Meurigite, a new fibrous iron phosphate resembling kidwellite

WILLIAM D. BIRCH

Department of Mineralogy and Petrology, Museum of Victoria, 328 Swanston Street, Melbourne, Victoria, 3000, Australia

ALLAN PRING

Department of Mineralogy, South Australian Museum, North Terrace, Adelaide, South Australia, 5000, Australia

PETER G. SELF

CSIRO Division of Soils, Private bag 2, Glen Osmond, South Australia, 5064, Australia

RONALD B. GIBBS

PO Box 448, Tyrone, New Mexico, 88065, U.S.A.

ERICH KECK

Algunderweg 3, 92694 Etzenricht, Germany

MARTIN C. JENSEN

2855 Idlewild, #121, Reno, Nevada, 89509, U.S.A.

AND

EUGENE E. FOORD

U.S. Geological Survey, Box 25046, MS 905, Denver Federal Centre, Denver, Colorado, U.S.A.

Abstract

Meurigite is a new hydrated potassium iron phosphate related to kidwellite and with structural similarities to other late-stage fibrous ferric phosphate species. It has been found at four localities so far – the Santa Rita mine, New Mexico, U.S.A.; the Hagendorf-Sud pegmatite in Bavaria, Germany; granite pegmatite veins at Wycheproof, Victoria, Australia; and at the Gold Quarry Mine, Nevada, U.S.A. The Santa Rita mine is the designated type locality. Meurigite occurs as tabular, elongated crystals forming spherical and hemispherical clusters and drusy coatings. The colour ranges from creamy white to pale yellow and yellowish brown. At the type locality, the hemispheres may reach 2 mm across, but the maximum diameter reached in the other occurrences is usually less than 0.5 mm. A wide variety of secondary phosphate minerals accompanies meurigite at each locality, with dufrenite, cyrilovite, beraunite, rockbridgeite and leucophosphite amongst the most common. Vanadates and uranates occur with meurigite at the Gold Quarry mine.

Electron microprobe analysis and separate determination of H_2O and CO_2 on meurigite from the type locality gave a composition for which several empirical formulae could be calculated. The preferred formula, obtained on the basis of 35 oxygen atoms, is $(K_{0.85}Na_{0.03})_{\Sigma 0.88}(Fe^{3+}_{7.01}Al_{0.16}Cu_{0.02})_{\Sigma 7.19}$ $(PO_4)_{5.11}(CO_3)_{0.20}(OH)_{6.7} \cdot 7.25H_2O$, which simplifies to $KFe^{3+}_7(PO_4)_5(OH)_7 \cdot 8H_2O$. Qualitative analyses only were obtained for meurigite from the other localities, due to the softness and openness of the aggregates. Because of the fibrous nature of meurigite, it was not possible to determine the crystal structure, hence the

exact stoichiometry remains uncertain. The lustre of meurigite varies from vitreous to waxy for the Santa Rita mine mineral, to silky for the more open sprays and internal surfaces elsewhere. The streak is very pale yellow to cream and the estimated Mohs hardness is about 3. Cleavage is perfect on {001} and fragments from the type material have a mean specific gravity of 2.96.

The strongest lines in the X-ray powder pattern for the type material are (d_{obs},I_{obs},hkl) 3.216(100)404; 4.84(90)111; 3.116(80)205; 4.32(70)112; 9.41(60)201; 3.470(60)800. The X-ray data were indexed on the basis of a monoclinic unit cell determined from electron diffraction patterns. The cell parameters, refined by least squares methods, are $a = 29.52(4)$, $b = 5.249(6)$, $c = 18.26(1)$ Å, $\beta = 109.27(7)°$, $V = 2672(3)$ Å^3, and $Z = 4$. The calculated density is 2.89 gcm^{-3}. The space group is either $C2$, Cm or $C2/m$. X-ray powder data for meurigite are closely similar to those for kidwellite and phosphofibrite, but meurigite appears to be characterised by a strong 14 Å reflection. The relationship between these three minerals remains uncertain in the absence of structural data. On the available evidence, meurigite and kidwellite are not the respective K and Na-endmembers of a solid solution series. The meurigite cell parameters suggest it belongs to a structural family of fibrous ferric phosphates, such as rockbridgeite, dufrenite and beraunite, which have a discrete 5 Å fibre axis. Meurigite occurs in widely varying environments, its formation probably favoured by late-stage solutions rich in K rather than Na.

Introduction

THE last minerals to crystallise in iron phosphate associations often include fibrous ferric phosphates with a discrete 5 Å fibre-axis structure. These include dufrenite, rockbridgeite, beraunite, lipscombite and barbosalite (Moore, 1970), souzalite, cacoxenite, kidwellite (Moore and Ito, 1978) and, probably, phosphofibrite (Walenta and Dunn, 1984). Two formerly accepted fibrous iron phosphate species, laubmannite and andrewsite, have been discredited as mixtures (Dunn, 1990).

During investigations of phosphate assemblages in pegmatites at Wycheproof, Victoria, Australia (Birch, 1993), small yellow fibrous spheres of a mineral resembling kidwellite were discovered. A similar mineral forming larger hemispheres had been collected in the Santa Rita mine, New Mexico, U.S.A. by one of the authors (RBG). As studies proceeded on these occurrences, similar material was obtained by another author (EK) in the Hagendorf-Sud pegmatite in Bavaria, Germany. Another occurrence, in a sediment-hosted gold deposit, was discovered at the Gold Quarry mine in northeast Nevada, U.S.A. (Jensen *et al.*, 1995). It is now confirmed that the mineral from these four localities is a new species, an hydrated potassium ferric phosphate. The mineral has been named meurigite, in recognition of Professor Sir John Meurig Thomas KB FRS (1932 -) eminent British crystal chemist at the University of Cambridge. The CNMMN approved meurigite as a new species in 1995.

Occurrence

The Santa Rita mine, near Silver City in south-western New Mexico, is the type locality for meurigite, as this occurrence provided the best material for characterizing the mineral. Meurigite occurs with dufrenite, beraunite and leucophosphite in fractures in hematitic fault gouge in the oxidised zone above copper sulphides. In the Hagendorf-Sud pegmatite the mineral was found at the 82-metre level in the southeast part of the mine. It occurs as small druses with nontronite and secondary phosphates, mainly rockbridgeite, but including apatite, vivianite, strengite, beraunite, robertsite/mitridatite, cyrilovite, laueite and stewartite. This suite had formed by alteration of the upper portion of a 2 × 2 × 4 m lens of triphylite. At Wycheproof, meurigite occurs in small etch cavities in granite pegmatite veins, accompanied by cyrilovite, rock-bridgeite and leucophosphite. At the Nevada occurrence, the mineral forms spherules on surfaces of silicified and brecciated sediments in the upper oxidised zone of a large, low-temperature hydrothermal (Carlin-type) system. Associated minerals include an assemblage of phosphates, vanadates and uranates, characterised mainly by fluellite, kingite, leucophosphite, tintiate, strengite/variscite, hewettite, tyuyamanite and torbernite.

At all these localities meurigite is present only in very small quantities. It is likely to occur, either undetected or possibly confused with kidwellite, in other phosphate occurrences. For example, Moore and Ito (1978) described a bright yellow fibrous mineral, 'Mineral B', resembling strunzite, as an alteration product of triphylite at McMahons pegmatite, South Australia. 'Mineral B' had X-ray powder diffraction data close to those of kidwellite. A semiquantitative microprobe analysis of a fragment of Mineral B in the South Australian Museum collection indicated it was a potassium iron phosphate, intimately mixed with jarosite (Birch,

unpublished data). Moore and Ito also described an unknown silky white mineral replacing rockbridgeite from the Sapucaia pegmatite in Minas Gerais, Brazil. This phase had an X-ray pattern identical to Mineral B, although no compositional data are available. It seems likely that Mineral B is meurigite.

Appearance and physical properties

At the Santa Rita mine, meurigite forms translucent yellowish brown hemispheres and globular aggregates up to about 2 mm across. When these are broken, they reveal a compact fibrous radiating structure, usually with a core of dark green dufrenite. At Hagendorf-Sud, meurigite occurs as cream to white spheres, rosettes and cavity linings of delicate silky fibres up to 0.5 mm long. At Wycheproof, meurigite spheres and hemispheres are up to 0.2 mm in diameter. The outer surface is pale to canary yellow, but broken internal surfaces are creamy white. At the Gold Quarry mine, the mineral occurs as isolated hemispheres to 0.2 mm and drusy crusts of pale yellow to pale orange fibrous crystals. 'Mineral B' at McMahons pegmatite formed silky straw-yellow fans and sprays of fine fibres, according to notes made by the original finder of the mineral (Mr J.E. Johnson).
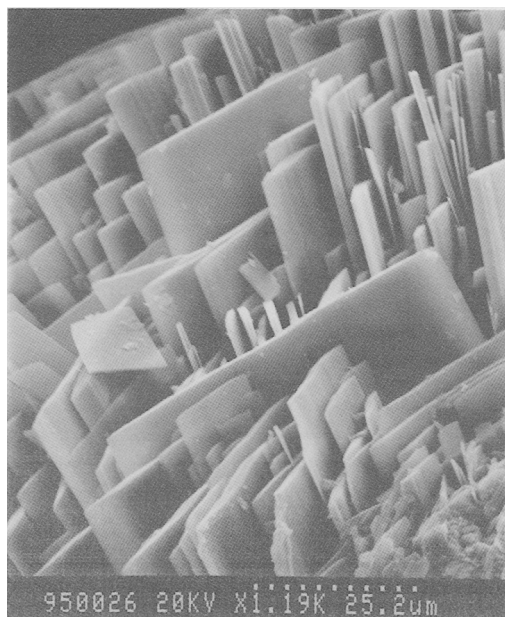
Scanning electron photomicrographs (Figs 1–3) show that meurigite fibres are tabular crystals which at the type locality may be 80 μm wide but only 2–3 μm thick. The crystals are tabular on {001} and elongated parallel to {010}. Crystals at the other localities are also tabular but are considerably smaller. Depending on the packing of the fibres, meurigite shows variable lustre. This may be vitreous to waxy for the Santa Rita mine spheres, or silky for more open sprays and internal surfaces at the other localities. The streak is very pale yellow to cream. The estimated Mohs hardness is about 3. Finely crushed fragments of meurigite from the type locality have a mean specific gravity of 2.96, obtained by heavy liquid methods. These fragments are platy, reflecting perfect cleavage on {001}.

Optically, meurigite is biaxial (+), with α = 1.780(5), β = 1.785(5), γ = 1.800(5) (589 nm). The 2V could not be measured, but $2V_{calc}$ = 60°. No pleochroism is observable.

Crystallography

Because of the fibrous nature of meurigite, it was not possible to determine the crystal structure, the space group or the unit cell by single crystal X-ray diffraction methods. Powder data were obtained for meurigite from the Santa Rita mine and Hagendorf-Sud using a 100 mm diameter Hagg-Guinier camera

FIG. 1. Meurigite crystal terminations on surface of spherical aggregate from Santa Rita mine. Scale bar is 25 μm. Largest crystal is 55 μm wide.

FIG. 2. Spherical aggregate of meurigite 0.13 mm in diameter from Wycheproof.
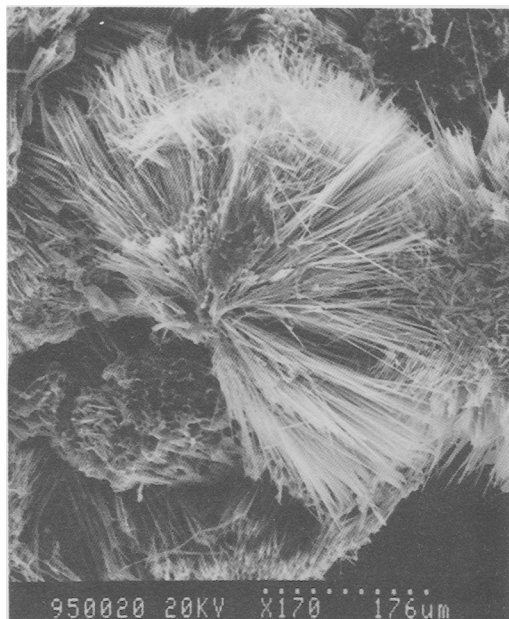
FIG. 3. Radiating fibres of meurigite, 0.25 mm long, from Hagendorf-Sud.

FIG. 4. Electron diffraction patterns of meurigite from Santa Rita mine. (*a*) [001] zone; (*b*) [011] zone, the tilt angle from |001] is 14°. Note that the distribution of reflections suggests a C-face centred lattice.

with monochromated $Cr-K\alpha_1$ (λ = 2.2897 Å) radiation, with elemental Si as an internal standard. The unit cell was determined directly with the aid of a series of electron diffraction patterns. Fragments of Santa Rita mine meurigite were finely ground with acetone in an agate mortar and deposited from suspension onto Cu grids with holey carbon support films. The crystal fragments were examined in a Philips EM400 electron microscope fitted with a double tilt goniometer $\pm45°$. A thin fracture fragment, in which the $a*$ axis was parallel with the main tilt axis of the goniometer was located and a series of diffraction zones was recorded (Fig. 4). A monoclinic unit cell, with $a = 29.32$, $b = 5.26$, $c = 18.22$ Å, $\beta = 108.6°$, was determined from the electron diffraction data. This cell was used to index the powder patterns and the cell parameters were refined by least squares methods. The final refined cell parameters for the type material are $a = 29.52(4)$, $b = 5.249(6)$, $c = 18.26(1)$ Å, $\beta = 109.27(7)°$, V = 2672(3) Å^3. The electron diffraction data indicate that the space group is either $C2$, Cm or $C2/m$. The indexed powder data for meurigite from Santa Rita and Hagendorf-Sud, together with the powder data for Mineral B from McMahons, kidwellite (Moore and Ito, 1978) and phosphofibrite (Walenta and Dunn, 1984) are tabulated in Table 1. There are close similarities between all powder patterns but -
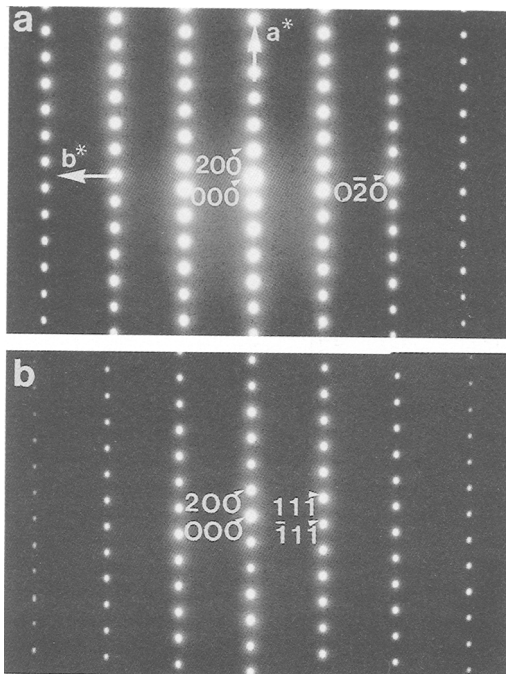
meurigite appears to be characterised by a strong 14 Å reflection.

Chemistry

Satisfactory electron microprobe analyses were obtainable only on meurigite from the Santa Rita mine, because these crystals are sufficiently large and in contact. The open fibrous structure and overall softness of the material from Wycheproof, Hagendorf-Sud and the Gold Quarry mine gave rise to low analytical totals. The analyses obtained using a Cameca SX50 instrument at 15 kV and 0.2 μA specimen current are shown in Table 2. Water and CO_2 were determined by CHN analysis on a small fragment from the type locality. Several empirical formulae can be obtained depending on the basis of the calculation. The three most likely formulae are given in Table 3, but without the aid of a structure determination, it is not possible to be certain of the stoichiometry of meurigite. Of the possible formulae, that calculated on the basis of 35 oxygen atoms gives the best agreement between the analysis and the measured and calculated density. The empirical

TABLE 1. X-ray powder diffraction data for meurigite from Santa Rita Mine and Hagendorf-Sud (this study) and McMahons Quarry (Mineral B of Moore and Ito 1978); kidwellite (Moore and Ito, 1978) and phosphofibrite (Walenta and Dunn, 1984)

hkl	Santa Rita			Hagendorf		McMahons		kidwellite		phosphofibrite	
	d_{obs}	d_{calc}	I/I_o	d_{obs}	I/I_o	d_{obs}	I/I_o	d_{obs}	I/I_o	d_{obs}	I/I_o
200	13.96	13.94	25	14.00	30	13.89	4	—	—	—	—
201	9.41	9.42	60	9.45	100	9.42	10	9.41	100	9.50	10
400	6.95	6.97	5	6.96	10	6.96	2	6.87	10	—	—
						6.50	3	6.43	30	—	—
								5.249	5	—	—
110		5.16								5.18	1
111?	5.09	5.03	15	5.09	15	5.10	2	—	—	—	—
111	4.84	4.86	90	4.85	30	4.86	4	4.792	12	4.91	2
311	4.63	4.61	5	4.63	5	—	—	—	—	4.65	1
								4.541	10	—	—
312		4.34									
112	4.32	4.31	70	4.32	30	4.31	5	—	—	4.35	5
311	4.25	4.25	50	4.26	10	—	—	—	—	—	—
601		4.15						4.141	10	4.11	1
								4.017	35	—	—
113	3.944	3.960	15	3.94	30	3.94	4	—	—	3.96	1
604	3.861	3.858	15	3.87	7	—	—	—	—	—	—
403		3.852									
512		3.829									
312		3.790						3.813	40	3.80	1
204	3.781	3.779	30	3.78	25	—	—	—	—	3.634	5
	3.61		0.5								
511	3.570	3.564	10	3.57	6	—	—	—	—	—	—
800	3.470	3.483	60	3.47	50	3.48	4	—	—	3.48	4
								3.413	55	—	—
711	3.277	3.283	5	3.27	5	—	—	—	—	3.29	2
404	3.216	3.219	100	3.215	100	3.21	1	3.193	40	3.23	6
801		3.215									
								3.173	35	—	—
205	3.116	3.115	80	3.115	20	3.11	6	—	—	3.13	6
406	3.038	3.031	2	3.045	5			3.078	15	—	—
711	2.980	2.983	7	2.984	10	2.99	5			2.99	5
115,714	2.944	2.950	4	—	—	—	—	2.943	10	—	—
								—	—	2.88	0.5
								2.846	15	—	—
								2.831	15	—	—
912	2.770	2.781	5	—	—	—	—	2.789	15	2.77	5
712	2.746	2.751	5	—	—	2.75	3	—	—	—	—
806	2.695	2.696	2	—	—	—	—	—	—	—	—
206	2.646	2.646	3	2.650	5	—	—	—	—	—	—
514	2.588	2.583	10	2.581	10	2.610	3	2.577	10	2.60	4
315	2.563	2.559	18	2.559	15	—	—	—	—	—	—
								2.484	15	—	—
222	2.432	2.430	10	2.434	5	—	—	2.424	5	2.41	2
								2.392	5	—	—
								2.183	5	—	—
518	2.090	2.090	5	—	—	—	—	—	—	2.10	5
715,516	2.078	2.080	5	—	—	—	—	—	—	—	—
						plus 3 lines to d=1.58Å		plus 10 lines to d=1.522Å		plus 9 lines to d=1.578Å	

TABLE 2. Chemical analysis and formula for meurigite

	1	2
Na_2O	0.07	0.03
K_2O	3.37	0.85
CuO	0.16	0.02
Fe_2O_3	47.40	7.01
Al_2O_3	0.70	0.16
P_2O_5	30.71	5.11
As_2O_5	0.03	–
CO_2	0.73	0.20
H_2O	16.2	21.2
Total	99.37	

1. Meurigite, average of 5 microprobe analyses. H_2O & CO_2 by microchemical methods.
2. Atomic proportions based on 35 O.

formula calculated on this basis is $(K_{0.85}Na_{0.03})_{\Sigma 0.88}$ $(Fe^{3+}_{7.01}Al_{0.16}Cu_{0.02})_{\Sigma 7.19}(PO_4)_{5.11}(CO_3)_{0.20}(OH)_{6.7}$ $\cdot 7.25H_2O$, which simplifies to $KFe^{3+}_7(PO_4)_5(OH)_7$ $\cdot 8H_2O$. For Z = 4 and the unit cell volume of 2672 Å^3, the calculated density is 2.89 gcm^{-3}, which is slightly lower than the measured density 2.96 gcm^{-3}. The Gladstone Dale compatibility is excellent, with $1-(K_p/K_C) = 0.025$.

Relationship to other minerals

As noted in the introduction there are a number of fibrous ferric phosphates with a discrete 5 Å fibre axis and meurigite is clearly a member of this group. Moore (1970) noted that many of these minerals have structures based on a common structural unit – a face-sharing cluster of three $Fe(O,OH)_6$ octahedra. These units are linked by the PO_4^{3-} tetrahedra, and the sum of the tetrahedral and octahedral edges define the ~5.1 Å fibre axis. The octahedral cluster also defines a ~13.8 Å which is observed in many ferric phosphate minerals. The meurigite cell parameters suggest that it is a member of this structural family with $a\sin\beta = 27.87$ Å i.e. 2×13.94 Å, and $b = 5.2$ Å.

In terms of composition, meurigite is most closely related to kidwellite and phosphofibrite, but the stoichiometry and cell parameters are distinct. Given that the structural data are not available for any of the three minerals, some uncertainty must remain about their stoichiometry and unit cells. On the evidence available it would appear that meurigite and kidwellite do not represent the potassium and sodium end-members of a solid-solution series. The relationship between phosphofibrite and meurigite is also uncertain; attempts to locate the phosphofibrite type material were unsuccessful and until material of this mineral becomes available the matter must remain unresolved.

Paragenesis

Meurigite has been found in small amounts in a wide range of late-stage environments. These include oxidised zones above copper sulphide ores and sediment-hosted hydrothermal gold systems, as well as granite pegmatites and hydrothermally altered massive pegmatoidal phosphates. It appears that meurigite crystallisation is favoured by solutions enriched in K rather than Na, in which case kidwellite would be the preferred phase. On this basis, meurigite should be as common as kidwellite in complex secondary phosphate assemblages.

Acknowledgements

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TABLE 3. Possible formulae and ideal analyses for meurigite

Formula	wt.% oxides (ideal)				density gcm^{-3}
	K_2O	Fe_2O_3	P_2O_5	H_2O	
$KFe^{3+}_7(PO_4)_5(OH)_7\cdot 8H_2O$	4.05	48.11	30.54	17.30	2.89
$KFe^{3+}_7(PO_4)_5(OH)_7\cdot 9H_2O$	3.97	47.13	29.11	18.97	2.95
$KFe^{3+}_8(PO_4)_6(OH)_7\cdot 8H_2O$	3.59	48.67	32.44	15.31	3.26

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