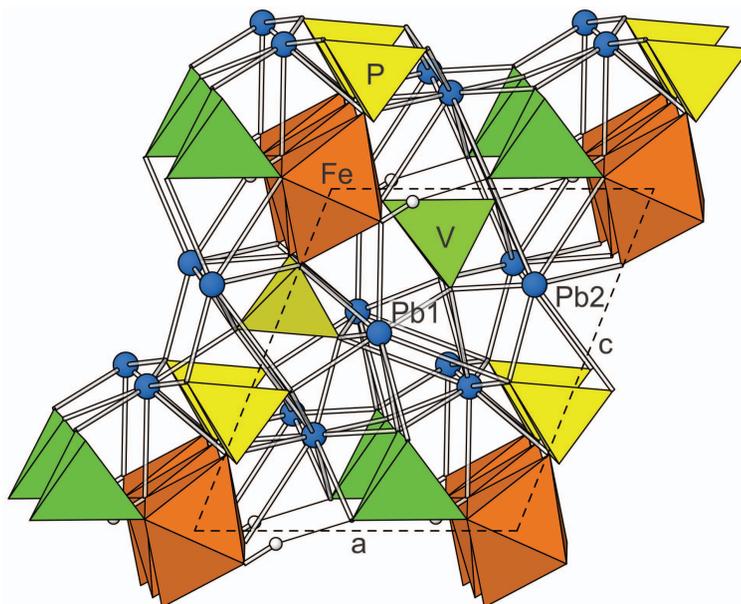


FIG. 4. The structure of ferribushmakinite viewed slightly canted along [010]. Hydrogen atoms are shown as spheres. Pb–O and O–H bonds are shown as sticks. Hydrogen bonds are shown as single lines. The outline of the unit cell is shown by thick dashed lines.

Ferribushmakinite is one of a growing list of minerals with a common structural motif (c.f. Cámara *et al.*, 2014; Hawthorne, 1998). The brackebuschite supergroup, as listed by Cámara *et al.* (2014), includes the vanadates (brackebuschite, calderónite, gamagarite and tokyoite), the arsenates (arsenbrackebuschite, feinglosite and grandaite), the phosphates (bearthite and goedkenite) and phases with mixed tetrahedral anions (tsumebite, arsenstumbite, bushmakinite and ferribushmakinite). The same structural topology is found in the mixed-anion minerals fornacite, molybdoformacite and vauquelinite and

the silicates törnebohmite-(Ce) and törnebohmite-(La); therefore, these could also be included in the brackebuschite supergroup.

Cámara *et al.* (2014) list heyite,  $\text{Pb}_5\text{Fe}_2^{2+}(\text{VO}_4)_2\text{O}_4$ , as a member of the brackebuschite supergroup with the qualification that the mineral needs further study. The cell parameters and powder XRD pattern of heyite (Williams, 1973) are consistent with it being a member of the brackebuschite supergroup; however, the chemical composition and ideal formula reported by Williams (1973) are not compatible with the brackebuschite structure. Symes and Williams

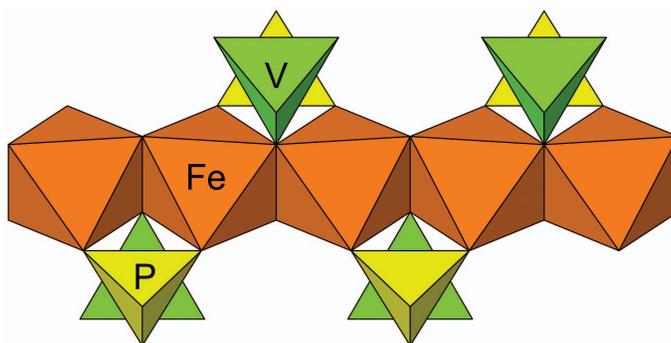


FIG. 5. The  $\text{Fe}^{3+}(\text{PO}_4)(\text{VO}_4)(\text{OH})$  structural unit in ferribushmakinite.

(1973) recognized the crystallographic similarities between heyite and brackebuschite, but ascribed them to “mere coincidence”. Calderónite (González del Tánago *et al.*, 2003),  $\text{Pb}_2\text{Fe}^{3+}(\text{VO}_4)_2(\text{OH})$ , another member of the brackebuschite supergroup that we have confirmed to occur at the Silver Coin mine, is so similar to heyite in cell parameters, powder pattern and chemical constituents that it is difficult to accept that they are not the same mineral and, indeed, recent examination of heyite crystals on the holotype specimen (BM1972,194) has confirmed the structural correspondence of heyite and calderónite (M.D. Welch, pers. comm.) and the identity of the two species.

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### References

- Breese, N.E. and O’Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, **B41**, 244–247.
- Burla, M.C., Caliendo, R., Camalli, M., Carozzini, B., Cascarano, G.L., De Caro, L., Giacovazzo, C., Polidori, G. and Spagna, R. (2005) SIR2004: an improved tool for crystal structure determination and refinement. *Journal of Applied Crystallography*, **38**, 381–388.
- Cámara, F., Ciriotti, M.E., Bittarello, E., Nestola, F., Massimi, F., Radica, F., Costa, E., Benna, P. and Piccoli, G.C. (2014) As-bearing new mineral species from Valletta mine, Maira Valley, Piedmont, Italy: I. Grandaitite,  $\text{Sr}_2\text{Al}(\text{AsO}_4)_2(\text{OH})$ , description and crystal structure. *Mineralogical Magazine*, **78**, 757–774.
- Chukanov, N.V., Pekov, I.V., Möckel, S., Zadov, A.E. and V.T. Dubinchuk (2006) Zinclipscumbite  $\text{ZnFe}^{3+}(\text{PO}_4)_2(\text{OH})_2$  – a new mineral. *Proceedings of the Russian Mineralogical Society*, **135**, 13–18.
- González del Tánago, J., La Iglesia, A., Rius, J. and Fernández Santín, S. (2003) Calderónite, a new lead-iron-vanadate of the brackebuschite group. *American Mineralogist*, **88**, 1703–1708.
- Hawthorne, F.C. (1998) Structure and chemistry of phosphate minerals. *Mineralogical Magazine*, **62**, 141–164.
- Higashi, T. (2001) *ABSCOR*. Rigaku Corporation, Tokyo.
- Kampf, A.R., Adams, P.M., Kolitsch, U. and Steele, I.M. (2009) Meurigite-Na, a new species, and the relationship between phosphofibrite and meurigite. *American Mineralogist*, **94**, 720–727.
- Kampf, A.R., Adams, P.M., Housley, R.M. and Rossman, G.R. (2014) Fluorowardite,  $\text{NaAl}_3(\text{PO}_4)_2\text{F}_2(\text{OH})_2(\text{H}_2\text{O})_2$ , the fluorine analogue of wardite from the Silver Coin mine, Valmy, Nevada. *American Mineralogist*, **98**, 804–810.
- Krivovichev, S.V. and Brown, I.D. (2001) Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Zeitschrift für Kristallographie*, **216**, 245–247.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *The Canadian Mineralogist*, **19**, 441–450.
- Mills, S.J., Kampf, A.R., Sejkora, J., Adams, P.M., Birch, W.D. and Plášil, J. (2011) Iangreyite: a new secondary phosphate mineral closely related to perhamite. *Mineralogical Magazine*, **75**, 329–338.
- Mills, S.J., Sejkora, J., Kampf, A.R., Grey, I. E., Bastow, T.J., Ball, N.A., Adams, P.M., Raudsepp, M. and Cooper, M.A. (2012) Krásnoite, the fluorophosphate analogue of perhamite, from the Huber open pit, Czech Republic and the Silver Coin mine, Nevada. *Mineralogical Magazine*, **76**, 625–634.
- Nespolo, M. and Ferraris, G. (2006) The derivation of twin laws in non-merohedric twins. Application to the analysis of hybrid twins. *Acta Crystallographica*, **A62**, 336–349.
- Pouchou, J.-L. and Pichoir, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model “PAP.” Pp. 31–75 in: *Electron Probe Quantitation* (K.F.J. Heinrich and D.E. Newbury (editors). Plenum Press, New York.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.
- Symes, R.F. and Williams, S.A. (1973) Heyite and brackebuschite compared. *Mineralogical Magazine*, **39**, 69–73.
- Thomssen, D. and Wise, W.S. (2004) Special list: Silver Coin Mine, Iron Point district, Edna Mountains, Humboldt Co., Nevada, USA. *International Micromounter’s Journal*, **13**, 7–8.
- Williams, S.A. (1973) Heyite,  $\text{Pb}_5\text{Fe}_2(\text{VO}_4)_2\text{O}_4$ , a new mineral from Nevada. *Mineralogical Magazine*, **39**, 65–68.
- Yakubovich, O.V., Massa, V. and Pekov, I.V. (2002) Crystal structure of the new mineral bushmakinitite,  $\text{Pb}_2\{(\text{Al,Cu})[\text{PO}_4][(\text{V,Cr,P})\text{O}_4](\text{OH})\}$ . *Doklady Earth Sciences*, **382**, 100–105.

