

# Wilhelmgümbelite, $[\text{ZnFe}^{2+}\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$ , a new schoonerite-related mineral from the Hagendorf Süd pegmatite, Bavaria

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## ABSTRACT

Wilhelmgümbelite, ideally  $[\text{ZnFe}^{2+}\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$ , is a new secondary phosphate mineral related closely to schoonerite,  $[\text{ZnMnFe}_2^+\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7]\cdot 2\text{H}_2\text{O}$ , from oxidized zones of the Hagendorf-Süd pegmatite, Hagendorf, Oberpfalz, Bavaria, Germany. Wilhelmgümbelite occurs as radiating sprays of needle-like rectangular laths, up to 0.2 mm long and with colour varying from light yellow brown to orange red. Cleavage is perfect parallel to  $\{010\}$ . The mineral is associated closely with an oxidized pseudomorph of phosphophyllite, recently named steinmetzite. Other associated minerals are albite, apatite, chalcophanite, jahnsite, mitridatite, muscovite and quartz. The calculated density of wilhelmgümbelite is  $2.82 \text{ g cm}^{-3}$ . It is optically biaxial (+) with  $\alpha = 1.560(2)$ ,  $\beta = 1.669(2)$ ,  $\gamma = 1.718(2)$ ,  $2V(\text{meas}) = 63(1)^\circ$  and  $2V(\text{calc.}) = 65^\circ$ . Dispersion is weak with  $r > v$ , orientation  $X = \mathbf{b}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{a}$ . Pleochroism is weak, with colours  $Z = \text{orange brown}$ ,  $Y = \text{yellow brown}$ ,  $X = \text{light yellow brown}$ ,  $Z \gg Y > X$ . Electron microprobe analyses (average of seven analyses, seven crystals) with  $\text{H}_2\text{O}$  and  $\text{FeO}/\text{Fe}_2\text{O}_3$  calculated on structural grounds, gave FeO 5.8,  $\text{Fe}_2\text{O}_3$  25.0, MnO 2.6, ZnO 16.4,  $\text{P}_2\text{O}_5$  28.7,  $\text{H}_2\text{O}$  23.4, total 101.9 wt.%. The empirical formula, scaled to 3 P and  $\text{OH}^-$  adjusted for charge balance is  $\text{Zn}_{1.50}\text{Mn}_{0.27}^{2+}\text{Fe}_{0.60}^{2+}\text{Fe}_{2.33}^{3+}(\text{PO}_4)_3\cdot(\text{OH})_{2.73}(\text{H}_2\text{O})_{8.27}$ . The structural formula is  $[\text{Zn}(\text{Mn}_{0.27}\text{Fe}_{0.73}^{3+})_{\Sigma 1.0}(\text{Zn}_{0.25}\text{Fe}_{0.15}^{2+}\text{Fe}_{0.60}^{3+})_{\Sigma 1.0}(\text{Zn}_{0.25}\text{Fe}_{0.45}^{2+})_{\Sigma 0.7}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH},\text{H}_2\text{O})_9]\cdot 2\text{H}_2\text{O}$ . Wilhelmgümbelite has orthorhombic symmetry,  $Pmab$ ,  $Z = 4$ , with the unit-cell parameters of  $a = 10.987(7) \text{ \AA}$ ,  $b = 25.378(13) \text{ \AA}$ ,  $c = 6.387(6) \text{ \AA}$  and  $V = 1781(2) \text{ \AA}^3$ . The strongest lines in the powder X-ray diffraction pattern are [ $d_{\text{obs}}$  in  $\text{Å}$  ( $I_{\text{obs}}$ ) ( $hkl$ )] 12.65 (100) (020); 8.339 (5) (120); 6.421 (14) (001); 6.228 (8) (011); 4.223 (30) (120) and 2.111 (7) (0 12 0). Wilhelmgümbelite is an oxidized form of schoonerite, with the  $\text{Mn}^{2+}$  replaced principally by  $\text{Fe}^{3+}$ . Its structure differs from that of schoonerite in having the Zn partitioned between two different sites, one five-coordinated as in schoonerite and the other tetrahedrally coordinated. Wilhelmgümbelite also differs structurally from schoonerite in having partial occupation of one of the Fe sites, which appears to be correlated with the Zn partitioning.

**KEYWORDS:** new mineral, new secondary phosphate, new schoonerite-related mineral, crystal structure.

## Introduction

As part of a study on secondary phosphate minerals from the Hagendorf-Süd pegmatite in Bavaria, we have recently described the new mineral steinmetzite,  $\text{Zn}_2\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})\cdot 3\text{H}_2\text{O}$ , which occurs as

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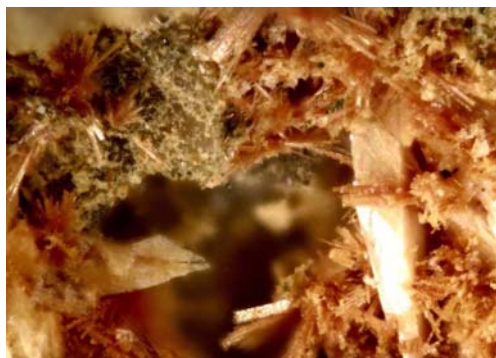


FIG. 1. Thin rectangular laths of wilhelmgümbelite (orange-red), associated with large laths of altered phosphophyllite (off-white). The field of view is 2.5 mm × 3 mm.

part of an oxidized pseudomorph after phosphophyllite (Grey *et al.*, 2015b). Steinmetzite was found by EK when collecting specimens containing opaque yellowish altered phosphophyllite crystals in a highly oxidized zone of the Cornelia mine open cut at the Hagendorf-Süd pegmatite. The altered phosphophyllite crystals were associated closely with radiating clusters of orange-red needles of a mineral that gave a powder X-ray diffraction (XRD) pattern similar to that for schoonerite,  $[\text{ZnMnFe}_2^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7] \cdot 2\text{H}_2\text{O}$  (Moore and Kampf, 1977), but for which electron microprobe analyses showed a replacement of most of the Mn by Fe. A single-crystal structure determination on the mineral showed it was isostructural with

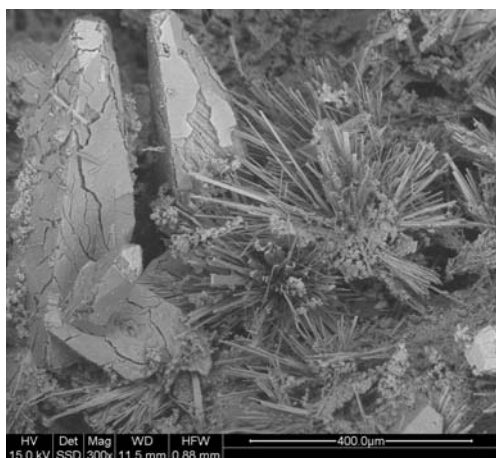


FIG. 2. Radiating sprays of wilhelmgümbelite crystals associated with laths of altered phosphophyllite, showing typical cracked weathering rinds.

schoonerite (Kampf, 1977) but with significant differences in the coordination of the Zn site.

The new mineral is named wilhelmgümbelite. The name is for Dr. Carl Wilhelm von Gümbel, born 1823 in Dannenfels and died in 1898, Munich. He was appointed to Munich in 1851 by King Maximilian II to lead the geological studies of the kingdom of Bavaria for more than 47 years. Geological mapping of Bavaria became his life's work, published in a number of comprehensive volumes that were printed between 1861 and 1891. His second volume "Geognostische Beschreibung des Ostbayerischen Grenzgebirges oder des Bayerischen und Oberpfälzer Waldgebirges", published in 1868, became an essential contribution to the mineralogical and geological investigation of pegmatites and their minerals in the northeastern parts of Bavaria. His work continues to be cited in modern publications. We wished to honour the memory of Dr. Gümbel but we were also aware that the obsolete name gümbelite (Bayliss, 2000) still appears in the literature as a synonym for illite-2M2. To avoid confusion we have chosen the name wilhelmgümbelite, because Dr. Gümbel was known as Wilhelm to all who were associated with him. The new mineral and name have been approved by the IMA Commission on new Minerals, Nomenclature and Classification (IMA 2015-072). The holotype specimen of wilhelmgümbelite is housed in the mineralogical collections of Museum Victoria, Melbourne, Victoria, Australia, registration number M53512.

### Occurrence, mineral assemblage and paragenesis

Wilhelmgümbelite was found in specimens collected by one of the authors (EK) from the 67 metre level of the Cornelia mine open cut at the Hagendorf-Süd pegmatite, Hagendorf, Oberpfalz, Bavaria, Germany (49°39'1"N, 12°27'35"E). It is confined to highly oxidized zones, mainly at depths of 60 to 76 metres in the mine. Samples were collected over the period 1974 to 1978. Since 1984 the mine has been flooded and no further specimens can be collected.

The new mineral is associated intimately with altered phosphophyllite, which has been transformed, in part, to steinmetzite (Grey *et al.*, 2015b). Other associated minerals that have been identified by X-ray diffraction are albite, Sr-bearing apatite, chalcophanite, jahnsite, mitridatite, muscovite and quartz. Goethite and cryptomelane are also abundant in the oxidized zone.

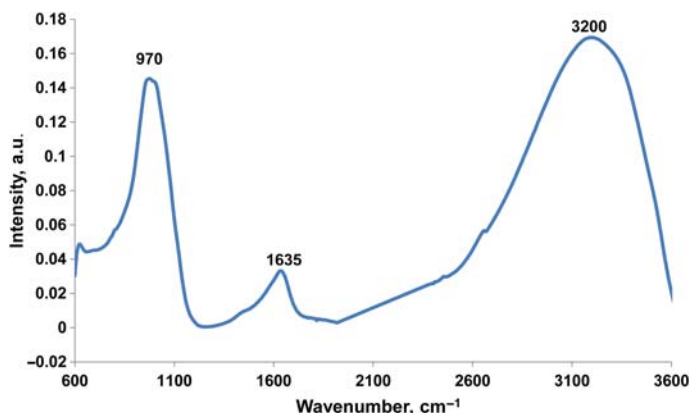


FIG. 3. Infrared spectrum for wilhelmgümbelite.

Wilhelmgümbelite is a secondary phosphate mineral that has probably formed from schoonerite by metal replacement reactions (enrichment of Zn and Fe, depletion of Mn) together with oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

### Physical and optical properties

Wilhelmgümbelite occurs as radiating sprays of needle-like rectangular laths up to 0.2 mm long. The crystals are light yellow brown to orange red in colour (Fig. 1). The mineral is associated closely with highly altered phosphophyllite crystals showing cracked yellow to orange weathering rinds and internal platy morphology (Fig. 2). The thin wilhelmgümbelite laths are elongated on [100] and flattened on {010}. They have perfect cleavage parallel to {010}. Their streak is pale yellow brown. The crystals are brittle, and have a dull lustre and uneven fracture. The crystals remain suspended in bromoform (density =  $2.89 \text{ g cm}^{-3}$ ) and have a

calculated density of  $2.82 \text{ g cm}^{-3}$ , based on the empirical formula and the single-crystal unit-cell parameters.

Wilhelmgümbelite is optically biaxial (+) with measured indices of refraction  $\alpha = 1.560(2)$ ,  $\beta = 1.669(2)$  and  $\gamma = 1.718(2)$  (white light).  $2V$ , measured using extinction data analysed with *EXCALIBUR* (Gunter *et al.*, 2004) is  $63(1)^\circ$ , while  $2V(\text{calc.})$  is  $65^\circ$ . Dispersion is weak with  $r > v$ . The optical orientation is  $X = \mathbf{b}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{a}$ . Pleochroism is weak, with colours  $Z =$  orange brown,  $Y =$  yellow brown,  $X =$  light yellow brown,  $Z \gg Y > X$ . The Gladstone-Dale compatibility index (Mandarino, 1981) is 0.030 (excellent) based on the empirical formula and density calculated from the single-crystal unit-cell parameters (at 100 K). Using the room temperature unit-cell parameters calculated from refinement of the powder XRD data gives a compatibility index of 0.016 (superior).

Attenuated total reflection infrared spectroscopy on crushed crystals of wilhelmgümbelite was

TABLE 1. Analytical data (wt.%) for wilhelmgümbelite.

Constituent	Mean	Range	Standard deviation	Probe standard
ZnO	16.4	15.4–17.2	0.6	phosphophyllite
MnO	2.6	2.4–2.8	0.1	rhodonite
$\text{Fe}_2\text{O}_3(\text{TOT})$	31.4	29.9–34.3	1.6	hematite
$\text{FeO}^*$	5.8			
$\text{Fe}_2\text{O}_3^*$	25.0			
$\text{P}_2\text{O}_5$	28.7	27.6–29.3	0.6	berlinite
$\text{H}_2\text{O}^{**}$	23.4			
Total	101.9			

\*Calculated from total Fe based on structure.

\*\*Calculated from structure.

TABLE 2. Powder diffraction data for wilhelmgümbelite.

$I_{obs}^*$	$d_{obs}$	$d_{calc}$	$h$	$k$	$l$
100	12.650	12.670	0	2	0
5	8.339	8.349	1	2	0
14	6.421	6.425	0	0	1
8	6.228	6.228	0	1	1
2	5.494	5.502	1	4	0
2	5.420	5.431	1	1	1
5	5.098	5.092	1	2	1
2	4.505	4.511	0	4	1
30	4.223	4.223	0	6	0
2	3.980	3.979	0	5	1
2	3.743	3.746	1	5	1
3	3.527	3.529	0	6	1
5	3.166	3.167	0	8	0
1	3.116	3.114	0	2	2
2	3.062	3.063	1	1	2
3	3.032	3.034	1	7	1
2	2.840	2.841	0	8	1
2	2.774	2.774	1	4	2
2	2.756	2.751	2	8	0
1	2.710	2.711	4	2	0
3	2.542	2.542	4	4	0
1	2.510	2.512	1	9	1
1	2.353	2.357	0	10	1
1	2.207	2.205	2	7	2
1	2.131	2.128	1	11	1
7	2.111	2.111	0	12	0
2	2.076	2.074	1	12	0
1	1.989	1.989	0	10	2
2	1.910	1.910	0	6	3
1	1.840	1.839	1	13	1
3	1.810	1.810	0	14	0
1	1.786	1.786	1	14	0
1	1.704	1.705	0	9	3
2	1.603	1.603	0	1	4
2	1.584	1.584	0	16	0

\*Intensities influenced by preferred orientation on  $\{0k0\}$ .

conducted using a Bruker IFS55 fitted with a MCT detector and Specac diamond ATR. A hundred co-added scans were employed at a spectral resolution of  $4\text{ cm}^{-1}$ . The infrared spectrum is shown in Fig. 3. The presence of water is confirmed by the H–O–H bending vibration at  $1635\text{ cm}^{-1}$ . The O–H stretching region contains a broad featureless peak centred at  $1620\text{ cm}^{-1}$ , corresponding to H-bonded water molecules. The only other feature in the spectrum is a peak at  $970\text{ cm}^{-1}$ , with shoulders at  $2010$  and  $1120\text{ cm}^{-1}$ , corresponding to P–O stretching vibrations of the  $\text{PO}_4$  groups.

## Chemical composition

Electron microprobe analyses (EMPA) on crystals of wilhelmgümbelite were conducted using wavelength-dispersive spectrometry on a JEOL JXA 8500F Hyperprobe operated at an accelerating voltage of  $12\text{ kV}$  and a beam current of  $4\text{ nA}$ . The beam was defocused to  $2\text{ }\mu\text{m}$  for the analyses. The data were corrected for matrix effects using the  $\Phi\rho Z$  method implemented in the JEOL system. Water was not analysed directly because of the paucity of sample. It was calculated from the empirical formula, based on the crystal structure analysis showing  $11(\text{H}_2\text{O} + \text{OH}^-)$  per formula unit with adjustment of  $\text{OH}^-$  for charge balance. The results of seven analyses on seven separate crystals are given in Table 1.

The empirical formula, scaled to 3 P with ferric and ferrous iron consistent with bond lengths/bond valence sums and  $\text{OH}^-$  adjusted for charge balance is:  $\text{Zn}_{1.50}\text{Mn}_{0.27}\text{Fe}_{0.60}^{2+}\text{Fe}_{2.33}^{3+}(\text{PO}_4)_3(\text{OH})_{2.73}(\text{H}_2\text{O})_{8.27}$ .

The structural formula is  $[\text{Zn}(\text{Mn}_{0.27}^{2+}\text{Fe}_{0.73}^{3+})_{\Sigma 1.0}(\text{Zn}_{0.25}\text{Fe}_{0.15}^{2+}\text{Fe}_{0.60}^{3+})_{\Sigma 1.0}(\text{Zn}_{0.25}\text{Fe}_{0.45}^{2+})_{\Sigma 0.7}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH},\text{H}_2\text{O})_9]\cdot 2\text{H}_2\text{O}$ . It was established by using calculated bond-valence sums to determine site valencies and by assigning minor elements (Zn, Mn) based on reported site occupancies for the structurally related minerals schoonerite (Kampf, 1977) and flurlite  $[\text{Zn}_3\text{MnFe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7]\cdot 2\text{H}_2\text{O}$  (Grey *et al.*, 2015a).

The idealized formula is  $[\text{ZnFe}^{2+}\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$ . This formula has 4  $\text{OH}^-$ , rather than 3  $\text{OH}^-$  from rounding of the empirical value, because the ideal formula has full occupation of the metal atom sites, whereas one site is only 0.7 occupied in the empirical and structural formulae.

## Crystallography

### Powder X-ray diffraction

Powder X-ray diffraction data for wilhelmgümbelite were collected at room temperature using a Philips diffractometer with a graphite monochromator, and employing  $\text{CuK}\alpha$  radiation. The small quantity of crystals available was dispersed, without grinding, on a zero-background silicon disk, using ethanol as the dispersant. This inevitably introduced some preferred orientation, resulting in enhancement of the  $\{0k0\}$  reflections. The indexed powder pattern is given in Table 2. The unit-cell parameters were refined using the positions of 36 reflections in *CELLREF* (Laugier and Bochu, 2000), giving the following orthorhombic unit-cell parameters:  $a = 11.099(5)$ ,  $b = 25.338(4)$ ,  $c = 6.425(2)\text{ \AA}$ ,  $V = 1806.9(1)\text{ \AA}^3$ .

## WILHELMGÜMBELITE, A NEW SCHOONERITE-RELATED MINERAL

TABLE 3. Data collection and structure refinement details for wilhelmgümbelite.

Ideal formula	[ZnFe <sup>2+</sup> Fe <sup>3+</sup> (PO <sub>4</sub> ) <sub>3</sub> (OH) <sub>4</sub> (H <sub>2</sub> O) <sub>5</sub> ]·2H <sub>2</sub> O
Formula weight	767.8
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pmab</i>
Unit-cell dimensions	<i>a</i> = 10.987(7) Å <i>b</i> = 25.378(13) Å <i>c</i> = 6.387(6) Å
Volume	1781(2) Å <sup>3</sup>
Z	4
Density (calc, from empirical formula)	2.82 g cm <sup>-3</sup>
Absorption coefficient	4.90 mm <sup>-1</sup>
Crystal size (mm)	0.03 × 0.05 × 0.18
Theta range for data collection	2.45 to 29.92°
Index ranges	-13 ≤ <i>h</i> ≤ 13, -34 ≤ <i>k</i> ≤ 35, -8 ≤ <i>l</i> ≤ 8
Reflections collected	26,412
Independent reflections	1030 [ <i>R</i> (int) = 0.12]
Reflections with <i>I</i> > 2σ( <i>I</i> )	869
Completeness of data	93%
Refinement method	Full-matrix least-squares on <i>F</i>
Data/restraints/parameters	1030/1/161
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>obs</sub> = 0.072, w <i>R</i> <sub>obs</sub> = 0.076
<i>R</i> indices (all data)	<i>R</i> <sub>obs</sub> = 0.090, w <i>R</i> <sub>obs</sub> = 0.077
Extinction coefficient	0.7(1)

### Single-crystal studies

In common with crystals of schoonerite (Kampf, 1977) and schoonerite-related flurlite (Grey *et al.*, 2015a) that have layer structures, the wilhelmgümbelite crystals are poorly diffracting. The diffraction patterns show strong streaking of the reflections normal to the plane of the layers. A further complication with the diffraction data for wilhelmgümbelite is the apparent presence of multiple diffraction, manifested by weak reflections systematically having  $F_{obs} \gg F_{calc}$ , and by the appearance of symmetry forbidden reflections. The effect is enhanced in wilhelmgümbelite by having relatively large unit-cell parameters, particularly  $b = 25.4$  Å, and using short wavelength radiation (flattened Ewald sphere), so that there is a high probability of multiple reflections being simultaneously in a position to diffract.

Eventually, a crystal was chosen for a data collection that had less severe streaking of the reflections. Single-crystal studies were carried out 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 0.71073 Å. A

phi scan was employed with a framewidth of 1° and a counting time per frame of 1 s. The crystal was 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 *JANA2006* (Petříček *et al.*, 2014). Further details of the data collection are given in Table 3.

### Crystal structure refinement

The atomic coordinates for schoonerite (Kampf, 1977) were used to initiate the structure refinement in space group *Pmab*, a reorientation of *Pbcm* (#57). The same atom labelling as for schoonerite was used, with Zn at the 5-coordinated Zn site and with Fe in the other metal atom sites. After refinement in *JANA2006* (Petříček *et al.*, 2014) using isotropic displacement parameters, it was observed that the Zn and Fe2 sites had elevated displacement parameters compared to the other sites, and a difference-Fourier map showed a strong peak (13  $e$  Å<sup>-2</sup>) displaced by 1 Å from the Zn site. Zinc was thus partitioned between the two sites, Zn1A and Zn1B, and restrained to have equal displacement

TABLE 4. Refined coordinates, equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) and calculated bond-valence sums (BVS) for wilhelmgümbelite.

	s.o.f.	x	y	z	$U_{eqi}$	BVS
Zn1A	0.699(4)	0.25	0.1026(1)	0.8492(5)	0.0304(9)	2.00(3)
Zn1B	0.301(4)	0.25	0.0656(3)	0.8806(11)	0.0304(9)	2.07(3)
Fe	1	0.25	0.41618(9)	0.2249(4)	0.0281(9)	2.61(3)
Fe1	1	0	0.25	0.0720(3)	0.0240(8)	2.58(2)
Fe2	0.69(1)	0	0.25	0.5623(5)	0.022(1)	2.06(2)
Fe3	1	0.25	0.18729(9)	0.3156(3)	0.0272(9)	3.06(3)
P1	1	0.0315(3)	0.1186(1)	0.1385(4)	0.025(1)	4.99(6)
O1	1	0.0253(7)	0.3300(3)	0.0440(12)	0.029(3)	1.58(3)
O2	1	0.0688(8)	0.4155(3)	0.2291(12)	0.032(3)	1.83(3)
O3	1	0.0896(8)	0.0878(3)	0.9592(12)	0.035(3)	1.82(3)
O4	1	0.1215(7)	0.1309(3)	0.3155(10)	0.026(3)	1.74(3)
P2	1	0.25	0.2170(1)	0.8220(6)	0.021(1)	5.06(7)
O5	1	0.25	0.1795(4)	0.0049(16)	0.025(4)	2.04(4)
O6	1	0.25	0.1823(4)	0.6273(18)	0.036(4)	1.88(5)
O7	1	0.1319(7)	0.2500(3)	0.8289(13)	0.033(3)	1.77(3)
OH	1	0.1221(9)	0.2424(3)	0.3046(13)	0.038(3)	1.26(2)
Ow1	1	0.0367(1)	0.3299(4)	0.6040(15)	0.056(4)	0.28(1)
Ow2	1	0.25	0.3463(4)	0.4106(17)	0.036(4)	0.36(1)
Ow3	1	0.25	0.3660(5)	0.9643(17)	0.034(4)	0.39(1)
Ow4	1	0.25	0.4592(5)	0.5008(17)	0.041(5)	0.42(1)
Ow5	1	0.25	0.4846(5)	0.0475(17)	0.037(4)	0.52(1)
Ow6	1	0.25	0.0649(5)	0.5853(18)	0.047(5)	0.56(1)
Ow7	1	0.0591(9)	0.4812(3)	0.7524(14)	0.046(4)	0

s.o.f. – site occupancy factor.

parameters and have the sum of the occupancies constrained to 1. The Fe2 site occupancy was also refined. A refinement with anisotropic displacement parameters for all atoms except the split pair of Zn atoms converged at  $wR_{obs} = 0.077$  for 1030 unique reflections to a resolution of 0.9  $\text{\AA}$ . Further details of the structure refinement are given in Table 3.

The refined coordinates, equivalent isotropic displacement parameters and bond-valence sums (BVS), calculated in *JANA2006*, are reported in Table 4. Hydrogen atoms were not located in the refinement, but the BVS values in Table 4 allow unambiguous assignment of hydroxyl ion (OH) and water molecules (Ow), consistent with the assignments reported by Kampf (1977) for schoonerite. Selected interatomic distances are reported in Table 5. The BVS values are consistent with site Fe2 being occupied by divalent cations ( $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$ ), and site Fe3 containing  $\text{Fe}^{3+}$  only, as in schoonerite. The bond valence of 2.6 for the Fe site (occupied by  $\text{Mn}^{2+}$  in schoonerite) and the Fe1 site (containing  $\text{Fe}^{2+}$  in schoonerite) indicates that these sites are predominantly occupied by  $\text{Fe}^{3+}$  in wilhelmgümbelite. This is also reflected in the

average bond length of 2.06  $\text{\AA}$  for both sites, considerably shorter than the average bond length of 2.16  $\text{\AA}$  for the Mn site and 2.12  $\text{\AA}$  for the Fe1 site in schoonerite (Kampf, 1977). In establishing the structural composition, we were guided by results for flurlite,  $[\text{Zn}_3\text{Mn}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7] \cdot 2\text{H}_2\text{O}$ , a Zn-rich mineral with a schoonerite-related structure (Grey *et al.*, 2015a). In flurlite the extra Zn atoms are ordered in the chains of edge-shared octahedra, which correspond to Fe1 and Fe2 in wilhelmgümbelite. With the extra Zn in Fe1 and Fe2 sites, the residual  $\text{Mn}^{2+}$  in the Fe site, and with  $\text{Fe}^{3+}$  allocated to sites Fe, Fe1 and Fe3 to satisfy the calculated bond valences, the structural composition is:  $[\text{Zn}(\text{Mn}_{0.27}^{2+}\text{Fe}_{0.73}^{3+})_{\Sigma 1.0}(\text{Zn}_{0.25}\text{Fe}_{0.15}^{2+}\text{Fe}_{0.60}^{3+})_{\Sigma 1.0}(\text{Zn}_{0.25}\text{Fe}_{0.45}^{2+})_{\Sigma 0.7}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH},\text{H}_2\text{O})_9] \cdot 2\text{H}_2\text{O}$ . The two water molecules per formula unit, outside the brackets, are interlayer water molecules, Ow7 in Table 4 and Fig. 4.

## Discussion

The structure for wilhelmgümbelite differs from that for schoonerite in that the Zn atoms in

TABLE 5. Selected bonds and interatomic distances (Å) in wilhelmgümbelite.

P1–O1	1.565(8)	P2–O5	1.508(11)
P1–O2	1.516(9)	P2–O6	1.525(12)
P1–O3	1.527(8)	P2–O7	1.545(8)
P1–O4	1.534(8)	P2–O7	1.546(8)
Av.	1.536	Av.	1.531
Zn1A–O3	1.934(9)	Zn1B–O3	1.917(9)
Zn1A–O3	1.934(9)	Zn1B–O3	1.917(9)
Zn1A–O5	2.191(10)	Zn1B–Ow5	2.106(13)
Zn1A–O6	2.469(11)	Zn1B–Ow6	1.886(14)
Zn1A–Ow6	1.937(12)	Av.	1.957
Av.	2.093		
Fe–O2	1.991(9)	Fe1–O1	2.058(7)
Fe–O2	1.991(9)	Fe1–O1	2.058(7)
Fe–Ow2	2.133(11)	Fe1–O7	2.124(8)
Fe–Ow3	2.096(12)	Fe1–O7	2.124(8)
Fe–Ow4	2.073(12)	Fe1–Oh	2.011(9)
Fe–Ow5	2.074(12)	Fe1–Oh	2.011(9)
Av.	2.060	Av.	2.064
Fe2–O7	2.235(9)	Fe3–O4	2.010(8)
Fe2–O7	2.235(9)	Fe3–O4	2.010(8)
Fe2–Oh	2.132(9)	Fe3–O5	1.994(11)
Fe2–Oh	2.132(9)	Fe3–O6	1.994(13)
Fe2–Ow1	2.085(10)	Fe3–OH	1.984(9)
Fe2–Ow1	2.085(10)	Fe3–OH	1.984(9)
Av.	2.151	Av.	1.996
Zn1A···Zn1B	0.959(7)	Fe1···Fe2	3.133(4)
Zn1A···P1	3.057(4)	Fe1···P2	3.286(4)
Zn1A···P2	2.910(6)	Fe2···P2	3.316(4)
Zn1B···P1	3.207(5)	Fe3···P1	3.175(4)
Fe···P1	3.263(5)	Fe3···P2	3.321(7)

wilhelmgümbelite are partitioned between two sites, 1 Å apart. The majority Zn1A site (70% occupied) is five coordinated, as in schoonerite. This site, described as a tetrahedron with one split vertex (Kampf, 1977) is unusual in that it shares the split vertex edge (O5–O6) with a PO<sub>4</sub> tetrahedron, with a resulting short Zn–P distance of 2.91 Å (Zn1A–P2 in Table 5). The distances of Zn1A to anions O5 and O6 of the split vertex are much longer (2.11, 2.47 Å) than to the other 3 anions (1.93–1.94 Å), and the O5–Zn1A–O6 angle is very narrow at 63°. The minority Zn1B site (30% occupied) retains the Zn1A coordination to 2× O3 of two PO<sub>4</sub> tetrahedra and the terminal Ow6 anion but the fourth anion of the tetrahedron, Ow5, is corner-shared with the Fe octahedron of an adjacent layer. The Zn1B tetrahedron thus bridges the

heteropolyhedral layers, forming a 3-D framework, whereas the Zn1A site is confined to the layer surface, thus retaining a 2-D layer structure. The local structure corresponding to the two different locations of the Zn atom are compared in Fig. 4.

A feature of the crystal structure analysis is that the refined site occupancy for the Fe2 site, of 0.69(1) matches the occupancy of the Zn1A site, 0.699(4). This suggests that locally, when the Zn occupies the Zn1B tetrahedral site, the Fe2 site is empty. The Fe2 octahedron has the composition FeO<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and in schoonerite it alternates with the Fe1 octahedron of composition FeO<sub>4</sub>(OH)<sub>2</sub>, forming edge-shared chains along [001]. These chains are disrupted locally when Zn occupies the tetrahedral site, so that Fe1 octahedra alternate with empty octahedral sites along [001], as shown in Fig. 5. The Fe2 site has *trans* coordination to 2× Ow1 water molecules. To check if these sites are vacant when the Fe2 site is vacant, the site occupancy of Ow1 was refined, but it did not deviate from full occupancy. Apparently the Ow1 molecules remain, held by hydrogen bonding, when the Fe2 site is vacant.

It is possible that more highly altered crystals of schoonerite have Zn dominantly in the tetrahedral site. In this case the ideal formula would be [ZnFe<sub>3</sub><sup>3+</sup>□(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>]·2H<sub>2</sub>O, where □ indicates a vacant Fe2 site. In the case where the 5-coordinated Zn site is fully occupied in wilhelmgümbelite, the ideal composition is [ZnFe<sup>2+</sup>Fe<sub>3</sub><sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>5</sub>]·2H<sub>2</sub>O, which compares with the ideal composition for schoonerite, [ZnMnFe<sub>2</sub><sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>]·2H<sub>2</sub>O. It is seen that, apart from the replacement of Mn by Fe and the oxidation of Fe, there is an increase in the hydroxyl ion content when schoonerite is altered to wilhelmgümbelite. The extra hydroxyl ions most likely replace coordinated water at the MO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> site. An analogous situation occurs in sigloite, Fe<sup>3+</sup>Al<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>, the oxidized equivalent of paravauxite, Fe<sup>2+</sup>Al<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>, where the Fe<sup>2+</sup>O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> octahedra in paravauxite become Fe<sup>3+</sup>O<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(OH) octahedra in sigloite (Hawthorne, 1988).

### Relationship to other species

Wilhelmgümbelite is related chemically and structurally to schoonerite. It can be considered as an oxidized form of schoonerite, with the Mn<sup>2+</sup> chiefly replaced by Fe<sup>3+</sup>. The structure of wilhelmgümbelite differs from that of schoonerite

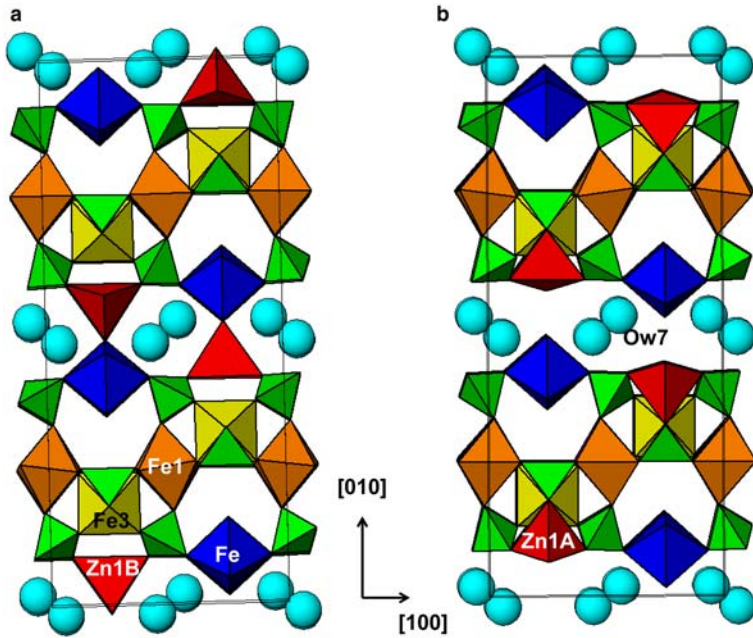


FIG. 4. [001] projection of wilhelmgümbelite structure for (a) Zn in tetrahedral site Zn1B and (b) Zn in 5-coordinated site Zn1A.

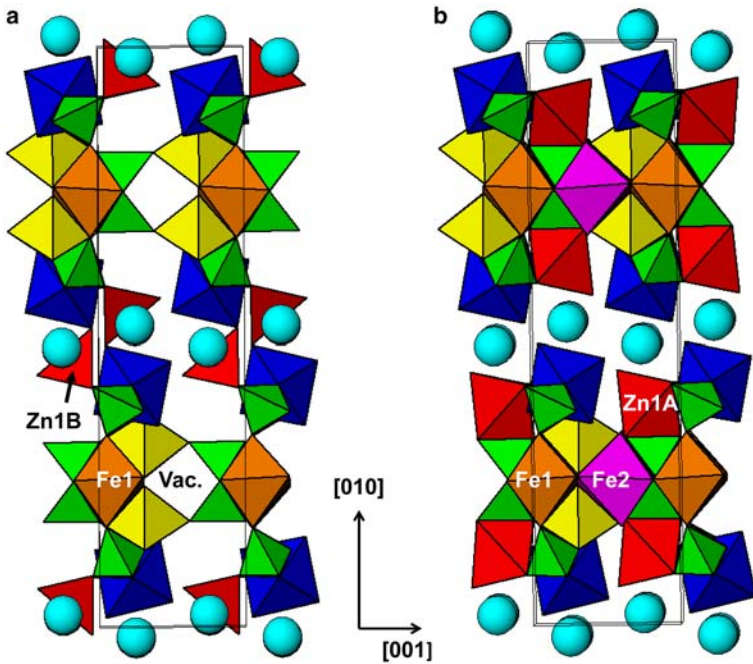


FIG. 5. [100] projection of the local structure of wilhelmgümbelite with (a) Zn in the tetrahedral site Zn1B and (b) Zn in the 5-coordinated site Zn1A.



TABLE 6. Comparative data for schoonerite, wilhelmgümbelite and flurlite.

	schoonerite	wilhelmgümbelite	flurlite
Formula (ideal)	$[\text{ZnMnFe}_2^+\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7] \cdot 2\text{H}_2\text{O}$	$[\text{ZnFe}^{2+}\text{Fe}_3^+(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$	$[\text{Zn}_3\text{MnFe}^{3+}(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7] \cdot 2\text{H}_2\text{O}$
Symmetry	Orthorhombic, <i>Pmab</i>	Orthorhombic, <i>Pmab</i>	Monoclinic, <i>P2<sub>1</sub>/m</i>
Cell	$a = 11.119(4) \text{ \AA}$ , $b = 25.546(11) \text{ \AA}$ $c = 6.437(3) \text{ \AA}$ $V = 1828.4 \text{ \AA}^3$	$a = 10.987(7) \text{ \AA}$ , $b = 25.378(13)$ , $c = 6.387(6) \text{ \AA}$ $V = 1781(2) \text{ \AA}^3$	$a = 6.371(1)$ , $b = 11.020(2)$ , $c = 13.016(3) \text{ \AA}$ , $\beta = 99.34(3)^\circ$ $V = 901.7(3) \text{ \AA}^3$
Z	4	4	2
Strongest powder pattern lines $d$ (Å), $I$ , ( $hkl$ )	12.77, 100, (020) 8.33, 70, (120) 6.43, 40, (001) 3.761, 40, (151) 3.182, 40, (311) 2.768, 90, (400)	12.65, 100, (020) 8.339, 5, (120) 6.421, 14, (001) 6.228, 8, (011) 4.223, 30, (060) 2.111, 7, (0120)	12.900, 100, (001) 8.375, 10, (011) 6.072, 14, (-101) 5.567, 8, (012) 4.297, 21, (003) 2.763, 35, (040)
Optics	Biaxial (-). $\alpha = 1.618(5)$ , $\beta = 1.652(3)$ , $\gamma = 1.682(3)$ $2V(\text{meas}) = 70\text{--}80^\circ$	Biaxial (+). $\alpha = 1.650(2)$ , $\beta = 1.669(2)$ , $\gamma = 1.718(2)$ $2V(\text{calc}) = 65^\circ$	Biaxial (-). $\alpha = 1.60(1)$ , $\beta = 1.65(1)$ , $\gamma = 1.68(1)$ $2V(\text{calc}) = 74^\circ$

in having Zn partitioned between two different sites, one five-coordinated as in schoonerite and the other tetrahedrally coordinated. Wilhelmgümbelite also differs structurally from schoonerite in having partial occupation of one of the Fe sites, which appears to be correlated with the Zn partitioning. There is also a relationship between the chemical and structural properties of wilhelmgümbelite and schoonerite and those of flurlite (Grey *et al.*, 2015a). Flurlite has the same heteropolyhedral layer composition as wilhelmgümbelite and schoonerite but has a different topology of the connections between the polyhedra as discussed by Grey *et al.* (2015a). The distribution of the dominant cations in the Zn, Mn, Fe1, Fe2 and Fe3 sites differs considerably for the three minerals, being  $(\text{Zn}^{2+}\text{Mn}^{2+}\text{Fe}^{2+}\text{Fe}^{2+}\text{Fe}^{3+})$  in schoonerite,  $(\text{Zn}^{2+}\text{Fe}^{3+}\text{Fe}^{3+}\text{Fe}^{2+}\text{Fe}^{3+})$  in wilhelmgümbelite and  $(\text{Zn}^{2+}\text{Mn}^{2+}\text{Zn}^{2+}\text{Zn}^{2+}\text{Fe}^{3+})$  in flurlite. Only the Zn and Fe3 sites remain unchanged chemically between the three minerals. The properties of the three minerals are compared in Table 6.

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