

Manganflurlite, $\text{ZnMn}_3^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$, a new schoonerite-related mineral from the Hagendorf-Süd pegmatite

ANTHONY R. KAMPF^{1,*}, IAN E. GREY², COLIN M. MACRAE² and ERICH KECK³

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

*Corresponding author, e-mail: akampf@nhm.org

²CSIRO Mineral Resources, Private Bag 10, Clayton South, Victoria 3169, Australia

³Algunderweg 3, 92694 Etzenricht, Germany

Abstract: The ideal formula for flurlite has been revised to $\text{Zn}_4\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$ and its Mn analogue, manganflurlite (IMA2017-076), $\text{ZnMn}_3^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$ has been found on two specimens of phosphophyllite from the Hagendorf-Süd pegmatite, Oberpfalz, Bavaria, Germany. Manganflurlite occurs as long, very thin, rectangular laths, up to 0.5 mm long and less than 10 μm thick. Laths are elongated on [1 0 0], flattened on {0 0 1} and exhibit the forms {1 0 0}, {0 1 0} and {0 0 1}. The mineral is orange brown in colour and transparent with a vitreous iridescent lustre and buff streak. Crystals are flexible and elastic with irregular fracture, and three cleavages: perfect on {0 0 1}, good on {1 0 0} and {0 1 0}. The Mohs' hardness is *ca.* 2½. The measured density is 2.73(2) g cm^{-3} . At room temperature, the mineral dissolves rapidly in dilute HCl. Optically, manganflurlite is biaxial (–), with $\alpha = 1.623(\text{calc})$, $\beta = 1.649(2)$, $\gamma = 1.673(2)$ (white light); $2V = 86(1)^\circ$. The dispersion is $r > v$, slight; the optical orientation is $X = c$, $Y = b$, $Z = a$. The pleochroism is $X = \text{pale yellow brown}$, $Y = \text{orange brown}$, $Z = \text{light yellow brown}$, $Y > Z > X$. Electron microprobe analyses for crystals from the holotype specimen gave the empirical formula $\text{Zn}(\text{Mn}_{1.51}^{2+}\text{Fe}_{0.69}^{2+}\text{Zn}_{0.68}\text{Mg}_{0.08})_{\Sigma 2.96}(\text{Fe}_{0.95}^{3+}\text{Al}_{0.05})_{\Sigma 1.00}(\text{PO}_4)_3(\text{OH})_{1.92}(\text{H}_2\text{O})_{9.08}$. Manganflurlite is monoclinic, $P2_1/m$, $a = 6.4546(8)$, $b = 11.1502(9)$, $c = 13.1630(10)$ Å, $\beta = 99.829(5)^\circ$, $V = 933.44(16)$ Å³ and $Z = 2$. The crystal structure, refined including all protons to $R_{\text{obs}} = 0.034$ for 2219 observed reflections [$I > 3\sigma(I)$], shows the mineral to be isostructural with flurlite. These minerals have a heteropolyhedral layer structure that is a topological isomer of the schoonerite structure.

Key-words: manganflurlite; new mineral; crystal structure; manganese zinc iron phosphate; flurlite; schoonerite; Hagendorf-Süd pegmatite, Germany.

1. Introduction

Schoonerite-group minerals (SGMs), with general formula $^{[4]}\text{Zn}_x^{[5]}\text{Zn}_{1-x}^{[6]}(\text{M1 M2 M3}_{1-x}\square_x\text{Fe}^{3+})(\text{PO}_4)_3(\text{OH})_y(\text{H}_2\text{O})_{9-y} \cdot 2\text{H}_2\text{O}$, represent an interesting class of secondary phosphate minerals in which different distributions of Fe^{2+} , Fe^{3+} , Mn^{2+} and Zn over the three octahedral sites M1 to M3, and partitioning of Zn between adjacent 4-coordinated and 5-coordinated sites reflect different paragenesis and weathering environments (Grey *et al.*, 2018a). Schoonerite, with dominant cations $\text{M1} = \text{Mn}^{2+}$, $\text{M2} = \text{M3} = \text{Fe}^{2+}$, is an example of a relatively unoxidized SGM, for which $x = 0$, $y = 2$ and only the $^{[5]}\text{Zn}$ site is occupied (Kampf, 1977), whereas wilhelmumbelite, schmidite, and wildenauerite are oxidized SGMs, with the iron predominantly as Fe^{3+} , and with partial partitioning of the Zn from the $^{[5]}\text{Zn}$ site to the $^{[4]}\text{Zn}$ site, accompanied by vacancies in the M3 site (Grey *et al.*, 2018a).

We have recently reported a new variation of the schoonerite structure in the Zn-rich secondary phosphate mineral flurlite (Grey *et al.*, 2015). Its structure can be

described as a topological isomer of the schoonerite structure due to different corner-connected linkages of PO_4 tetrahedra with M2 and M3-centred octahedra. This results in M2 and M3 becoming equivalent in flurlite ($= \text{M2}$) and the symmetry is lowered from orthorhombic $Pmab$ to monoclinic $P2_1/m$ (Grey *et al.*, 2015). In the original description of flurlite, dominant Mn^{2+} was assigned to M1 by analogy with schoonerite and dominant Zn was assigned to M2, but a reanalysis of the data, using the same bond-valence-sum approach used for SGMs, showed that Zn was dominant in both M1 and M2 sites. The revised ideal formula for flurlite is $\text{Zn}_4\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$. This revised formula for flurlite has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association.

Recently, we have encountered a mineral that is isostructural with flurlite, but with Mn^{2+} dominant in both the M1 and M2 sites. For this new manganese analogue of flurlite, described herein, we have proposed the name manganflurlite. The new mineral and its name were approved by the

Table 1. Comparative data for flurlite and manganflurlite.

	Flurlite	Manganflurlite
Formula	$\text{Zn}_4\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$	$\text{ZnMn}_3^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$
Symmetry	Monoclinic, $P2_1/m$	Monoclinic, $P2_1/m$
Cell parameters	$a = 6.3710(13) \text{ \AA}$	$a = 6.4546(8) \text{ \AA}$
	$b = 11.020(2) \text{ \AA}$	$b = 11.1502(9) \text{ \AA}$
	$c = 13.016(3) \text{ \AA}$	$c = 13.1630(10) \text{ \AA}$
	$\beta = 99.34(3)^\circ$	$\beta = 99.829(5)^\circ$
	$V = 901.7(3) \text{ \AA}^3$	$V = 933.44(16) \text{ \AA}^3$
Z	2	2
Optics	Biaxial(–)	Biaxial (–).
	$\alpha = 1.60(1)$	$\alpha = 1.623(\text{calc})$
	$\beta = 1.65(1)$	$\beta = 1.649(2)$
	$\gamma = 1.68(1)$	$\gamma = 1.673(2)$
	$2V(\text{calc}) = 74^\circ$	$2V(\text{meas}) = 86(1)^\circ$

Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA2017-065). The original description approved by the CNMNC was based on one holotype specimen. Subsequently, a second specimen containing the mineral was found in the collection of one of the authors (EK) and this specimen is now designated as a cotype. Both specimens are deposited in the collections of the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA, catalogue numbers 66682 (holotype) and 66731 (cotype). Comparative data for flurlite and manganflurlite are provided in Table 1.

2. Occurrence

The holotype specimen of manganflurlite is from the collection of Gabriela (Kay) Robertson. The specimen is documented to have come from the Hagendorf-Süd pegmatite, Hagendorf, Oberpfalz, Bavaria, Germany ($49^\circ 39' 1''\text{N}$, $12^\circ 27' 35''\text{E}$) and was obtained by Mrs. Robertson from August Hartlaub of Regensburg, Germany, in 1965. The cotype specimen was collected by EK in the open cut mine at the Hagendorf-Süd pegmatite at a depth of about 60–67 m and the holotype is likely to have originated from the same part of the pegmatite.

The holotype specimen (Fig. 1) consists of one euhedral 3-cm-long phosphophyllite crystal intergrown with smaller phosphophyllite crystals, plates of hematite and fairfieldite, veinlets of kryshanovskite, and massive quartz and muscovite. The manganflurlite is relatively abundant on the specimen, occurring in vugs with lacework hydroxylapatite and tiny blocky crystals of jahnsite-(CaMnFe). Note that we also found small blocky crystals of an intermediate whiteite-jahnsite phase apparently corresponding to the not-yet-described mineral whiteite-(CaMnFe) (Grey *et al.*, 2010). On the specimen collected by EK, manganflurlite is associated with apatite, mitridatite and Zn-bearing rockbridgeite (Fig. 2).

On the holotype specimen, the new mineral apparently crystallized contemporaneously with phosphophyllite, as

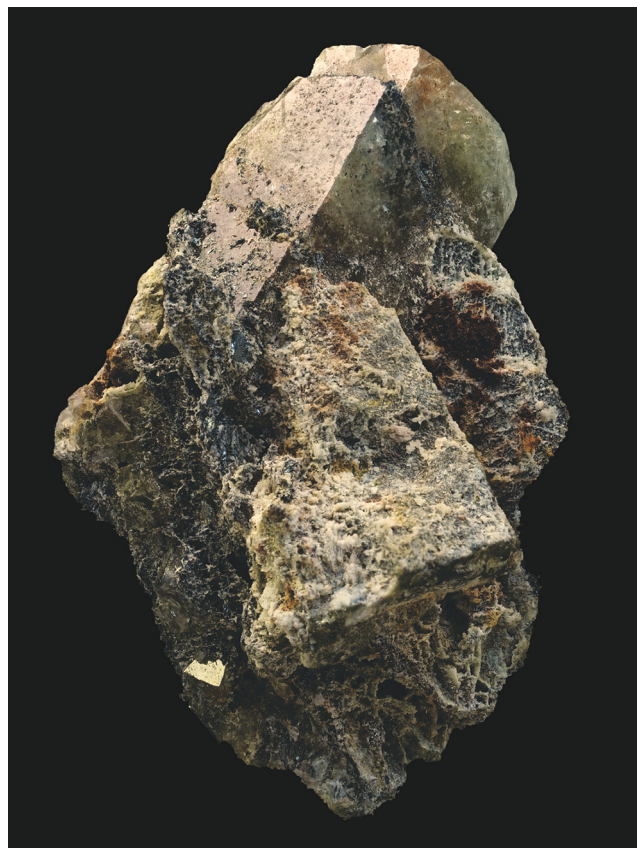


Fig. 1. Large 3-cm crystal of phosphophyllite with associated minerals including manganflurlite. The field of view is 3 cm across.

laths of manganflurlite are found both on and included within crystals of phosphophyllite. The secondary phosphate mineral assemblages on both specimens has formed from the reaction of earlier formed phosphate minerals with late-stage relatively low-temperature hydrothermal solutions. A detailed study of the secondary Zn-bearing phosphate minerals associated with the alteration of phosphophyllite at Hagendorf-Süd was reported by Grey *et al.* (2018b).

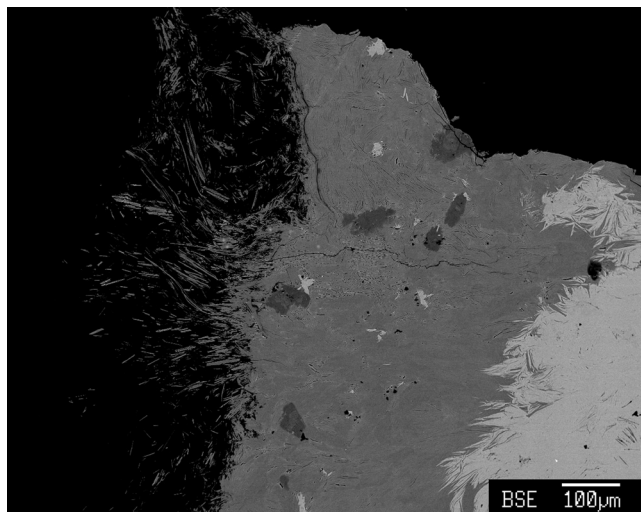


Fig. 2. Backscatter SEM image of the electron-microprobe mount of manganflurlite (grey) on Zn-bearing rockbridgeite (light grey), with individual manganflurlite laths separating at the surface.

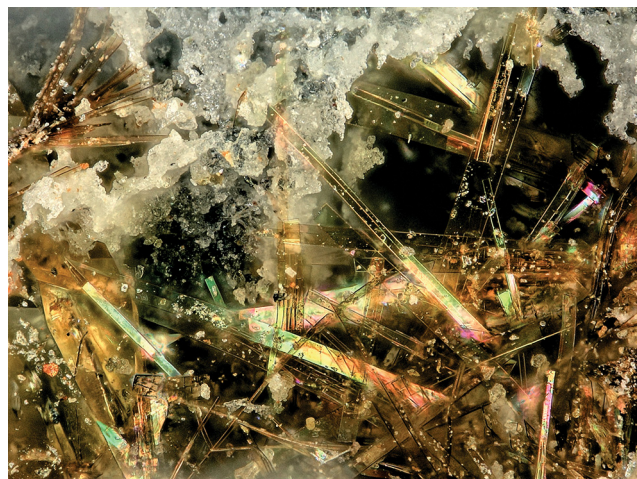


Fig. 3. Laths of manganflurlite with hydroxylapatite (white) on specimen in Fig. 1. The field of view is 1.14 mm across.

Table 2. Analytical data (in wt%) for manganflurlite.

	66682 (holotype)			66731 (cotype)			Probe standard
	Mean	Range	SD	Mean	Range	SD	
MgO	0.39	0.27–0.60	0.09	0.28	0.14–0.37	0.06	Spinel
CaO	0.02	0.00–0.11	0.04	0.04	0.00–0.13	0.05	Wollastonite
MnO	13.54	12.76–14.60	0.43	14.20	13.31–15.19	0.49	Rhodonite
ZnO	17.29	16.01–18.84	0.67	13.68	12.68–14.80	0.58	Phosphophyllite
Fe ₂ O ₃	(16.52)	15.50–17.33	0.59	(20.92)	19.30–22.79	0.97	Hematite
FeO*	6.26			9.78			
Fe ₂ O ₃ *	9.57			10.05			
Al ₂ O ₃	0.32	0.17–0.50	0.08	0.20	0.09–0.32	0.06	Berlinite
P ₂ O ₅	26.85	26.08–27.68	0.43	27.61	25.13–29.17	1.22	Berlinite
H ₂ O**	22.79			23.48			
Total	97.03			99.32			

*Apportioned in accord with the structure.

**Calculated from the structure.

3. Physical and optical properties

Manganflurlite occurs as long, very thin, rectangular laths, up to 0.5 mm long and less than 10 μm thick. Laths are elongated on [1 0 0], flattened on {0 0 1} and exhibit the forms {1 0 0}, {0 1 0} and {0 0 1}. Crystals usually occur in random (jackstraw) arrangements, but occasionally form divergent fans (Fig. 3). No twinning was observed.

Crystals are orange brown in colour and have a buff streak. They exhibit vitreous lustre and common iridescence. The mineral is non-fluorescent. Crystals are flexible and elastic with irregular fracture and three cleavages: {0 0 1} perfect, {1 0 0} and {0 1 0} good. The Mohs' hardness is estimated to be about 2½. The measured density is 2.73(2) g cm⁻³ determined by flotation in a mixture of methylene iodide and toluene. The calculated density is 2.737 g cm⁻³, based on the empirical formula for the holotype, and 2.729 g cm⁻³ for the ideal formula. At room temperature, the mineral is rapidly soluble in dilute HCl.

Optically, manganflurlite is biaxial (–), with the indices of refraction $\alpha = 1.623(\text{calc})$, $\beta = 1.649(2)$, $\gamma = 1.673(2)$ measured on the holotype in white light. The 2V measured directly on a spindle stage is 86(1)°. The thinness of the blades prevented the accurate measurement of α ; consequently, it was calculated from β , γ and 2V. The dispersion is $r > v$, slight. The optical orientation is $X = c$, $Y = b$, $Z = a$. The pleochroism is $X = \text{pale yellow brown}$, $Y = \text{orange brown}$, $Z = \text{light yellow brown}$, $Y > Z > X$. The Gladstone–Dale compatibility, $1 - (K_P/K_C)$, (Mandarino, 2007) is –0.026 (excellent) based upon the empirical formula for the holotype.

4. Chemical composition

Chemical analyses (16 and 21 points on crystals from the holotype and cotype, respectively) were performed on a JEOL JXA 8500F Hyperprobe using wavelength dispersive

Table 3. Powder X-ray diffraction data (d in Å) for holotype manganflurlite (66682).

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
100	12.89	12.9698	100	0 0 1	3	2.423	2.4330	2	$\bar{2}$ 1 4	6	1.6748	1.6814	1	$\bar{1}$ 5 5
38	8.43	8.4551	29	0 1 1	6	2.347	2.4163	1	2 3 0	6	1.6453	1.6764	4	2 4 4
		6.3599	2	1 0 0	9	2.270	2.3519	6	0 2 5			1.6621	1	$\bar{2}$ 5 4
22	6.14	6.1396	16	$\bar{1}$ 0 1	6	2.1533	2.2758	8	$\bar{2}$ 2 4			1.6565	2	$\bar{2}$ 2 7
28	5.57	5.6058	17	0 1 2			2.1616	4	0 0 6			1.6500	1	3 0 4
		5.5244	6	1 1 0	22	2.1001	2.1227	2	$\bar{1}$ 1 6			1.6450	1	3 4 1
18	5.35	5.3782	10	$\bar{1}$ 1 1			2.1080	5	$\bar{1}$ 3 5			1.6439	1	$\bar{3}$ 1 6
		5.3600	6	1 0 1			2.1025	2	1 2 5			1.6123	3	0 6 4
14	5.10	5.1219	8	0 2 1			2.0962	5	2 4 0	21	1.6045	1.6093	4	$\bar{2}$ 6 1
26	4.241	4.3233	10	0 0 3	10	2.0540	2.0621	4	2 1 4			1.6045	3	$\bar{2}$ 6 0
		4.2276	7	0 2 2			2.0375	1	3 0 1			1.5973	4	$\bar{2}$ 4 6
		4.1274	2	$\bar{1}$ 2 1			2.0336	2	2 4 1			1.5900	2	4 0 0
19	3.897	3.9277	8	1 1 2	8	1.9720	1.9754	3	$\bar{2}$ 4 3	12	1.5811	1.5878	1	3 4 4
		3.8981	6	$\bar{1}$ 0 3			1.9693	1	1 5 2			1.5815	2	3 4 2
		3.8639	2	1 2 1			1.9638	1	2 2 4			1.5740	2	4 1 0
12	3.680	3.6798	9	$\bar{1}$ 1 3			1.9491	2	$\bar{2}$ 0 6			1.5475	1	2 4 5
		3.2424	3	0 0 4	11	1.9331	1.9422	3	1 4 4	7	1.5432	1.5452	1	1 7 0
		3.2247	5	0 3 2			1.9357	2	$\bar{1}$ 5 3			1.5431	1	0 4 7
29	3.206	3.2089	7	1 3 0			1.9318	2	$\bar{3}$ 0 4			1.5290	1	4 2 0
		3.1833	2	1 1 3			1.8528	2	0 0 7			1.5107	2	0 6 5
		3.1795	4	$\bar{1}$ 3 1			1.8409	1	$\bar{1}$ 1 7			1.5042	1	3 4 3
8	3.099	3.1135	3	0 1 4	9	1.8463	1.8396	2	0 6 1	10	1.5023	1.4985	2	$\bar{2}$ 2 8
		3.0919	2	$\bar{2}$ 1 1			1.8374	1	0 5 4			1.4900	1	$\bar{2}$ 6 4
		3.0580	3	2 1 0			1.8351	1	2 1 5			1.4892	1	1 7 2
7	3.004	2.9971	5	$\bar{1}$ 1 4			1.8272	2	2 3 4			1.4618	1	4 3 0
		2.8729	5	2 1 1	10	1.8181	1.8158	1	$\bar{3}$ 2 2	7	1.4597	1.4601	2	$\bar{3}$ 5 4
15	2.844	2.8535	4	1 2 3			1.8126	1	$\bar{1}$ 5 4			1.4579	1	1 2 8
		2.8184	3	0 3 3			1.8080	3	2 4 3			1.4478	1	$\bar{1}$ 1 9
		2.8029	9	0 2 4			1.7927	1	$\bar{3}$ 3 3			1.4313	1	$\bar{1}$ 5 7
95	2.776	2.7876	33	0 4 0	7	1.7854	1.7865	4	0 6 2	7	1.4288	1.4286	1	2 5 5
		2.7622	24	2 2 0			1.7840	1	2 5 1			1.4267	1	2 4 6
		2.7253	2	0 4 1			1.7759	1	$\bar{3}$ 1 5			1.4251	1	0 5 7
27	2.713	2.7171	8	$\bar{1}$ 2 4	3	1.7150	1.7282	2	$\bar{2}$ 4 5			1.3989	1	$\bar{3}$ 6 2
		2.7077	4	1 0 4			1.7082	1	0 4 6			1.3953	1	4 4 1
		2.6891	4	$\bar{2}$ 2 2						8	1.3908	1.3938	2	0 8 0
												1.3858	1	0 8 1
												1.3811	1	4 4 0

spectrometry. Analytical conditions were 15 kV accelerating voltage, 2.2 nA beam current and a beam diameter of 5 μm . Because insufficient material is available for a direct determination of H_2O , it is calculated based upon the structure determination. There was minor beam damage, which could account for the low analytical total. Analytical results are given in Table 2.

The empirical formulas (calculated on the basis of 3 P and 23 O *apfu*) are $\text{Zn}(\text{Mn}_{1.51}^{2+}\text{Fe}_{0.69}^{2+}\text{Zn}_{0.68}\text{Mg}_{0.08})_{\Sigma 2.96}(\text{Fe}_{0.95}^{3+}\text{Al}_{0.05})_{\Sigma 1.00}(\text{PO}_4)_3(\text{OH})_{1.92}(\text{H}_2\text{O})_{9.08}$ and $\text{Zn}(\text{Mn}_{1.54}^{2+}\text{Fe}_{1.05}^{2+}\text{Zn}_{0.30}\text{Mg}_{0.05}\text{Ca}_{0.01})_{\Sigma 2.95}(\text{Fe}_{0.97}^{3+}\text{Al}_{0.03})_{\Sigma 1.00}(\text{PO}_4)_3(\text{OH})_{1.88}(\text{H}_2\text{O})_{9.12}$ for the holotype and cotype, respectively. The ideal

end-member formula is $\text{ZnMn}_3^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$, which requires ZnO 10.61, MnO 27.74, Fe_2O_3 10.41, P_2O_5 27.76, H_2O 23.48, total 100 wt%.

5. X-ray crystallography and crystal structure determination

Powder X-ray diffraction data for manganflurlite were obtained on a Rigaku R-Axis Rapid II curved-imaging-plate microdiffractometer utilising monochromatised Mo $K\alpha$ radiation. A Gandolfi-like motion on the ϕ and ω axes was used

Table 4. Data collection and refinement details for cotype manganflurlite (66731).

X-ray radiation	Synchrotron ($\lambda = 0.7107 \text{ \AA}$)
Temperature	100(2) K
Structural formula	$\text{Zn}(\text{Mn}_{1.54}\text{Fe}_{1.06}^{2+}\text{Zn}_{0.30}\text{Mg}_{0.05})(\text{Fe}_{0.96}^{3+}\text{Al}_{0.04})(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_9$
Space group	$P2_1/m$
Unit-cell dimensions	$a = 6.4070(10) \text{ \AA}$ $b = 11.074(2) \text{ \AA}$ $c = 13.085(3) \text{ \AA}$ $\beta = 99.62(3)^\circ$
V	$915.3(16) \text{ \AA}^3$
Z	2
Density (for above formula)	2.778 g cm^{-3}
Absorption coefficient	4.66 mm^{-1}
$F(0\ 0\ 0)$	757
Crystal size	$50 \times 15 \times 5 \text{ }\mu\text{m}$
θ range	$1.58\text{--}32.17^\circ$
Resolution for refinement	$0.7 \text{ \AA}$
Index ranges	$-8 \leq h \leq 8, -12 \leq k \leq 13,$ $-17 \leq l \leq 17$
Reflections collected/unique	16853/2294; $R_{\text{int}} = 0.031$
Reflections with $I > 3\sigma I$	2219
Completeness to $0.7 \text{ \AA}$	98%
Refinement method	Full-matrix least-squares on F^2
Parameters/constraints	188/59
GoF (obs/all)	3.28/3.28
Final R indices [$I > 3\sigma I$]	$R_{\text{obs}} = 0.0337, wR_{\text{obs}} = 0.0452$
R indices (all data)	$R_{\text{obs}} = 0.0353, wR_{\text{obs}} = 0.0456$
Largest diff. peak/hole	$+1.00/-1.39 \text{ e \AA}^{-3}$

to randomize the sample. Observed d values and intensities were derived by profile fitting using JADE 2010 software (Materials Data Inc.). Data are given in Table 3. The unit-cell parameters refined from the powder data using JADE 2010 with whole-pattern fitting are $a = 6.435(4)$, $b = 11.163(5)$, $c = 13.175(5) \text{ \AA}$, $\beta = 99.96(2)^\circ$ and $V = 932.1(8) \text{ \AA}^3$.

Initial single-crystal structure data for a crystal from the holotype specimen were obtained on the same instrument noted above. The refined cell parameters for this crystal are $a = 6.4546(8)$, $b = 11.1502(9)$, $c = 13.1630(10) \text{ \AA}$, $\beta = 99.829(5)^\circ$ and $V = 933.44(16) \text{ \AA}^3$. The Rigaku CrystalClear software package was used for processing of structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi, 2001). An initial structure model with most atoms located was obtained by the charge-flipping method using SHELXT (Sheldrick, 2015). This data set only allowed a structure refinement to $R_1 = 8.9\%$ for 900 observed ($I > 2\sigma I$) reflections and the O atoms could not be refined anisotropically. Subsequently, much better single-crystal data were obtained for a crystal from the cotype specimen on the macromolecular beam line MX2 of the Australian Synchrotron. Data were collected using an ADSC Quantum 315r detector and monochromatic radiation with a wavelength of $0.7107 \text{ \AA}$. A ϕ scan was employed with a framewidth of 1° and a counting time per frame of 1 s. The crystals were maintained at 100 K in an open-flow nitrogen cryostream. The intensity data sets were processed using XDS software to produce data files, which were analysed using WinGX

(Farrugia, 1999). The structure was refined using JANA2006 (Petříček *et al.*, 2014).

The crystal used for the synchrotron data collection exhibited twinning by 180° rotation on $[1\ 0\ 3]$. Introduction of this twinning in the data analysis improved R_1 from 11% to 5%. A difference Fourier map showed a significant peak about $1 \text{ \AA}$ from the ^{15}Zn site (Zna). This appears to represent a low occupancy Zn site (Znb) surrounded by four O atoms in approximately tetrahedral coordination. The same type of splitting of the ^{15}Zn site into $^{15}\text{Zn}/^{41}\text{Zn}$ sites occurs in the oxidized SGMs, schmidite, wildenauerite, and wilhelmgümbelite (Grey *et al.*, 2018a). The cation sites were assigned occupancies guided by a site-scattering refinement and the EPMA. All H atom sites were located in difference Fourier maps and were subsequently refined using an O–H distance constraint of $0.90(2) \text{ \AA}$ and an H–O–H angle constraint of $109.47(2)^\circ$. The refinement converged to a final R_{obs} of 0.034 for 2215 $I > 3\sigma I$ observed reflections.

Data collection and refinement details are given in Table 4, atom coordinates and displacement parameters in Table 5, site assignments and scattering values in Table 6, selected bond distances and angles in Table 7, and bond-valence sums (BVS) in Table 8. The Crystallography Information File (CIF), including reflection data, is available online as supplementary material linked to this article on the GSW website of the journal, <https://pubs.geoscienceworld.org/eurjmin>.

6. Discussion of the structure

Manganflurlite is isostructural with flurlite (Grey *et al.*, 2015) and their general formula can be given as $^{15}\text{ZnM1}^{2+}\text{M2}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$, where the ^{15}Zn site has trigonal bipyramidal coordination and the M1, M2 and Fe sites have octahedral coordination. For manganflurlite, we assigned the cations indicated in the empirical formula to the structural sites (Table 6) based upon site scattering, bond lengths and BVS values. The M1(Mn1) and M2(Mn2) sites have nearly identical mean bond distances and BVS values; consequently, they were assigned equivalent cation occupancies.

Manganflurlite has a heteropolyhedral layer structure (Fig. 4), with layers parallel to $\{0\ 0\ 1\}$ and with water molecules between the layers. The slab-like layers contain two types of polyhedral chains parallel to $[1\ 0\ 0]$: (a) chains of edge-sharing M2-centred octahedra and (b) chains in which Fe^{3+} -centred octahedra share their apices with edge-sharing units comprised of one ^{15}Zn -centred trigonal bipyramid and one P2-centred PO_4 tetrahedron. The two types of chains are interconnected by corner-sharing along $[0\ 1\ 0]$. A second type of PO_4 tetrahedron (P1-centred) connects the chains to $\text{M1O}_2(\text{H}_2\text{O})_4$ octahedra along $[0\ 1\ 0]$ to complete the $\{0\ 0\ 1\}$ slabs.

Flurlite and manganflurlite have formulas similar to the SGMs, schoonerite, schmidite, wildenauerite, and wilhelmgümbelite (Grey *et al.*, 2018a), but are different topological isomers according to the definition of Krivovichev (2004). The structure of flurlite/manganflurlite

Table 5. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for cotype manganflurlite (66731).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}		
Zna	0.58420(7)	0.75	0.79062(3)	0.01539(14)		
Znb	0.5728(16)	0.75	0.8686(7)	0.0247(19)		
Mn1	0.21349(8)	0.25	0.83343(4)	0.01244(15)		
Mn2	0.24954(5)	0.50073(3)	0.50888(3)	0.01400(12)		
Fe	0.04594(8)	0.75	0.62679(4)	0.01165(15)		
P1	0.27813(9)	0.53120(6)	0.76516(4)	0.01152(17)		
P2	0.52969(13)	0.75	0.56790(6)	0.0099(2)		
O1	0.2120(3)	0.43460(18)	0.83661(13)	0.0167(5)		
O2	0.3350(3)	0.47360(17)	0.66607(14)	0.0155(5)		
O3	0.0911(3)	0.61938(17)	0.73574(13)	0.0150(5)		
O4	0.4747(3)	0.59605(17)	0.82336(13)	0.0179(5)		
O5	0.3595(4)	0.75	0.63754(19)	0.0141(7)		
O6	0.7405(4)	0.75	0.64689(18)	0.0123(7)		
O7	0.5105(3)	0.63463(18)	0.50212(13)	0.0166(5)		
Oh	0.0042(3)	0.62450(18)	0.51614(15)	0.0175(5)		
Ow1	0.2298(3)	0.52944(18)	0.34108(15)	0.0164(5)		
Ow2	0.4431(4)	0.25	0.9756(2)	0.0209(8)		
Ow3	−0.0404(4)	0.25	0.9234(2)	0.0183(7)		
Ow4	0.4568(4)	0.25	0.7349(2)	0.0188(8)		
Ow5	−0.0283(4)	0.25	0.6900(2)	0.0168(7)		
Ow6	0.8717(5)	0.75	0.8717(2)	0.0401(12)		
Ow7	0.7229(3)	0.44360(18)	0.96424(15)	0.0212(6)		
Hoh	−0.004(7)	0.670(3)	0.458(2)	0.038(4)		
H1a	0.140(5)	0.478(3)	0.302(3)	0.038(4)		
H1b	0.361(3)	0.515(3)	0.332(3)	0.038(4)		
H2	0.5240(18)	0.1848(13)	0.982(4)	0.038(4)		
H3	−0.121(2)	0.1833(13)	0.925(4)	0.038(4)		
H4	0.453(7)	0.1836(13)	0.6949(9)	0.038(4)		
H5	−0.107(3)	0.1841(13)	0.695(4)	0.038(4)		
H6	0.957(9)	0.75	0.824(4)	0.038(4)		
H7a	0.662(7)	0.493(3)	0.915(2)	0.038(4)		
H7b	0.780(7)	0.486(3)	1.019(2)	0.038(4)		
	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²
Zna	0.0146(2)	0.0121(3)	0.0177(2)	0	−0.00229(16)	0
Mn1	0.0116(2)	0.0106(3)	0.0155(2)	0	0.00339(18)	0
Mn2	0.01226(19)	0.0162(2)	0.01294(19)	0.00195(12)	0.00026(14)	−0.00071(10)
Fe	0.0069(2)	0.0157(3)	0.0125(2)	0	0.00212(17)	0
P1	0.0095(3)	0.0118(3)	0.0132(3)	0.0013(2)	0.00157(19)	0.0009(2)
P2	0.0074(3)	0.0112(4)	0.0110(3)	0	0.0014(3)	0
O1	0.0161(8)	0.0177(10)	0.0167(8)	0.0012(6)	0.0038(6)	0.0030(6)
O2	0.0172(8)	0.0137(9)	0.0162(8)	0.0013(6)	0.0045(6)	−0.0004(6)
O3	0.0095(7)	0.0153(9)	0.0207(8)	0.0016(6)	0.0039(6)	0.0035(6)
O4	0.0151(8)	0.0181(10)	0.0187(8)	−0.0025(6)	−0.0021(6)	0.0014(6)
O5	0.0089(11)	0.0163(14)	0.0177(11)	0	0.0038(9)	0
O6	0.0100(10)	0.0127(13)	0.0135(10)	0	0.0001(8)	0
O7	0.0160(8)	0.0171(10)	0.0154(8)	0.0024(6)	−0.0009(7)	−0.0056(6)
Oh	0.0160(8)	0.0173(10)	0.0198(8)	−0.0021(6)	0.0045(6)	−0.0046(6)
Ow1	0.0104(8)	0.0149(10)	0.0226(8)	−0.0003(6)	−0.0004(6)	−0.0001(6)
Ow2	0.0189(12)	0.0149(14)	0.0293(13)	0	0.0056(11)	0
Ow3	0.0156(11)	0.0147(14)	0.0252(12)	0	0.0048(10)	0
Ow4	0.0233(13)	0.0118(14)	0.0215(11)	0	0.0047(10)	0
Ow5	0.0153(11)	0.0169(14)	0.0180(11)	0	0.0023(9)	0
Ow6	0.0151(13)	0.095(3)	0.0101(11)	0	0.0026(10)	0
Ow7	0.0246(10)	0.0195(11)	0.0180(8)	0.0043(7)	−0.0007(7)	−0.0002(7)

differs from that of schoonerite in the same way that the structure of strunzite differs from that of laueite (Krivovichev, 2004). In both cases, due to different octahedra-tetrahedra linkages, two independent octahedra

(*M2* and *M3* in SGMs) with coordinations of $M2O_4(OH)_2$ and $M3O_2(OH)_2(H_2O)_2$ are replaced by a single octahedron (*M2*) with intermediate coordination $M2O_3(OH)_2(H_2O)$ in flurlite/manganflurlite.

Table 6. Site occupancies and scattering values (*epfu*) for metal atom sites in cotype manganflurlite (66731).

Site	<i>apfu</i>	Assigned site occupancy	Site scattering value	
			Assigned	Refined
Zna	1	0.95 Zn	28.5	27.7(1)
Znb	1	0.05 Zn	1.5	1.44(6)
Mn1 (M1)	1	0.51 Mn ²⁺ + 0.37 Fe ²⁺ + 0.10 Zn + 0.02 Mg	25.6	24.6(1)
Mn2 (M2)	2	0.51 Mn ²⁺ + 0.37 Fe ²⁺ + 0.10 Zn + 0.02 Mg	51.2	51.3(2)
Fe	1	0.96 Fe ³⁺ + 0.04 Al	25.5	25.17(5)

Table 7. Selected interatomic distances (Å) in cotype manganflurlite (66731).

Zna–O4 (×2)	1.919(2)	Mn1–O1 (×2)	2.045(2)	Fe–O3 (×2)	2.0176(19)
Zna–O5	2.263(3)	Mn1–Ow2	2.171(3)	Fe–O5	1.990(3)
Zna–O6	2.274(3)	Mn1–Ow3	2.162(3)	Fe–O6	2.018(3)
Zna–Ow6	1.966(3)	Mn1–Ow4	2.183(3)	Fe–Oh (×2)	1.992(2)
<Zn–O>	2.068	Mn1–Ow5	2.225(3)	<Fe–O>	2.002
		<Mn1–O>	2.157		
Znb–O4 (×2)	1.878(4)			P1–O1	1.526(2)
Znb–Ow2	2.058(10)	Mn2–O2	2.060(2)	P1–O2	1.542(2)
Znb–Ow6	1.908(11)	Mn2–O7	2.247(2)	P1–O3	1.5439(19)
<Zn–O>	1.931	Mn2–O7	2.169(2)	P1–O4	1.5365(19)
		Mn2–Oh	2.100(2)	<P1–O>	1.537
		Mn2–Oh	2.120(2)		
		Mn2–Ow1	2.201(2)	P2–O5	1.533(3)
		<Mn1–O>	2.167	P2–O6	1.558(2)
				P2–O7 (×2)	1.534(2)
				<P2–O>	1.540
Hydrogen bonds					
<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	< <i>DHA</i>	
Oh–Hoh...Ow5	0.91(3)	2.17(3)	3.061(3)	167(4)	
Ow1–H1a...O3	0.91(3)	1.83(3)	2.695(3)	159(4)	
Ow1–H1b...O2	0.89(3)	1.95(2)	2.806(3)	163(3)	
Ow2–H2...Ow7	0.885(14)	1.951(17)	2.815(3)	165(3)	
Ow3–H3...Ow7	0.905(16)	1.84(2)	2.730(3)	166(4)	
Ow4–H4...O2	0.901(14)	1.91(2)	2.705(2)	146(3)	
Ow5–H5...Ow1	0.893(17)	1.910(17)	2.761(2)	158(3)	
Ow6–H6...O3	0.90(6)	2.12(4)	2.840(3)	136.8(11)	
Ow7–H7a...O4	0.88(3)	1.93(3)	2.793(3)	167(4)	
Ow7–H7b...O1	0.89(3)	2.07(3)	2.902(3)	155(4)	

Table 8. Bond valence sums in valence units (*vu*) for cotype manganflurlite (66731). The Znb site is not included.

	Zna	Mn1	Mn2	Fe	P1	P2	Hydrogen bonds		Σ
							accepted	donated	
O1		0.45 × 2↓			1.28		0.15		1.88
O2			0.43		1.23		0.18, 0.22		2.06
O3				0.49 × 2↓	1.22		0.23, 0.17×½		2.03
O4	0.54 × 2↓				1.24		0.19		1.97
O5	0.22			0.53		1.25			2.00
O6	0.21			0.49		1.18			1.88
O7			0.28, 0.33			1.25 × 2↓			1.86
Oh			0.39, 0.38	0.53 × 2↓				–0.12	1.18
Ow1			0.31				0.20	–0.23, –0.18	0.10
Ow2		0.33						–0.18×2	–0.03
Ow3		0.34						–0.21×2	–0.08
Ow4		0.33						–0.22×2	–0.11
Ow5		0.29					0.12	–0.20×2	0.01
Ow6	0.48							–0.17×2	0.14
Ow7							0.18, 0.21	–0.19, –0.15	0.05
Σ	1.99	2.19	2.12	3.06	4.97	4.93			

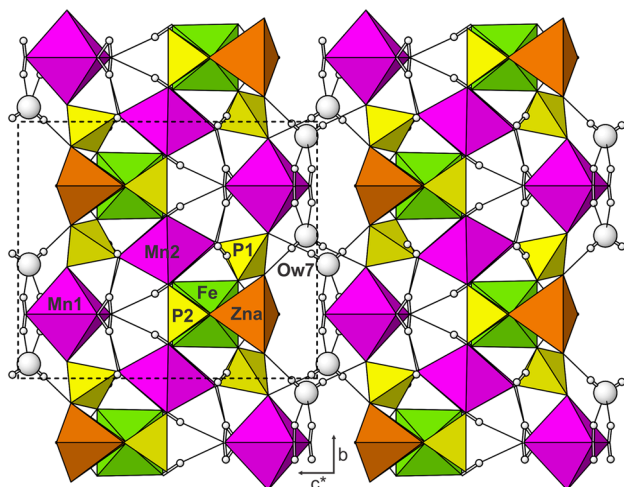


Fig. 4. Manganflurlite structure viewed along $[1\ 0\ 0]$. O–H bonds are shown as sticks; hydrogen bonds are shown as black lines. The unit-cell outline is shown with dashed lines.

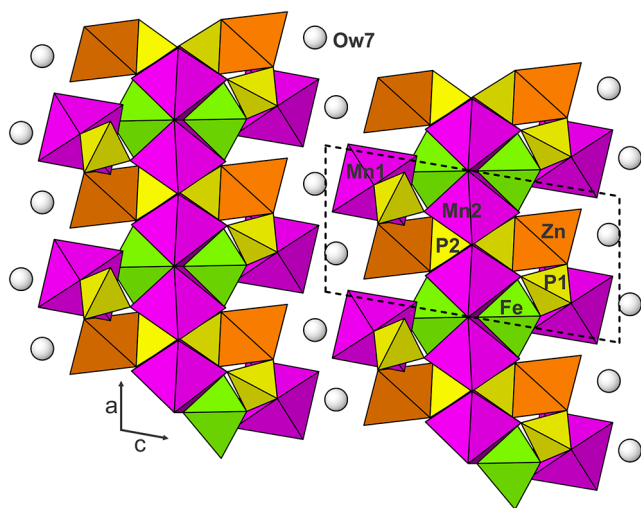


Fig. 5. Manganflurlite structure viewed along $[0\ 1\ 0]$. The H atoms are omitted for clarity.

Acknowledgements: The paper benefited from comments by two anonymous referees. Rob Lavinsky is thanked for

the donation of the holotype specimen. This study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County. This research was undertaken in part using the MX2 beamline at the Australian Synchrotron, part of ANSTO, and made use of the Australian Cancer Research Foundation (ACRF) detector.

References

- Farrugia, L.J. (1999): WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.*, **32**, 837–838.
- Grey, I.E., Mumme, W.G., Neville, S.M., Wilson, N.C., Birch, W.D. (2010): Jahnsite–whiteite solid solutions and associated minerals in the phosphate pegmatite at Hagendorf-Süd, Bavaria, Germany. *Mineral. Mag.*, **74**, 969–978.
- Grey, I.E., Keck, E., Mumme, W.G., Pring, A., MacRae, C.M. (2015): Flurlite, $\text{Zn}^3\text{Mn}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2 \cdot 9\text{H}_2\text{O}$, a new mineral from the Hagendorf Süd pegmatite, Bavaria, with a schoonerite-related structure. *Mineral. Mag.*, **79**, 1175–1184.
- Grey, I.E., Kampf, A.R., Keck, E., Cashion, J.D., MacRae, C.M., Gozokara, Y. (2018a): Crystal chemistry of schoonerite-group minerals. *Eur. J. Mineral.*, **30**, 621–634.
- Grey, I.E., Keck, E., MacRae, C.M., Glenn, A.M., Kampf, A.R., Cashion, J.D. (2018b): Secondary Zn-bearing phosphate minerals associated with alteration of phosphophyllite at Hagendorf-Süd, Bavaria. *Eur. J. Mineral.*, **30**, 1007–1020.
- Higashi, T. (2001): *ABSCOR*, Rigaku Corporation, Tokyo.
- Kampf, A.R. (1977): Schoonerite: its atomic arrangement. *Am. Mineral.*, **62**, 250–255.
- Krivovichev, S.V. (2004): Topological and geometrical isomerism in minerals and inorganic compounds with laueite-type heteropolyhedral sheets. *Neues Jahrb. Mineral. Monatsh.*, **2004**, 209–220.
- Mandarino, J.A. (2007): The Gladstone–Dale compatibility of minerals and its use in selecting mineral species for further study. *Can. Mineral.*, **45**, 1307–1324.
- Petríček, V., Dušek, M., Palatinus, L. (2014): Crystallographic Computing System JANA2006: General features. *Z. Kristallogr.*, **229**, 345–352.
- Sheldrick, G.M. (2015): SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr.*, **A71**, 3–8.

Received 20 April 2018

Modified version received 26 May 2018

Accepted 2 June 2018