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Meurigite-Na, a new species, and the relationship between phosphofibrite and meurigite

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ABSTRACT

The new mineral meurigite-Na, $[\mathrm{Na(H_2O)_{2.5}}][\mathrm{Fe^{3+}_8(PO_4)_6(OH)_7(H_2O)_4}]$, is monoclinic with space group *C*2/*c* and cell parameters a = 28.835(2), b = 5.1848(4), c = 19.484(1) Å, β = 106.983(6)°, V = 2785.8(2) Å^3, and Z = 4. It is the Na analog of meurigite, which is now named meurigite-K. The type locality of meurigite-Na is the Silver Coin mine, Valmy, Iron Point district, Nevada, where it occurs as radial sprays of cream-colored, flattened fibers (thin laths) to 0.4 mm in length. At the Silver Coin mine, meurigite-Na occurs very late in a paragenetic sequence that includes (in approximate order from early to late) quartz, barite, apatite-(CaF), goethite, rockbridgeite, cacoxenite, alunite, wardite, turquoise/chalcosiderite, leucophosphite, lipscombite/zinclipscombite, kidwellite, strengite/variscite, crandallite/perhamite, and jarosite. Meurigite-Na also occurs at Tom's quarry and Moculta quarry in South Australia, Australia, Lake Boga quarry and probably Rixon's Sandstone quarry in Victoria, Australia, and at an unnamed pegmatite prospect near Linopolis, Minas Gerais, Brazil. The streak is white, the luster is silky, and the Mohs hardness is about 3. The measured density is 2.94(2) g/cm^3 and the calculated density is 2.954 g/cm^3. Optical properties: biaxial (–), α = 1.740(3), β = 1.759(3), γ = 1.763(3), $2V_{\mathrm{meas}}$ = 50(10)°; X ≅ *c*, Z = *b*. The strongest powder X-ray diffraction lines are [*d*(*hkl*)*I*]: 13.8(200)20, 9.35(002)100, 4.843(111)20, 3.206($\bar{7}$12)40, 3.107($\bar{7}$13)30, 2.971(513)15, and 2.593(116)15. Meurigite-Na is insoluble in concentrated HCl. Evaluation of powder XRD and chemical-analytical data in light of the structure determination for meurigite-K leads to the conclusion that type phosphofibrite is isostructural with meurigite and represents the alkali-deficient member of a series with meurigite-K.

Keywords: Meurigite-Na, meurigite-K, phosphofibrite, new mineral, crystal chemistry, Silver Coin mine

INTRODUCTION

One of the authors (P.M.A.) first collected specimens of the new mineral described herein in 2003 at the Silver Coin mine, Valmy, Iron Point district, Nevada. The sprays of yellow to cream fibers resembled meurigite, which had been reported from the mine previously (Pullman and Thomssen 1999; Castor and Ferdock 2004), and an X-ray powder diffraction pattern showed a close match with meurigite; however, a check of the chemistry by energy-dispersive spectroscopy indicated that Na rather than K was dominant.

In their original description of meurigite from the Santa Rita mine, Grant County, New Mexico, Birch et al. (1996) were unable to determine its crystal structure, leaving some uncertainty as to the exact stoichiometry of the chemical formula. That, coupled with the possible identity of meurigite and phosphofibrite acknowledged by Birch et al. (1996) and more strongly pointed out by Kolitsch (1999), made it desirable to directly compare the Na-rich material from the Silver Coin mine with the original type meurigite and, in particular, to obtain Fourier transform infrared spectra of the two under equivalent conditions. Quite serendipitously, a small piece from the meurigite type specimen provided by the Museum of Victoria (Melbourne, Australia), also yielded a crystal fragment of sufficient quality for the determination of its crystal structure using a synchrotron source (Kampf et al. 2007).

The present study describes the new mineral meurigite-Na, reports on the renaming of the original meurigite to meurigite-K, and provides an analysis of the evidence for the possible identity of meurigite-K and phosphofibrite. Unfortunately, our lack of success in obtaining phosphofibrite type material must leave final clarification of the last of these issues open. The new mineral meurigite-Na and the renaming of the original meurigite to meurigite-K have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2007-024). Type material is deposited in the Natural History Museum of Los Angeles County under catalog numbers 57659 and 57660.

DESCRIPTION OF MEURIGITE-NA

Occurrences

The type locality of meurigite-Na is the Silver Coin mine (SW¼ Sec. 1 and SE¼ Sec. 2, T35N, R41E) Valmy, Iron Point district, Humboldt County, Nevada (Fig. 1). The following

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excerpt from Vanderburg (1988) provides background on the Silver Coin group of claims:

> The Silver Coin group of five unpatented claims is owned by the Kramer Estate, Lyle L. Kramer, of Golconda, Nevada, administrator. According to the records in possession of Kramer, the production of shipping ore from 1918 to 1924 by Kramer and lessees was 25 lots, totaling 693.5 dry tons containing 30,854 ounces of silver, or an average of 44.49 ounces per ton. The ore also contained a little lead and about 0.02 ounce gold per ton.
>
> Development consists of several shallow shafts, open cuts, and surface trenches totaling approximately 1200 feet. The principal working is the Silver Coin shaft inclined about 30° and 165 feet deep. There is no equipment on the property.
>
> The formations are silicified limestone and black shale intruded by andesite. The vein strikes north 15° east and dips 32° to the west, averaging 3 feet in width. The width of the shipping ore averaged about 20 inches. The principal economic mineral in the ore is silver occurring in cerargyrite, argentite, and tetrahedrite, associated with cerussite and oxidized copper minerals.

William S. Wise (personal communication 2008) describes the geology of the deposit as follows:

> The host rocks for the Pb-Zn-Ag containing veins exploited by the Silver Coin mine are thin bedded quartzite, argillite, and phosphatic-argillite of late Paleozoic age. Veins consisting of quartz, barite, pyrite, argentiferous-galena, and sphalerite filled a fault zone and associated fractures. Upon exposure to oxygenated vadose water, the pyrite and other sulfide minerals oxidized to acidic fluids. These solutions leached phosphate and Al from the argillite wall rocks leading to the formation of the prolific secondary phosphate assemblage, precipitated in fractures and bedding planes.

At the Silver Coin mine, meurigite-Na occurs very late in a paragenetic sequence that includes (in approximate order from early to late) quartz, barite, apatite-(CaF), goethite, rockbridgeite, cacoxenite, alunite, wardite, turquoise/chalcosiderite, leucophosphite, lipscombite/zinclipscombite, kidwellite, strengite/variscite, crandallite/perhamite, and jarosite. (Species separated by slashes exhibit variations in chemistry between the two species.) Note that the crandallite and perhamite examined contain significant amounts of F, apparently substituting for OH. These are currently under study as possible new F-analogs of these mineral species.

FIGURE 1. Entrance to the main decline at the Silver Coin mine. Photo by William S. Wise.

Other reported occurrences of meurigite-Na include several localities in Australia: Tom's quarry, Kapunda, Mt. Lofty Ranges, South Australia; Moculta quarry, Angaston, Mt. Lofty Ranges, South Australia; Lake Boga quarry, Lake Boga, Victoria; and probably Rixon's Sandstone quarry, Campbells Creek, Victoria. Meurigite-Na has also been confirmed in association with ruifrancoite, leucophosphite, muscovite, and quartz on a specimen from an unnamed pegmatite prospect near Linopolis, Minas Gerais, Brazil. Note that this latter locality is presumably not the Sapucaia mine, Minas Gerais, Brazil, the type locality of ruifrancoite (Atencio et al. 2007). We confirmed by EDS that meurigite-K is associated with ruifrancoite on the type specimen of that mineral.

At all of its occurrences meurigite-Na formed as a late-stage, low-temperature, secondary mineral in complex phosphate assemblages rich in Fe^{3+} and Na.

Physical and optical properties

At the Silver Coin mine, meurigite-Na forms radial sprays of cream-colored, flattened fibers (thin laths) to 0.4 mm in length (Figs. 2 and 3). The fibers are flattened on {001} and elongated parallel to [010]. Radial aggregates can reach 1 mm or more in diameter.

The color of the mineral is white, creamy, or yellow, and its streak is white. Longitudinal striations on the surfaces of laths give the mineral a silky luster. The laths are slightly flexible and have a splintery fracture. The crystal structure suggests a likely cleavage on {001}, but it is not observed because of the small crystal size. The Mohs hardness is estimated to be about 3. The density measured by the sink-float method in sodium polytungstate solution is 2.94(2) g/cm^3. The density calculated from the empirical formula and refined unit-cell data is 2.954 g/cm^3.

Meurigite-Na is biaxial (–) with indices of refraction α = 1.740(3), β = 1.759(3), and γ = 1.763(3) measured in light of a wavelength of 589 nm. The $2V$ estimated conoscopically is 50(10)°; the calculated $2V$ is 49°. No dispersion was observed. The optical orientation is $X \cong c$, $Z = b$. The mineral is nonpleochroic.

The Gladstone-Dale compatibility $[1 - (K_P/K_C)]$ is 0.0398, indicating excellent agreement between the chemistry, density, and average of the indices of refraction.

Chemical composition

Quantitative chemical analyses were performed by electron microprobe (EMP) in WDS mode at an accelerating voltage of 15 kV and beam current of 25 nA, slightly defocused beam. The standards used were: Amelia albite (Na), asbestos microcline (K), anorthite glass (Ca, Al), Mn- and Mg-bearing olivine (Fe, Mg), Cu metal (Cu), synthetic $Ca_2P_2O_7$ (P), and synthetic V_2O_3 (V).

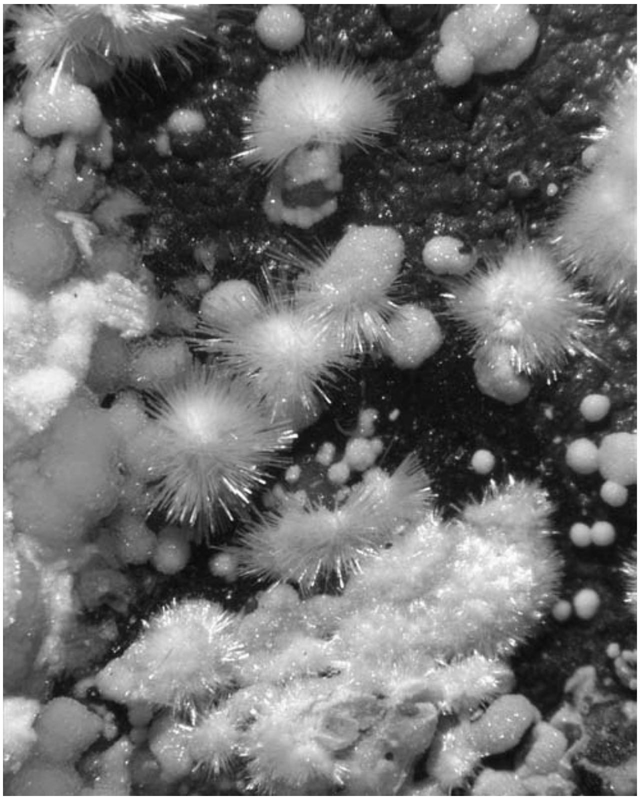

FIGURE 2. Sprays of meurigite-Na with turquoise, intergrown kidwellite/lipscombite, and crandallite on goethite from the Silver Coin mine. The largest spray is about 1 mm across.

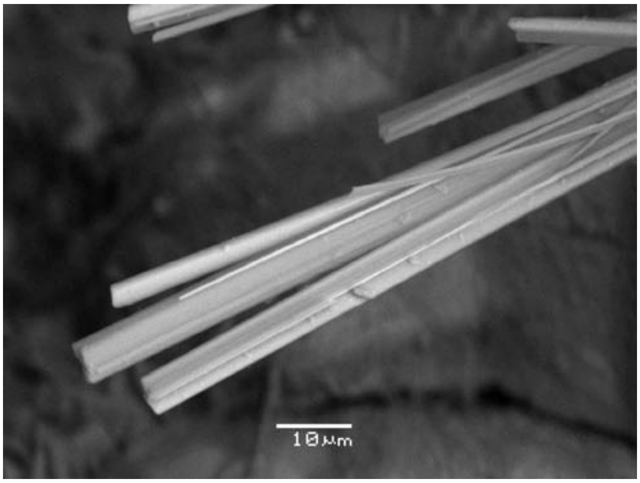

FIGURE 3. SEM image of meurigite-Na crystals.

TABLE 1. Chemical analyses of meurigite and phosphofibrite

	1	2	3	4	5	6
Na_2O	2.13 (1.27–2.96)	0.07	–	–	–	–
K_2O	0.32 (0.29–0.38)	3.37	2.78	2.33	1.90	1.55 (1.38–1.77)
CaO	0.21 (0.17–0.25)	–	–	–	–	0.16 (0.13–0.21)
CuO	0.27 (0.16–0.38)	0.16	0.25	–	2.60	2.84 (2.31–3.12)
Fe_2O_3	42.14 (40.67–42.67)	47.4	48.7	45.85	46.6	42.7 (41.8–43.6)
Al_2O_3	5.36 (4.67–5.86)	0.70	–	2.20	1.50	0.92 (0.20–1.54)
MgO	0.03 (0.03–0.04)	–	–	–	–	–
P_2O_5	32.48 (31.50–33.70)	30.7	30.9	32.06	34.0	29.7 (28.5–30.3)
As_2O_5	–	0.03	–	–	–	0.88 (0.77–1.03)
V_2O_5	0.92 (0.80–1.01)	–	–	–	–	–
CO_2	n.d.	0.73	n.d.	3.08	n.d.	n.d.
H_2O*	[16.14]	16.2	[17.37]	14.48	[13.4]	[21.25]
Total	100.00	99.37	100.00	100.00	100.00	100.00

Notes: 1 = Meurigite-Na (type), Silver Coin mine, Nevada; average and range of four analyses $[Na_{0.86}K_{0.09}Ca_{0.05}(H_2O)_{1.90}(H_3O)_{0.60}]_{\Sigma 3.50}[(Fe^{3+}_{6.63}Al_{1.32}Cu_{0.04}Mg_{0.01})_{\Sigma 8.00}(P_{0.96}V_{0.02}O_4)_6(OH)_7(H_2O)_4]$.
2 = Meurigite-K (type), Santa Rita mine, Grant Co., New Mexico (Birch et al. 1996) $[(K_{0.91}Na_{0.03})_{\Sigma 0.94}(H_2O)_{2.56}]_{\Sigma 3.50}[(Fe^{3+}_{7.52}Al_{0.17}Cu_{0.03})_{\Sigma 7.72}(PO_4)_{5.48}(CO_3)_{0.21}(OH)_{7.20}(H_2O)_{5.23}]$.
3 = Meurigite-K, Clara mine, Black Forest, Germany (Walenta and Theye 2001) $[K_{0.74}(H_2O)_{2.76}]_{\Sigma 3.50}[(Fe^{3+}_{7.66}Cu_{0.04})_{\Sigma 7.70}(PO_4)_{5.47}(OH)_{7.39}(H_2O)_{5.72}]$.
4 = Meurigite-K, Kněžská hora quarry, Bohemia, Czech Republic (Sejkora et al. 2000) $[K_{0.62}(H_2O)_{1.26}(CO_3)_{0.54}][(Fe^{3+}_{7.20}Al_{0.54})_{\Sigma 7.74}(PO_4)_{5.66}(CO_3)_{0.34}(OH)_{5.10}(H_2O)_{6.26}]$.
5 = Phosphofibrite (type), Clara mine, Black Forest, Germany (Walenta and Dunn 1984) $[K_{0.47}(H_2O)_{3.03}]_{\Sigma 3.50}[(Fe^{3+}_{6.87}Cu_{0.39}Al_{0.34})_{\Sigma 7.60}(PO_4)_{5.65}(OH)_{5.93}(H_2O)_{6.44}]$.
6 = Phosphofibrite (type), Clara mine, Black Forest, Germany (Kampf et al. 2007); average and range of nine analyses: $[K_{0.43}Ca_{0.04}(H_2O)_{3.03}]_{\Sigma 3.50}[(Fe^{3+}_{6.91}Cu_{0.45}Al_{0.24})_{\Sigma 7.60}(PO_4)_{5.41}(AsO_4)_{0.09}(OH)_{6.35}(H_2O)_{6.65}]$.
* H_2O values in brackets are by difference.

Water could not be directly determined because of the difficulty in separating enough pure material. The presence of H_2O was confirmed by infrared spectroscopy (see below). The small peak in the infrared spectrum between 1400 and 1470 cm^{-1} assignable to CO_2 in meurigite-K is not observed in the meurigite-Na spectrum, indicating little or no CO_2 in meurigite-Na. Water was calculated, based upon the structure of meurigite-K (Kampf et al. 2007). The results of four electron microprobe analyses are reported in Table 1. The samples were easily damaged by the beam. We attribute this largely to volatilization of H_2O. There appeared to be no significant Na burn-off; however, the large range in analyzed Na_2O content may, in part, be due to differential volatilization of this constituent. As discussed later, significant variability in Na_2O content is readily accommodated by the structure.

The empirical formula (based on Fe + Al + Cu + Mg = 8 apfu) is:

$$[Na_{0.86}K_{0.09}Ca_{0.05}(H_2O)_{1.90}(H_3O)_{0.60}][Fe^{3+}_{6.63}Al_{1.32}Cu_{0.04}Mg_{0.01}(P_{0.96}V_{0.02}O_4)_6(OH)_7(H_2O)_4].$$

Note that H_3O^+ is provided in the formula for charge balance, although there is no direct evidence for its presence. The ideal end-member formula is $[Na(H_2O)_{2.5}][Fe^{3+}_8(PO_4)_6(OH)_7(H_2O)_4]$, which requires: Na_2O 2.43, Fe_2O_3 50.07, P_2O_5 33.38, H_2O 14.12, Total 100.00 wt%. Meurigite-Na is insoluble in concentrated HCl.

Infrared and Raman spectroscopy

The FTIR and Raman spectra of meurigite-Na are given in Figures 4 and 5, respectively. Band assignments are made by analogy to those of giniite (Frost et al. 2007). In the infrared spectrum, there is a sharp band at 3579 cm^{-1} and two broad bands at 3390 and 3235 cm^{-1}. The former can be attributed to (OH) stretching and the later two to H_2O stretching, which is consistent with both (OH) and H_2O being present in the structure. A broad band at 1637 cm^{-1} can be attributed to the H_2O bending mode. The Raman spectrum shows only a very weak broad peak at 3270 cm^{-1}. A series of bands appear in the infrared and Raman spectra between 876 and 1125 cm^{-1}. These can be attributed to the $(PO_4)^{-3}$ stretching modes (ν_3 and ν_1). The Raman spectrum shows a peak at 568 cm^{-1} and a series of peaks at 490, 441, and 401 cm^{-1} that can be attributed to the $(PO_4)^{-3}$ (ν_4) and (ν_2)

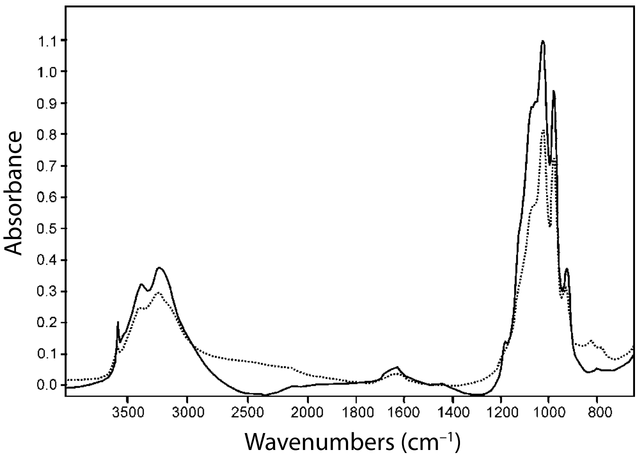

FIGURE 4. Fourier transform infrared spectra of meurigite-Na (dashed) and meurigite-K (type material) (solid). (NICPLAN FTIR microscope, diamond compression cell.)

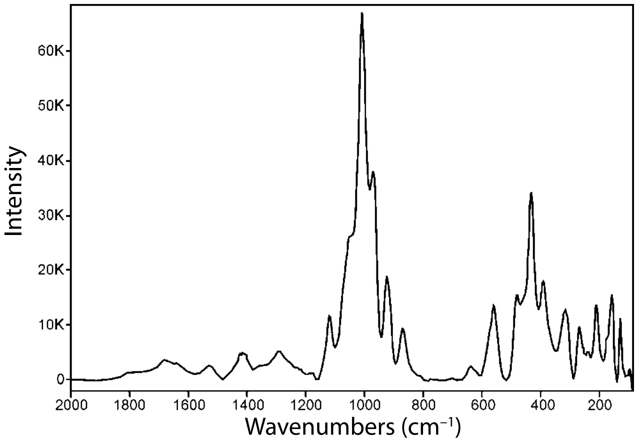

FIGURE 5. Raman spectrum of meurigite-Na.

bending modes, respectively. Additional bands in the Raman spectrum at 281, 222, and 170 cm^{-1} can probably be ascribed to Fe-O stretching vibrations.

Crystallography and structure

Single-crystal X-ray studies could not be carried out because of the small thickness and poor crystal quality of meurigite-Na fibers. X-ray powder-diffraction data (114.6 mm diameter Gandolfi camera, Cu*K*α) are provided in Table 2. Calculated intensities from the single-crystal structure of meurigite-K (with Na in place of K) are given for comparison. By analogy with meurigite-K, the mineral is monoclinic with space group *C*2/*c*. The unit-cell parameters refined from the powder data are provided in Table 3.

The structure of meurigite (Kampf et al. 2007) is a framework consisting of face-sharing octahedral $Fe^{3+}_2O_9$ dimers, which are linked by sharing corners with corner-sharing dimers and isolated $Fe^{3+}O_6$ octahedra to form thick slabs of octahedra parallel to the *a*-*b* plane. PO_4 tetrahedra further link octahedra within the slabs and also link slabs to one another perpendicular to the *a*-*b* plane. Relatively large channels through the framework along the *b* axis contain disordered alkali atoms (K/Na) and H_2O molecules. The meurigite structure is shown in Figure 6. The meurigite structure is related to those of other fibrous ferric phosphates with 5 Å fiber axes and shows a particularly close relationship with the structure of dufrénite.

Key to the distinction of the meurigite/phosphofibrite species is an understanding of the contents of the channels in the structure. Kampf et al. (2007) found partially occupied K and O(H_2O) sites in the channels. The K atoms (K1 and K2) form bonds to O atoms in the surrounding framework as well as to H_2O molecules (OW3 and OW4) in the channels. Based upon bond-length considerations, the K1, K2, OW3, and OW4 sites in the channels appear to represent two equivalent networks of atoms that are offset along the *b* axis (the channel direction) by one cell length with respect to one another. One such network is shown in Figure 7. If one of these networks of K and H_2O sites were fully occupied, there would be no space for any additional large ions in the channels. This would represent the theoretical upper limit on channel content based upon packing considerations; however, it would also mean twice as many K atoms in the formula as are indicated by the refined occupancies from the structure analysis and by the chemical analyses. Furthermore, it would lead to an excess positive charge in the formula. The solution suggested by Kampf et al. (2007) is to assume that H_2O molecules take the place (though not necessarily the exact positions) of approximately half of the K atoms in the channel network, with hydrogen bonds linking the H_2O molecules to one another. If this is the case, the channel would contribute 1 K and 2½ H_2O per formula unit (4 K and 10 H_2O per unit cell). Lower alkali (K/Na) content would allow higher H_2O content, with the total K + Na + O content of the channels being 3½ apfu (Z = 4).

RELATIONSHIP OF PHOSPHOFIBRITE AND MEURIGITE

Summary of previous work

Phosphofibrite was first described from the Clara mine, Black Forest, Germany, by Walenta and Dunn (1984). The ideal chemical formula $KCuFe^{3+}_{15}(PO_4)_{12}(OH)_{12}\cdot 12H_2O$ was given based upon electron microprobe analyses with H_2O calculated by difference due to the very meager amount of material. The powder X-ray diffraction pattern was indexed based upon a primitive orthorhombic unit cell with *a* = 14.4, *b* = 18.76, and *c* = 10.4 Å (*Z* = 2), with possible space groups *Pbmn* or *Pnmn*, obtained by trial and error indexing methods, although the authors noted that the optical properties suggested a lower symmetry (possibly monoclinic).

In their description of meurigite, Birch et al. (1996) provided the ideal formula $KFe^{3+}_7(PO_4)_5(OH)_7\cdot 8H_2O$. Although the authors recognized the strong similarities between meurigite and phosphofibrite, they cited several distinguishing characteristics: (1) the meurigite powder pattern includes a reflection at ~14 Å, which was not present in the originally published pattern for phosphofibrite; (2) transmission electron microscopic study showed that meurigite is monoclinic (pseudo-orthorhombic), with probable space groups *C*2, *Cm*, or *C*2/*m*, unit-cell parameters (refined from a powder X-ray diffraction pattern) of *a* = 29.52(4), *b* = 5.249(6), *c* = 18.26(1) Å, β = 109.27(7)°;

TABLE 2. Comparison of phosphofibrite and meurigite powder X-ray diffraction data

Meurigite-Na type Silver Coin mine		Meurigite-Na (calculated using meurigite-K structure: Kampf et al. 2007)			Meurigite-K type Santa Rita mine (Birch et al. 1996)		Meurigite-K Kněžská hora (Sejkora et al. 2000)		Phosphofibrite Clara mine (Kolitsch 1999)		Phosphofibrite type Clara mine (Walenta 1999)		Phosphofibrite type Clara mine (Walenta and Dunn 1984)	
I_{obs}	d_{obs}	I_{calc}	d_{calc}	*hkl*	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}
20	13.796	26	13.789	2 0 0	25	13.96	26	13.79	20	13.89	30	14.15		
100	9.349	100	9.317	0 0 2	60	9.41	100	9.36	100	9.40	100	9.54	100	9.50
		16	9.042	$\bar{2}$ 0 2			32	9.06						
									5b	8.01				
5	6.936	7	6.894	4 0 0	5	6.95	13	6.91	10	6.92	20	6.98		
							4	6.54						
5	5.091	12	5.096	1 1 0	15	5.09	6	5.07	15	5.08	30	5.15	10	5.18
							2	4.894						
20	4.843	21	4.849	1 1 1	90	4.84	12	4.831	30	4.85	50	4.90	20	4.91
		5	4.659	0 0 4			17	4.685			20	4.74		
		6	4.596	6 0 0	5	4.63	16	4.606			20	4.60	10	4.65
		5	4.576	$\bar{1}$ 1 2										
5	4.525	4	4.521	$\bar{4}$ 0 4					10b	4.578				
		6	4.516	3 1 0			16	4.544						
		21	4.314	$\bar{3}$ 1 2	70	4.32	15	4.306	30	4.325	60	4.35	50	4.35
10	4.266	14	4.252	3 1 1	50	4.25	12	4.243	10	4.246	10	4.30		
5	4.073	8	4.068	2 0 4			24	4.089	15	4.100	30	4.13	10	4.11
10	3.939	16	3.931	$\bar{3}$ 1 3	15	3.944	7	3.929	25b	3.940	60	3.95	40	3.96
		5	3.889	$\bar{6}$ 0 4			9	3.905						
							8	3.896						
		4	3.856	$\bar{5}$ 1 1	15	3.861	8	3.851						
		4	3.778	5 1 0										
5	3.782	6	3.774	$\bar{5}$ 1 2	30	3.781	9	3.771	15	3.779	20	3.81		
		5	3.593	$\bar{8}$ 0 2			13	3.601	10b	3.607	10	3.61	5	3.61
		2	3.566	5 1 1										
		3	3.559	$\bar{5}$ 1 3	10	3.570	9	3.561						
		3	3.504	$\bar{3}$ 1 4			3	3.505						
10	3.450	15	3.447	8 0 0	60	3.470	29	3.454	20	3.463	40	3.49	40	3.48
		2	3.424	4 0 4										
		3	3.280	5 1 2										
5	3.263	9	3.272	$\bar{5}$ 1 4					20	3.285	60	3.29	20	3.29
		2	3.264	$\bar{8}$ 0 4										
		9	3.239	$\bar{2}$ 0 6	5	3.277	36	3.262						
40	3.206	30	3.207	$\bar{7}$ 1 2	100	3.216	29	3.211	50	3.217	80	3.23	60	3.23
		4	3.204	$\bar{4}$ 0 6										
		5	3.137	7 1 0										
30	3.107	32	3.106	$\bar{7}$ 1 3	80	3.116	27	3.110	50	3.119	80	3.15	60	3.13
		4	3.101	$\bar{3}$ 1 5										
		4	3.032	3 1 4										
		3	3.014	$\bar{6}$ 0 6	2	3.038	14	3.033	5	3.048	5	3.0		
15	2.971	14	2.974	5 1 3	7	2.980	27	2.975	25	2.986	70	2.99	50	2.99
		11	2.964	8 0 2										
		3	2.934	1 1 5	4	2.944								
5	2.877	5	2.878	6 0 4			11	2.891	10	2.885	20	2.89	5	2.88
		3	2.856	2 0 6			12	2.872						
		2	2.784	7 1 2			7	2.788						
10	2.740	10	2.750	$\bar{3}$ 1 6	5	2.770	19	2.760	20b	2.762	40b	2.76	50b	2.77
		8	2.733	$\bar{7}$ 1 5	5	2.746	3	2.735						
		4	2.718	$\bar{1}$ 1 6										
		2	2.691	3 1 5										
		2	2.683	$\bar{9}$ 1 3	2	2.695	2	2.694	5	2.696				
		2	2.638	9 1 0	3	2.646	3	2.639	5	2.651				
		3	2.592	0 2 0										
15	2.593	14	2.591	1 1 6	10	2.588	18	2.599	20	2.608	40	2.62	40	2.60
							2	2.578						
5	2.572	6	2.568	0 2 1	18	2.563	3	2.557	5	2.568	10	2.59		
		2	2.456	10 0 2										
		3	2.452	$\bar{3}$ 1 7			14	2.460	5	2.467	10	2.48		
		3	2.439	$\bar{4}$ 2 1	10	2.45								
		3	2.422	5 1 5										
		3	2.415	$\bar{5}$ 1 7	10	2.432	13	2.426	5	2.434				
		3	2.392	0 2 3										
		3	2.386	9 1 2			9	2.395	15	2.397	30	2.41	20bb	2.41
10	2.378	5	2.376	$\bar{6}$ 0 8			21	2.387						
		3	2.343	$\bar{4}$ 2 3			6	2.332	5	2.343	10	2.34		
		3	2.327	$\overline{11}$ 1 3			6	2.277	5	2.294	5	2.29		
		2	2.188	$\bar{5}$ 1 8			10	2.204	10b	2.209	20	2.21	5b	2.21
		5	2.108	$\overline{11}$ 1 6	1	2.116	5	2.126	5	2.12				

Continued next page

TABLE 2.—CONTINUED

15	2.078	10	2.082	9 1 4	5	2.090	15	2.087	15	2.095	40	2.09	50	2.10
		3	2.078	$\bar{8}$ 2 3										
		2	2.077	1 1 8										
		7	2.067	$\bar{6}$ 2 5	5	2.078	2	2.066	5	2.073				
		5	2.052	2 2 5			10	2.043			5	2.06		
		2	2.035	$\overline{13}$ 1 2										
		3	2.021	8 2 1			1	2.017	5b	2.022	10	2.03		
		2	2.016	$\bar{9}$ 1 8			1	2.003						
		5	1.965	$\bar{6}$ 2 6			8	1.9655	10	1.973	30	1.972		
5	1.937	4	1.936	9 1 5			12	1.9440	10	1.948	30	1.954	20b	1.957
		2	1.935	$\bar{6}$ 0 10			2	1.9312						
		3	1.890	13 1 1										
		3	1.893	$\bar{4}$ 2 7					10b	1.905	20	1.903	10	1.899

TABLE 3. Unit-cell constants, density, and optical data for meurigite and phosphofibrite

	Meurigite-Na type	Meurigite-K type (Birch et al. 1996)	Meurigite-K type (Kampf et al. 2007)	Meurigite-K type* (Kolitsch 1999)*	Phosphofibrite type (Walenta and Dunn 1984)	Phosphofibrite type (based on meurigite cell)†
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
a (Å)	28.835(2)	29.52(4)	29.018(5)	~29.2	14.40	29.019(2)
b (Å)	5.1848(4)	5.249(6)	5.1892(6)	~5.17	18.76	5.1995(3)
c (Å)	19.484(1)	18.26(1)	19.695(3)	~19.7	10.40	19.718(1)
β (°)	106.983(6)	109.27(7)	106.987(1)	~107		107.037(6)
Space group	*C*2/*c*	*C*2, *Cm*, or *C*2/*m*	*C*2/*c*	*C*2/*c*	*Pbmn* or *Pnmn*	*C*2/*c*
Z	4	4	4	4	2	4
Density	2.94 (meas), 2.954 (calc)	2.96 (meas)	2.95 (calc)		2.90 (meas)	2.905 (calc)
n_α	1.740(3)	1.780(5)		1.760(5)	1.755(4)	
n_β	1.759(3)	1.785(5)		1.772(5)	n.d.	
n_γ	1.763(3)	1.800(5)		1.784(5)	1.790(4)	
Optic orientation	X ≅ *c*, Z = *b*	n.d.		X ≅ *c*, Y = *b* (Y = elongation)	Y = elongation	
Dispersion	none observed	n.d.		*r* << *v*	*r* << *v*	

* The data for the sample noted as Kolitsch (1999) are from that study and unpublished single-crystal studies of Kolitsch (see text), but were not included in that publication (conference abstract).

† Cell parameters were refined from the powder data of Walenta (1999) with reflections indexed in accord with the meurigite structure determination. The calculated density is based on the chemical analysis of Walenta and Dunn (1984) as explained in text.

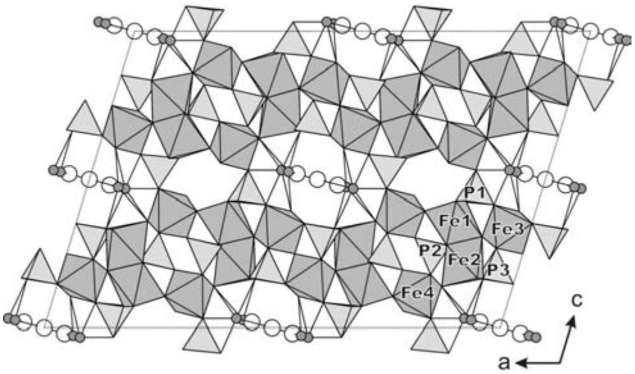

FIGURE 6. Structure of meurigite-K viewed down the *b* axis. Iron and P polyhedra are labeled. Small shaded circles are partially occupied K1 and K2 sites. Large open circles are partially occupied OW3 and OW4 sites.

and (3) meurigite contains much less Cu than phosphofibrite. Nonetheless they conclude, "The relationship between these three (including kidwellite) minerals remains uncertain in the absence of structural data." Attempts of Birch et al. (1996) to obtain the phosphofibrite type specimen for comparative studies were unsuccessful.

Walenta (1997) described a "Cu-free phosphofibrite" from the Clara mine. He detected only K, Fe, and P in this sample and pointed out that Cu has to be considered a non-essential component of phosphofibrite, as it obviously replaces Fe. He concluded that the chemical formula of phosphofibrite might have to be redefined, although it is not clear if Cu substitutes for Fe on a specific structural site, making a nomenclatorial distinction more difficult.

Kolitsch (1999) conducted a preliminary study to investigate the possible identity of meurigite and phosphofibrite. In the course of this study, several samples of meurigite and phosphofibrite, including type material of meurigite and cotype material of phosphofibrite (very small sample from a specimen in the Clara collection of the Oberwolfach, Black Forest, obtained with the help of Franz Hahn, Hohberg), as well as examples of the Na analog of meurigite, were studied by powder X-ray diffraction (Gandolfi technique to avoid preferred orientation), transmission electron microscopy, energy dispersive spectroscopy, and polarized-light microscopy. Kolitsch concluded that meurigite is identical to phosphofibrite.

Also, Walenta (1999) published a new powder XRD pattern for type phosphofibrite from the Clara mine, which now included a line at ~14 Å.

In their crystal structure determination of meurigite-K, Kampf et al. (2007) reported the space group *C*2/*c*, with *a* = 29.018(5), *b* = 5.1892(6), *c* = 19.695(3) Å, and β = 106.987(1)°. Tiny meurigite crystals from Santa Rita material were also studied with single-crystal X-ray diffractometry by Kolitsch (unpublished data). These crystals also showed *C*-centered monoclinic cells; approximate parameters of the two "best" fragments were *a* = 29.2, *b* = 5.17, *c* = 19.7 Å, β = 106.8° and *a* = 29.3, *b* = 5.2, *c* = 19.3 Å, β = ~106°, values similar to those reported by Kampf et al. (2007); transmission electron microscope-selected area electron diffraction studies of both Santa Rita meurigite

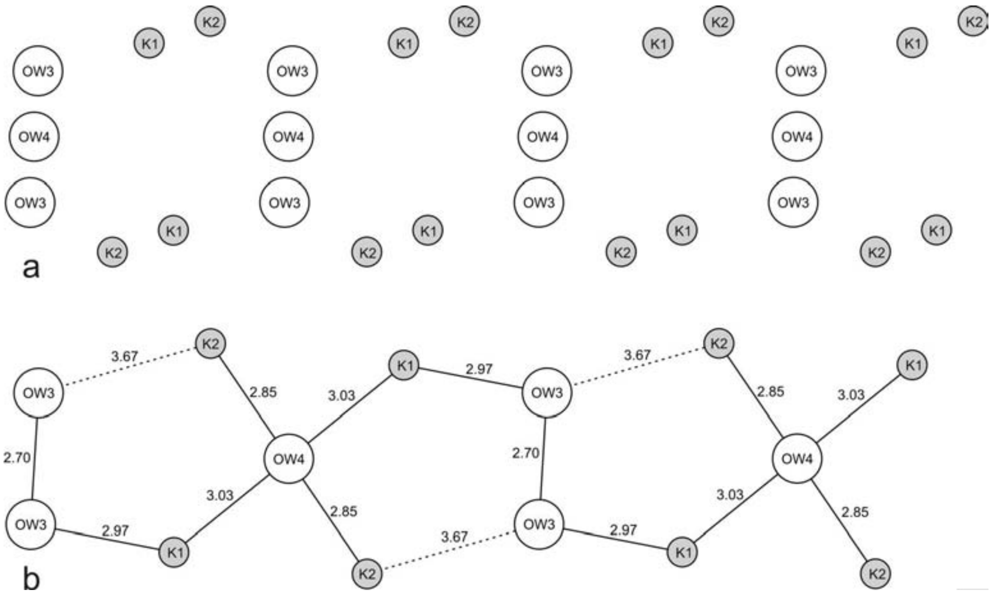

FIGURE 7. (**a**) Channel sites in meurigite structure viewed down the *c* axis with the channel direction (*b* axis) horizontal. (**b**) One network of K1, K2, OW3, and OW4 sites with distances in angstroms shown.

and Clara phosphofibrite (part of type material) by Kolitsch (1999) had yielded β = 107°, with systematic absences being in agreement with space-group symmetry *C*2/*c*. Based upon their structure determination, Kampf et al. (2007) provided the ideal formula $[K(H_2O)_{2.5}][Fe^{3+}_8(PO_4)_6(OH)_7(H_2O)_4]$. Kampf et al. (2007) reanalyzed type phosphofibrite using the original probe mount (NMNH no. 150230) and showed how this, as well as other published analyses for meurigite [K-poor meurigite from Kněžská hora (Sejkora et al. 2000) and meurigite from the Clara mine (Walenta and Theye 2001)], were compatible with their ideal formula. The findings of Kampf et al. (2007) suggested an empirical formula for type phosphofibrite with less than 0.5 K per formula unit.

Analysis of the evidence

Table 2 provides powder X-ray diffraction data for several meurigite and phosphofibrite samples. The data for the sample noted as Kolitsch (1999) is from that study, but was not included in that publication (conference abstract). The powder data for the various meurigite and phosphofibrite samples show strong similarities. With few exceptions, all major lines are consistently represented in all of the patterns. The line at ~14 Å is only missing from the original pattern of type phosphofibrite but, as mentioned above, this line was noted by Walenta (1999) in a subsequent pattern obtained from the type specimen. The minor differences noted are readily attributable to minor sample impurities, minor differences in chemistry (Al- and Cu-for-Fe substitutions; As- and V-for-P substitutions; variable alkali contents; very minor Ca contents), variation in sample preparation and differences in methods used for recording and analyzing the patterns. We note that the powder pattern published by Birch et al. (1996) is clearly affected by preferred orientation. The powder pattern of Walenta (1999) with reflections re-indexed in accord with the meurigite structure determination yields a refined monoclinic unit-cell that compares very closely to the cell reported by Kampf et al. (2007) for type meurigite (see Table 3).

Table 2 provides electron microprobe analyses for several meurigite and phosphofibrite samples. The only published analyses attributed to the species phosphofibrite are from the same polished probe mount of the type specimen. Because of the finely fibrous habit of phosphofibrite, a good polish for electron microprobe work could not be obtained. This, coupled with the marked tendency of the material to exhibit degassing under the electron beam, leads to analytical results that must be regarded as subject to considerable variability, depending on the spot analyzed and the analytical conditions. Walenta and Dunn (1984) published only an average of their analyses with no indication of ranges; however, Kampf et al. (2007) analyzed nine points on the same probe mount and the ranges they provided demonstrate significant variability, particularly with respect to K_2O, CuO, and Al_2O_3 (see Table 1). Despite those analytical problems, it is nevertheless clear that type phosphofibrite has a composition very similar to those of analyzed meurigite samples. The most significant differences are rather high Cu and rather low K contents in type phosphofibrite.

Kampf et al. (2007) showed that the original analysis by Walenta and Dunn (1984) for type phosphofibrite can be fit to the formula based upon the structure determination of type meurigite by assuming that the H_2O by difference is in error, by basing the formula on octahedral cations = 8, with K + O = 38.5 and sufficient H for charge balance to provide $[K_{0.50}(H_2O)_{3.00}]_{\Sigma 3.50}[(Fe^{3+}_{7.23}Cu_{0.41}Al_{0.36})_{\Sigma 8.00}(PO_4)_{5.94}(OH)_{6.29}(H_2O)_{4.97}]$, $Z = 4$. This formula yields a calculated density of 2.979 g/cm^3 somewhat higher than the measured density of 2.90 g/cm^3 reported by Walenta and Dunn (1984). However, if it is assumed that the octahedral sites are not fully occupied, as the structure solution suggested is the case for meurigite, a calculated density consistent with the measured density can be obtained (of course, it seems also probable that the finely fibrous habit of type phosphofibrite would lead to a measured density somewhat lower than the real one). Assuming octahedral cations = 7.6, the formula becomes $[K_{0.47}(H_2O)_{3.03}]_{\Sigma 3.50}[(Fe^{3+}_{6.87}Cu_{0.39}Al_{0.34})_{\Sigma 7.60}(PO_4)_{5.65}(OH)_{5.95}(H_2O)_{6.46}]$, yielding a calculated density of 2.905 g/cm^3.

The reanalysis of type phosphofibrite by Kampf et al. (2007) yielded an analytical total significantly lower than that obtained by Walenta and Dunn (1984); however, the relative amounts of the major components compare favorably. The empirical formula using the same constraints is $[K_{0.43}Ca_{0.04}(H_2O)_{3.03}]_{\Sigma 3.50}[(Fe^{3+}_{6.91}Cu_{0.45}Al_{0.24})_{\Sigma 7.60}(PO_4)_{5.41}(AsO_4)_{0.09}(OH)_{6.35}(H_2O)_{6.65}]$.

Finally, it should be noted that each of the four nonequivalent octahedral cation sites has an equipoint rank of 8. Even if all of the Cu and Al preferentially occupied one of these four sites, a highly unlikely possibility, that site would still be dominantly occupied by Fe. Therefore, the amount of Cu (and/or Al) in type phosphofibrite is certainly insufficient to distinguish it as a separate species from meurigite.

Table 3 provides a comparison of cell constants, density, and optical data reported for meurigite-K, meurigite-Na, and phosphofibrite.

CONCLUDING REMARKS

The conclusions that follow from the forgoing are: (1) phosphofibrite is isostructural with meurigite, and (2) phosphofibrite is the alkali-deficient member of a series with meurigite-K. Because the name phosphofibrite has chronological priority, it might be argued that the three closely related species, meurigite-K, meurigite-Na, and phosphofibrite, should be named phosphofibrite-□, phosphofibrite-K, and phosphofibrite-Na; however, we do not propose such renaming in the absence of a more complete study of phosphofibrite type material, involving structure analysis or at least water determination. Unfortunately, virtually all of the phosphofibrite type material was consumed for the original microprobe mount and only one minute fragment with traces of the mineral remains at the Universität Stuttgart (Kurt Walenta, personal communication).

To date meurigite-K, meurigite-Na, and/or phosphofibrite have been reported from numerous localities (see www.mindat.org). Indeed, both meurigite-K and phosphofibrite have been reported from the Clara mine, and all three species have been reported from the Silver Coin mine. In many cases, earlier reports have not been based upon chemical analyses and, therefore, the specific identity of the member(s) of the group present must be considered tentative. We have not been able to confirm either meurigite-K or phosphofibrite as occurring at the Silver Coin mine.

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