

Secondary Zn-bearing phosphate minerals associated with alteration of phosphophyllite at Hagendorf-Süd, Bavaria

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Abstract: At the Hagendorf-Süd pegmatite, Bavaria, phosphophyllite plays an important paragenetic role in the formation of numerous Zn-bearing secondary phosphate minerals. We report the results of studies conducted on the alteration of phosphophyllite in a heavily corroded triphylite nodule from the 67 m level of the pegmatite mine. The most abundant secondary phosphate minerals associated with phosphophyllite are oxidized schoonerite-group minerals, including the new mineral schmidite, $^{[5]}Zn^{[6]}((Fe_{0.5}^{3+}Mn_{0.5}^{2+})_2ZnFe^{3+})(PO_4)_3(OH)_3(H_2O)_6 \cdot 2H_2O$, whose formation is contemporaneous with phosphophyllite. The phosphophyllite crystals in the nodule are characteristically covered with a composite rind of epitactic Zn-rich jahnsite crystals on the phosphophyllite surface overlain by an orange-yellow amorphous Zn-bearing ferric phosphate and/or green mitridatite. The jahnsite crystals are compositionally zoned into two-phase domains based on their Ca/Zn contents. The low-Zn domains are jahnsite-(CaMnMn) whereas the high-Zn domains correspond to a potentially new species, “jahnsite-(CaMnZn)”. The amorphous phase coating the jahnsite crystals has Zn levels similar to those in jahnsite, and is probably derived from its alteration. Its properties are consistent with it being a Zn-bearing santabarbaraite. Younger idiomorphic crystals of laueite, earlshannonite and zincostrunzite occur on the phosphophyllite rind. The laueite crystals have a surface layer, ~5 µm thick, in which Mn is replaced completely by a 1:1 atomic mixture of Zn + Mg, giving a composition $(Zn_{0.5}Mg_{0.5})Fe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$. The composition of the surface phase is explained by configurational-entropy stabilisation. The earlshannonite crystals commonly grow epitactically on the laueite, yet despite the close association, they are Zn-bearing only, with very low Mg contents. Single-crystal structure refinements have been done on both (Zn + Mg)-bearing laueite and Zn-bearing earlshannonite and all H atoms were located in both cases. Structural models are presented for the epitactic growth of jahnsite on phosphophyllite and earlshannonite on laueite.

Key-words: Hagendorf-Süd pegmatite; secondary phosphate minerals; zinc; phosphophyllite alteration; santabarbaraite; (Zn + Mg)-rich laueite; earlshannonite; jahnsite; epitaxy; crystal structure; configurational-entropy stabilisation.

1. Introduction

The Hagendorf-Süd granitic pegmatite in Bavaria is renowned industrially for having been a major supplier of high-grade feldspar for the European ceramics industry during its mining life, from 1894 to 1984. In the 1950s, it also supplied more than 1,000 tons of triphylite for Li production (Keck, 1983). In addition, it is renowned scientifically for the diversity of minerals that became accessible to collectors during mining, with shafts going down to 115 m, and intersecting rich phosphate pods below 50 m. It ranks 15th in the list of most prolific type localities in the world (Mindat.org) and is the most highly ranked type locality for the number of secondary phosphate minerals that have been discovered (22 of the 23 type specimens). Only the Palermo #1 and Tip Top

mines in the USA come close in having phosphates as the majority of their type minerals, 13 and 12, respectively.

A significant factor contributing to the diversity of new secondary phosphate minerals in the Hagendorf pegmatite body is the high activity in solution of Zn from the breakdown of sphalerite, and its low-temperature (epithermal and supergene) reaction with primary and metasomatically altered phosphates. The first Zn-phosphate mineral to be named from Hagendorf was phosphophyllite, $Zn_2(Fe,Mn)(PO_4)_3 \cdot 4H_2O$ (Laubmann & Steinmetz, 1920). It was found at the Hagendorf-North pegmatite, which is 0.5 km from Hagendorf-Süd (Dill *et al.*, 2013). At Hagendorf-Süd, half (11 out of 22) of the type phosphate minerals contain essential Zn. They are the dimorphs scholzite (Strunz, 1950) and parascholzite, $CaZn_2(PO_4)_2 \cdot 2H_2O$ (Sturman *et al.*, 1981), jungite, $Ca_2Zn_4Fe_8$

$(\text{PO}_4)_9(\text{OH})_9 \cdot 16\text{H}_2\text{O}$ (Moore & Ito, 1980), flurlite, $^{[5]}\text{Zn}^{[6]}(\text{Mn}^{2+}\text{Zn}_2\text{Fe}^{3+})(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$ (Grey *et al.*, 2015), zincoberaunite, $\text{ZnFe}_5^{3+}(\text{PO}_4)_4(\text{OH})_5(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ (Chukanov *et al.*, 2017), zincostrunzite, $\text{ZnFe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6.5\text{H}_2\text{O}$ (Kampf *et al.*, 2017a), steinmetzite, $\text{Zn}_2\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH}) \cdot 3\text{H}_2\text{O}$ (Grey *et al.*, 2017a), three oxidized schoonerite-group minerals, wilhelmgümbelite, $^{[5]}\text{Zn}^{[6]}\text{Fe}_2^{3+}\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})_5 \cdot 2\text{H}_2\text{O}$ (Grey *et al.*, 2017b), schmidite, $^{[5]}\text{Zn}^{[6]}((\text{Fe}_{0.5}^{3+}\text{Mn}_{0.5}^{2+})_2\text{ZnFe}^{3+})(\text{PO}_4)_3(\text{OH})_3(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$ (Grey *et al.*, 2017c) and wildenauerite, $^{[5]}\text{Zn}^{[6]}((\text{Fe}_{0.5}^{3+}\text{Mn}_{0.5}^{2+})_2\text{Mn}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3(\text{OH})_3(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$ (Grey *et al.*, 2017d), and manganflurlite, $^{[5]}\text{Zn}^{[6]}(\text{Mn}_3^{2+}\text{Fe}^{3+})(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_7 \cdot 2\text{H}_2\text{O}$ (Kampf *et al.*, 2017b). In addition, two other type minerals at Hagendorf-Süd have been described as being Zn-bearing. These are keckite, $(\text{Ca}, \text{Mg})(\text{Mn}, \text{Zn})_2\text{Fe}_3^{3+}(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ (Mücke, 1979), and wilhelmvierlingite, $(\text{Ca}, \text{Zn})\text{MnFe}^{3+}[\text{OH}(\text{PO}_4)_2]2\text{H}_2\text{O}$ (Mücke, 1983).

In ongoing studies of secondary phosphate minerals from Hagendorf-Süd, we have encountered a number of unusual occurrences of Zn-bearing minerals in an altered triphylite nodule, in which the triphylite has been altered predominantly to phosphophyllite. The new occurrences, which include a Zn-rich jahnsite, Zn-bearing santabarbarite and earlshannonite, and a (Zn + Mg)-substituted laueite, have all formed on the surface of altered phosphophyllite, and their crystals display epitactic relationships with the phosphophyllite and/or with one another. We report here the results of studies of these minerals using electron microprobe analyses, powder and single-crystal structure refinements, optical measurements and Mössbauer spectroscopy.

2. Experimental procedure

Electron microprobe (EMP) analyses were done using wavelength-dispersive spectrometry on a JEOL JXA 8500F Hyperprobe operated at an accelerating voltage of 15 kV and a beam current of 4 nA. The beam was defocused to 5 μm for the analyses.

Powder X-ray diffraction (PXRD) data on ground samples were collected at room temperature in the two-theta range 5–80° using a Philips diffractometer and $\text{Co K}\alpha$ radiation. Refinement of the PXRD data was done using the Rietveld program Fullprof (Rodriguez-Carvajal, 1990).

Single-crystal data collections were made at 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 Å. A ϕ scan was used with a framewidth of 1° and a count time per frame of 1 s. The crystals were kept 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, 2012). Crystal-structure refinements were done using JANA2006 (Petříček *et al.*, 2014).

The Mössbauer spectrum for Zn-rich jahnsite was collected using a conventional constant acceleration drive with a symmetrical sawtooth waveform (Wissel). The source of ^{57}Co in rhodium was maintained at room temperature. The spectrum was fitted using four Voigtian doublets (three for Fe^{3+} , one for Fe^{2+}) with a Lorentzian half-width at half-maximum component of 0.16(4) mm/s and a variable Gaussian component to deal with line broadening. The isomer shifts are given relative to $\alpha\text{-Fe}$ at room temperature.

3. The 67-metre triphylite nodule

The triphylite nodule containing the minerals to be described here was found by one of us (E.K.) at the 67-metre level of the open-cut mine at Hagendorf-Süd in 1977 and a preliminary description of it was given by Keck (2000). The location of the nodule in the open pit is shown in Fig. 1. The nodule, measuring $50 \times 50 \times 120 \text{ cm}^3$, was heavily corroded and only a $\sim 20 \text{ cm}$ -thick shell remained, surrounding a central cavity measuring $30 \times 40 \times 50 \text{ cm}^3$. On one side of the cavity, residual primary phosphates, triphylite and fluorapatite, were present with vivianite and mitridatite, whereas on the opposite side, the triphylite had been converted to predominantly (98%) phosphophyllite, together with aggregates of oxidized schoonerite-group minerals (1%). A wide variety of sparsely distributed secondary phases, including stewartite, laueite, whitmoreite, scholzite, parascholzite, strunzite, hopeite, parahopeite, mitridatite, chalcophanite and jahnsite make up the remaining 1%.

The phosphophyllite crystals vary in size up to a maximum of 5–6 cm, but more typically form interlocking aggregates of mm-sized crystals. They rarely have the colourless to blue-green, transparent appearance of fresh phosphophyllite; more typically, the crystals are translucent to opaque with a milky-white to off-white colour. Mücke (1981) has previously noted that at Hagendorf-Süd, phosphophyllite frequently “has a muddied and opaque appearance, and it is white, yellow or brownish-yellow”. The crystals are generally corroded by leaching, often to the extent of leaving only a shell of a yellow rind as shown in Fig. 2. Despite their altered appearance, PXRD patterns on crushed crystals give sharp diffraction peaks corresponding to phosphophyllite, suggesting that their milky-white colour is due to recrystallization as microcrystals.

4. Zn-bearing secondary phosphate minerals associated with phosphophyllite

The most common secondary phosphate minerals associated with phosphophyllite in the 67-m nodule are oxidized schoonerite-group minerals, including the new mineral schmidite, as discussed by Grey *et al.* (2017c). The next most commonly encountered minerals on the surface of altered phosphophyllite are (Zn + Mg)-bearing laueite, Zn-bearing whitmoreite and Zn-rich jahnsite. Figure 3 shows a typical occurrence of yellow laueite laths and



Fig. 1. Open pit at Hagendorf-Süd in 1976. The excavator is at the 60 m level. The cross marks the location of the 67-m nodule, unearthed 7 m below, when freshly blasted material was removed. (Online version in color)



Fig. 2. Leached phosphophyllite crystals from the 67-m nodule. Extensive leaching has left shells of yellow rind. Residual white phosphophyllite in twinned crystal. The surrounding red mineral is the schoonerite-group mineral schmidite. Field of view (FOV) ~10 mm. Photo V. Betz. (Online version in color)



Fig. 3. Amber-yellow laueite laths and orange-brown earlshannonite mounds on a beige-coloured rind (mitridatite plus amorphous ferric phosphate) covering phosphophyllite. FOV 1 mm. Photo M. Reinhardt. (Online version in color)

orange-brown whitmoreite mounds sitting on a greenish-yellow surface crust on phosphophyllite. Zn-rich jahnsite forms epitactic growths on the surface of phosphophyllite, as shown in Fig. 4, although the crystals are often hidden under coatings of mitridatite and an amorphous Zn-bearing ferric phosphate mineral. The jahnsite crystals in Fig. 4 show two different orientations, due to epitactic relations with the phosphophyllite substrate, as will be discussed below.

A noteworthy feature of phosphophyllite crystals in the 67-m nodule is the presence of a rind, on the order of 0.1–0.5 mm thick, and usually of an orange-yellow colour, but sometimes green due to finely precipitated mitridatite. A

thin air-gap was often present between the rind and the crystal, due to leaching of phosphophyllite at the interface. This allowed the rinds to be readily detached for further study. Microscopic examination showed the rind to have a composite structure. The upper surface has an earthy appearance, as shown in Fig. 3, with no crystallinity evident, even at high magnification in a scanning electron microscope (SEM). The under-surface, which had been in contact with the phosphophyllite, comprises two almost orthogonal orientations of rectangular laths of jahnsite, shown in Fig. 5.

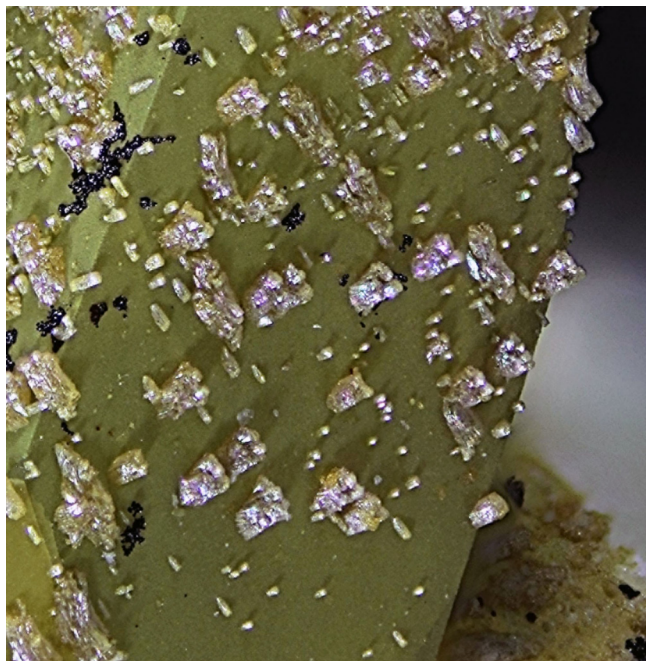


Fig. 4. Two different orientations of Zn-bearing jahnsite crystals on the surface of phosphophyllite. The green colour is a film of mitridatite on the surface. FOV 2 mm. Photo V. Betz. (Online version in color)

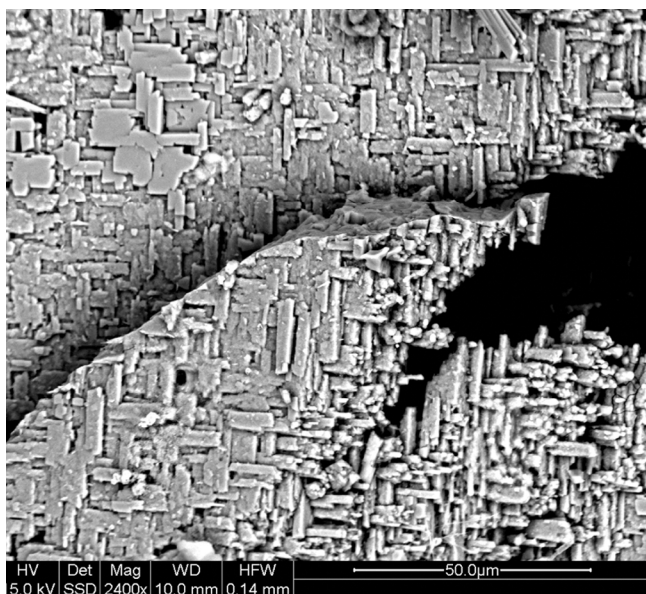


Fig. 5. Back-scattered electron (BSE) image of epitaxial jahnsite crystals on the underside of yellow rind on altered phosphophyllite.

4.1. Zn-bearing “santabarbaraite”

The upper-surface orange-yellow phase in the rinds on phosphophyllite is X-ray amorphous and optically isotropic, with a measured index of refraction of 1.645 (5). The EMP analyses given in Table 1 (Amorph. 1) are identical, within the standard deviations, to analyses obtained on an amorphous ferric-phosphate phase found in association with the new mineral steinmetzite, $\text{Zn}_2\text{Fe}^{3+}$

$(\text{PO}_4)_2(\text{OH}) \cdot 3\text{H}_2\text{O}$, in pseudomorphed phosphophyllite at Hagendorf-Süd (Grey *et al.*, 2017a). Table 1 also reports analyses for the amorphous ferric-phosphate mineral santabarbaraite, $\text{Fe}_3^{3+}(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, from Wannon Falls, Australia (Pratesi *et al.*, 2003). The wt% of the main components of santabarbaraite, Fe_2O_3 and P_2O_5 , closely match those for the amorphous phase in the phosphophyllite rind. Scaling the metal atoms in the latter to 3M as in santabarbaraite, with OH adjusted to give charge balance, gives the empirical formula: $(\text{Ca}_{0.24}\text{Zn}_{0.34}\text{Mn}_{0.08}\text{Mg}_{0.03}\text{Fe}_{2.31}^{3+})_{\Sigma 3}(\text{PO}_4)_{1.85}(\text{OH})_{2.76}(\text{H}_2\text{O})_{2.14}$.

This formula is close to the empirical formula reported for the Wannon Falls santabarbaraite, allowing for minor substitution of Zn for Fe. It has a small phosphate deficiency relative to santabarbaraite, common in altered phosphate minerals, where H_4O_4 substitutes for PO_4 (Wambeke, 1971). Using the EMP analyses and the measured index of refraction in the Gladstone-Dale relation (Mandarino, 1981) gives an estimated density of 2.45 g/cm^3 , close to the measured density of santabarbaraite of 2.42 g/cm^3 . In addition, the positions of broad humps in the PXRD pattern match those in santabarbaraite. Although it is not possible to be certain regarding the identification of amorphous minerals, all the results obtained support the amorphous component of the rind on altered phosphophyllite being a Zn-bearing santabarbaraite.

4.2. Zn-bearing jahnsite

A SEM back-scattered-electron (BSE) image of two almost-orthogonal orientations of Zn-bearing jahnsite crystals located on the underside of a yellow rind covering altered phosphophyllite is shown in Fig. 5. The sectioned and polished crystals show a mottled texture in SEM BSE images, due to fine-scale compositional zoning. Separate analyses of the two compositional domains are given in Table 2, showing that the BSE contrast variation between the two domains is due primarily to Zn/Ca variations. Within the zones, however, the dominant element substitution is Fe replacing Mn plus Zn (linear trendline slope = -1 , $R^2 = 0.67$). This substitution accounts for the high standard deviations for these three elements in Table 2. Formulae for the two domains are given below, scaled to 4 P *apfu*, with site assignments according to the Moore & Ito (1978) procedure for jahnsite, in which cations with decreasing size successively occupy sites X, M1, M2 and M3 in the structural formula $\text{XM1}(\text{M2})_2(\text{M3})_2(\text{PO}_4)_4(\text{OH})_2(\text{H}_2\text{O})_8$:

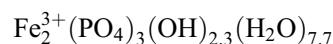
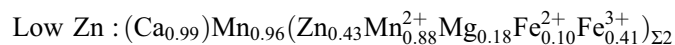
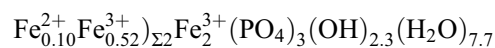
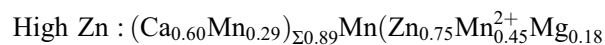


Table 1. Electron microprobe analyses (wt%) of amorphous ferric-phosphate rind on phosphophyllite.

Constituent	Amorph. 1 [*] Av. of 8		Amorph. 2 [*] Av. of 5		Santabarbaraite Wannon Falls [*]		Standard
	Mean	SD	Mean	SD	Mean	SD	
ZnO	6.5	0.4	6.7	1.7	n.d.		Phosphophyllite
MnO	1.3	0.3	0.4	0.4	n.d.		Rhodonite
MgO	0.29	0.06	n.d.		0.69	0.06	Spinel
CaO	3.1	0.2	3.2	0.5	2.9	0.1	Wollastonite
Fe ₂ O ₃	43.3	0.4	43.8	2.6	43.2	0.3	Hematite
P ₂ O ₅	30.7	0.5	29.6	1.6	28.6	0.2	Berlinite
H ₂ O ^{**}	14.8		16.3		23.0	0.2	
Total	100.0		100.0		98.4		

^{*} Amorph. 1. Orange-yellow rind on phosphophyllite (this work); Amorph. 2. Amorphous ferric-phosphate associated with steinmetzite (Grey *et al.*, 2017a); Santabarbaraite from Wannon Falls, Australia (Pratesi *et al.*, 2003).

^{**} H₂O in Amorph. to give total = 100%.

Table 2. EMP analyses, optical measurements and Mössbauer spectroscopy results for Zn-bearing jahnsite.

EMP analyses	High Zn/low Ca (6 zones)		Low Zn/high Ca (6 zones)		
	Mean wt%	SD	Mean wt%	SD	
ZnO	6.8	1.1	3.9	1.0	
CaO	3.7	0.2	6.2	0.2	
MnO	13.7	1.7	14.6	1.5	
MgO	0.8	0.2	0.8	0.1	
Fe ₂ O ₃ (total)	23.3	3.1	22.3	3.2	
FeO [*]	0.6		0.6		
Fe ₂ O ₃ [*]	22.4		21.4		
P ₂ O ₅	31.7	0.3	31.7	0.5	
H ₂ O ^{**}	18.2		18.3		
Total	97.9		97.5		
Optical parameters					
Zn-bearing jahnsite		Jahnsite-(CaMnMn) (Grice <i>et al.</i> , 1990)			
Biaxial(−). α = 1.675(2), β = 1.686(2), γ = 1.691(2), 2V (calc.) = 68°		Biaxial(−). α = 1.643(1), β = 1.659(1), γ = 1.671(1), 2V (meas.) = 80(2)°			
Dispersion: could not be observed		Dispersion not observed			
Orientation: Z = b		Z = b			
Pleochroism: imperceptible		Slight pleochroism, yellow-green to brown-green			
Mössbauer parameters ^{***}					
δ, mm/s	Δ, mm/s	σ(Δ), mm/s	A (%)	Atoms	Assignments
0.37(1)	0.37(9)	0.0	28	0.7	Fe ³⁺ in M3A
0.38(1)	0.60(6)	0.0	41	1.0	Fe ³⁺ in M3B
0.37(1)	0.95(6)	0.13	27	0.7	Fe ³⁺ in M2A, M2B
0.95(11)	2.50(22)	0.28	4	0.1	Fe ²⁺ in M2A, M2B

^{*} FeO/Fe₂O₃ from Mössbauer.

^{**} H₂O from structure.

^{***} δ = isomer shift, Δ = quadrupole splitting, $\sigma(\Delta)$ = Gaussian component, A = doublet area.

The low-Zn compositional domains correspond to jahnsite-(CaMnMn), first reported by Grice *et al.* (1990). The high-Zn domains correspond to a potentially new species, “jahnsite-(CaMnZn)” for which IMA approval is required. The compositional change from the low-Zn to the high-Zn domains involves a coupled substitution of Mn for Ca at the *X* site and Zn for Mn at the *M2* site.

An alternative interpretation of the analyses in Table 2, involving Zn substituting for Ca at the *X* site would seem improbable given the large size difference, although Mücke (1983) has reported a similar inverse correlation between Ca and Zn in the jahnsite-related mineral wilhelmvierlingite, $(\text{Ca,Zn})\text{MnFe}^{3+}(\text{OH})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ from Hagendorf. Such a substitution would require a local displacement of Zn to adopt a lower coordination. This occurs, for example, in Zn-bearing kintoreite, in which Zn atoms displace from the centre of hexagonal rings in hexagonal-tungsten-bronze (HTB) type layers of octahedral to adopt 5-coordination (Grey *et al.*, 2009), whereas in pyrochlore, Ca atoms sit at the centres of the HTB rings.

Both compositional domains contain high levels of Fe^{3+} at the *M2* site. This differs from other jahnsite minerals, which contain Fe^{2+} at the *M2* sites, but is consistent with the assignment of Fe^{3+} to *M2* sites in the jahnsite-related mineral keckite, $\text{CaMn}(\text{Fe}^{3+}, \text{Mn})_2\text{Fe}_2^{3+}(\text{PO}_4)_4(\text{OH})_3(\text{H}_2\text{O})_7$ (Hochleitner & Fehr, 2010). Fitting of the Mössbauer spectrum for the jahnsite-rich rind on phosphophyllite gave fitting parameters and site assignments that agree closely with those for keckite by Hochleitner & Fehr (2010). The Mössbauer results are given in Table 2. We note that the linewidths are larger than those of other related samples that we have measured because of the close geometry required by the small (5 mg) sample, giving some $\cos\theta$ broadening. The Fe^{3+} assigned to the *M2* sites from the Mössbauer spectrum is higher than in the above formulae, and this is most likely due to the presence of minor admixed amorphous ferric phosphate in the ground rinds used for the Mössbauer measurement. The high Fe^{3+} content in the Zn-bearing jahnsite is reflected in the indices of refraction (Table 2), which are considerably higher than those reported for jahnsite-(CaMnMn) by Grice *et al.* (1990), also given in Table 2.

The PXRD pattern for an accumulation of ground jahnsite-bearing rinds is shown in Fig. 6. An interesting aspect, which was reproducible in a number of PXRD patterns of different rinds and surface aggregates, is incipient splitting of the (00*l*) reflections, shown in the insert in Fig. 6. The heights of the split components are the same, suggesting that the splitting is due to different *c* axis lengths for the high-Zn and low-Zn compositions, since there are approximately equal volumes of the two compositions. Two-phase Rietveld refinement of the PXRD data with *a*, *b* and β constrained to be equal gave the following refined unit-cell parameters:

$$a \ 15.054(1), b \ 7.1889(6), c \ 9.952(2) \text{ \AA}, \beta \ 111.27(1)^\circ$$

$$a \ 15.054(1), b \ 7.1889(6), c \ 10.029(2) \text{ \AA}, \beta \ 111.27(1)^\circ.$$

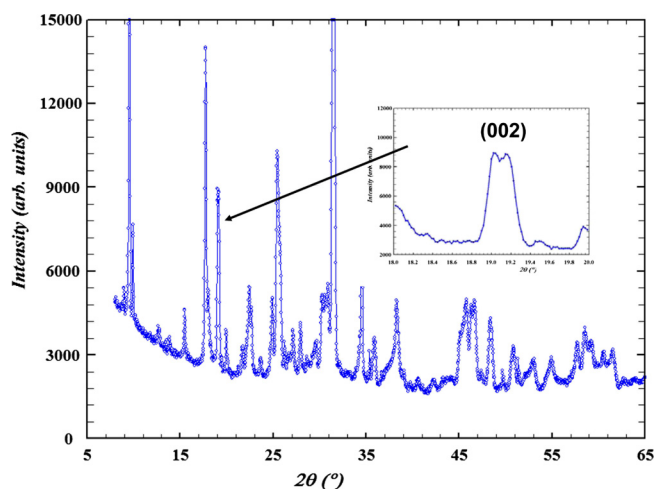


Fig. 6. PXRD pattern of yellow rinds on phosphophyllite (jahnsite plus amorphous phase). Inset shows splitting of the (002) reflection of jahnsite. (Online version in color)

The consistency between the analytical data, the refractive indices and the unit-cell parameters for Zn-bearing jahnsite can be checked using the Gladstone-Dale compatibility index (Mandarino, 1981). Combining the mean analytical results and cell dimensions, averaged for the high-Zn and low-Zn phases, with the indices of refraction in Table 2 gives a Gladstone-Dale index of 0.027 (excellent).

The observed epitaxy of jahnsite crystals on phosphophyllite can be understood in terms of the close match of their structural metrics. Phosphophyllite has monoclinic symmetry, $P2_1/c$, with $a = 10.378(3)$, $b = 5.084(2)$, $c = 10.553(3) \text{ \AA}$, $\beta = 121.14(2)^\circ$ (Hill, 1977). The structure comprises (100) layers of corner-shared ZnO_4 and PO_4 tetrahedra that are interconnected via corner-sharing along [100] of the PO_4 tetrahedra with Fe-centred octahedra. Redefining the axes in the (100) planes by the vectors [2 1 0] and [2 -1 0] gives an almost orthogonal face-centred array with axial lengths of 14.65 Å (angle between the axes = 92.2°), shown in Fig. 7a. For comparison *a* and 2*b* in Zn-bearing jahnsite are 15.05 and 14.38 Å (Fig. 7b), with a mismatch relative to the phosphophyllite dimensions of 2.6% and 1.8%, respectively. The relatively close match of the intralayer lattice metrics between the two structures provides the basis for epitactic growth of jahnsite on phosphophyllite. A comparison of Figs. 7a and 7b shows that there is a close correspondence of the positions and orientations of the PO_4 tetrahedra in the two structures, enabling one mineral to form an epitactic overgrowth on the other by connectivity of the PO_4 tetrahedra to the interlayer octahedra. The two equal repeat distances in the (100) phosphophyllite layers, $b' = c' = 14.65 \text{ \AA}$ means that $a \parallel b'$ and $a \parallel c'$ are equally probable, giving rise to the two orientations of jahnsite shown in Figs. 4 and 5.

4.3. Zn + Mg substitution in laueite

Amber-coloured laueite laths on the surface rind of phosphophyllite crystals (Fig. 3) were initially subjected to

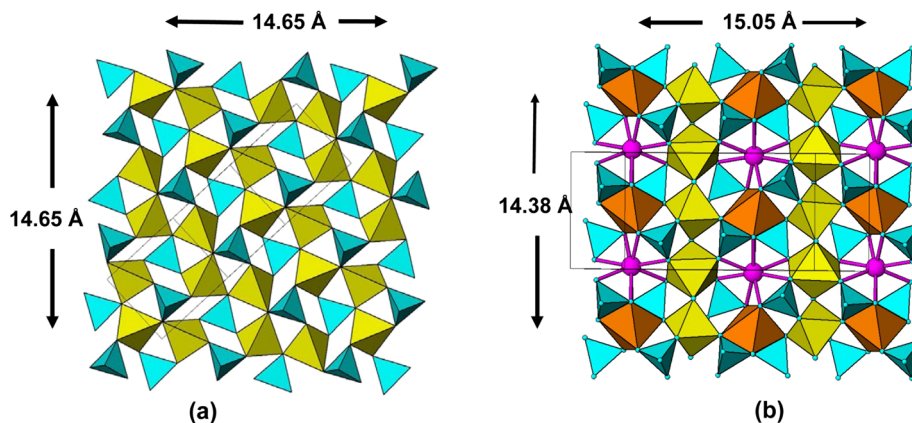
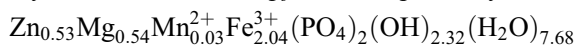


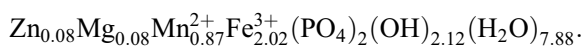
Fig. 7. Structural basis for epitaxy of jahnsite on phosphophyllite: (a) (1 0 0) layer of phosphophyllite; (b) (0 0 1) layer of jahnsite. Intralayer cell structure-metrics are shown. In jahnsite, the pink circles are X , brown octahedra are $M1$, yellow octahedra are $M3$. (Online version in color)

energy-dispersive spectral (EDS) analysis in a SEM. A surprising result from analysing the flat surfaces of the crystals was that they consistently gave a 1:1 Zn:Mg atomic ratio, and with the MnO content an order-of-magnitude smaller than ZnO and MgO. However, when the crystals were sectioned and polished for EMP analyses, it was found that the high Zn and Mg analyses were confined to a thin surface layer $\sim 5 \mu\text{m}$ thick and that the bulk of the crystals conformed to a laueite composition.

The EMP analyses were made along line scans, starting within $1 \mu\text{m}$ of the surface and analysing every μm into the crystal until the ZnO and MgO contents decreased to low, constant values. Resulting plots of Zn vs. Mg atoms per formula unit (apfu) and Zn + Mg vs. Mn apfu are shown in Fig. 8. The results are striking in showing an almost exact 1:1 atomic ratio of [Zn] to [Mg] is maintained and there is a progressive replacement of [Zn + Mg] by [Mn], moving into the crystal. The latter can be interpreted in terms of the laueite crystals having an overgrowth of a $\sim 5 \mu\text{m}$ thick surface layer with (Zn + Mg) in place of Mn, and due to the electron-beam spread, the analyses are a composite of the surface and bulk compositions. Full EMP analyses are given in Table 3. The mean sum of oxides is 79%, whereas based on the structural formula for laueite, the sum of oxides should only be 70%, with 30% H_2O . The high total is due to dehydration under vacuum as discussed for the laueite-group minerals ushkovite (Galliski & Hawthorne, 2002) and kummerite (Grey *et al.*, 2016). Using the structure-based water contents, the empirical formulae for the surface phase and for the interior of the crystal, scaled to 2 P apfu, are respectively:



and



The ideal surface-phase composition is $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, whereas the interior of the crystals is a (Zn + Mg)-bearing laueite. Charge

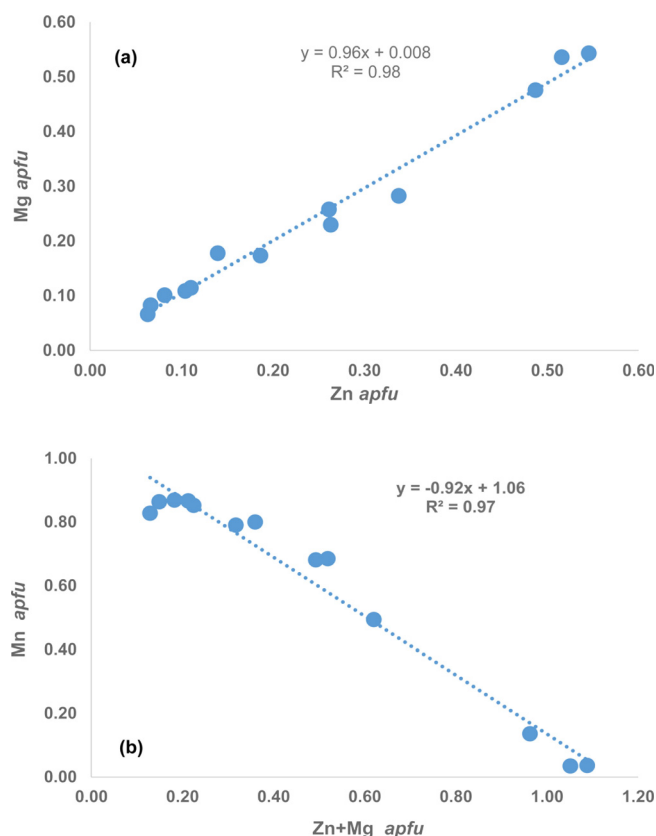


Fig. 8. Scatter plots for (a) Mg apfu vs. Zn apfu and (b) Zn + Mg apfu vs. Mn apfu from EMP analyses of (Zn + Mg)-bearing laueite crystals. (Online version in color)

balance in the above formulae is consistent with all Mn being 2+; however, single-crystal structure analysis shows that a small amount of Mn is in the trivalent state, as discussed below.

A PXRD pattern of ground crystals showed that, in addition to strong peaks due to the bulk laueite phase, a number of weak peaks corresponding to the surface phase were present, with a significantly smaller b axis, where b

Table 3. EMP analyses (wt%) for (Zn + Mg)-substituted laueite and Zn-bearing earlshannonite.

ZnO	MnO	MgO	Fe ₂ O ₃	P ₂ O ₅	Total
(Zn + Mg)-substituted laueite					
9.16	0.54	4.71	36.50	30.96	81.87
9.99	0.58	4.93	35.83	31.94	83.27
8.44	2.05	4.08	35.41	30.20	80.19
5.85	7.45	2.42	33.33	30.20	79.25
4.38	9.88	1.89	34.84	29.01	80.00
4.65	10.63	2.27	33.08	31.05	81.69
2.31	11.41	1.46	31.61	28.90	75.69
3.17	11.87	1.46	33.10	29.68	79.27
1.04	11.94	0.54	34.26	28.87	76.66
1.82	12.23	0.93	31.97	28.71	75.66
1.11	12.55	0.68	33.48	29.08	76.90
1.77	12.81	0.91	35.18	29.58	80.26
1.39	12.94	0.85	33.87	29.79	78.84
Zn-bearing earlshannonite					
3.05	5.59	0.33	39.19	28.99	77.14
2.28	5.14	0.25	42.50	29.26	79.43
2.05	5.78	0.08	40.20	30.39	78.51

Table 4. Refined unit-cell parameters for (Zn + Mg)-substituted laueite and Zn-bearing earlshannonite.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
Surface-phase, PXRD	5.339(4)	10.568(4)	7.247(8)	107.95(8)	112.00(7)	71.74(3)
Zn + Mg laueite, PXRD	5.342(1)	10.687(2)	7.221(2)	107.85(1)	111.49(1)	71.86(1)
Zn + Mg laueite, single crystal, 293 K	5.346(1)	10.685(1)	7.2299(1)	107.84(1)	111.44(1)	71.82(1)
Zn + Mg laueite Single crystal, 100 K	5.316(1)	10.610(3)	7.118(1)	107.33(3)	111.33(3)	72.22(2)
Epitactic earlshannonite on laueite						
Laueite, PXRD	5.371(2)	10.663(2)	7.256(2)	107.44(3)	111.85(3)	71.39(2)
Earlshannonite, PXRD	9.913(2)	9.697(2)	5.450(1)	90	93.94(1)	90
Earlshannonite Single crystal, 100 K	9.984(2)	9.595(2)	5.437(1)	90	92.85(3)	90

corresponds to the interlayer separation. Unit-cell parameters for both phases obtained from Rietveld refinement (Rodriguez-Carvajal, 1990) of the PXRD pattern are reported in Table 4. Also given in Table 4 are the unit-cell parameters obtained by refinement of diffraction data obtained on a single crystal at ambient temperature and at 100 K. The ambient-temperature unit-cell parameters agree closely with those obtained from PXRD refinement of the peaks due to the bulk (non-surface) laueite.

The only published structure refinements for laueite were done in the 1960s using photographic film methods (Moore, 1965; Plieth *et al.*, 1965). The standard deviations in the atom coordinates are high (or in the case of Plieth *et al.*, not reported) and the H atoms were not located. To remedy this, we refined synchrotron single-crystal data on a (Zn + Mg)-bearing laueite crystal of high diffracting quality ($R_{\text{int}} = 0.018$) and located all H atoms in difference-Fourier maps. The H atoms were refined using soft restraints, $\text{O}-\text{H} = 0.85(2)$ Å and $\text{H}-\text{O}-\text{H} = 109.47(2)^\circ$, and with a common isotropic-displacement parameter, which refined to $0.036(2)$. Fe was ordered at the trivalent cation sites *M2* and *M3*, and the occupancy of the *M1* site

was fixed at values obtained from the EMP analyses. The data-collection and refinement details are given in Table 5. Refined coordinates, equivalent isotropic-displacement parameters and calculated bond valence sums (BVS) (Gagné & Hawthorne, 2015) are reported in Table 6, selected bond-distances in Table 7 and hydrogen bonds in Table 8. The hydrogen bonds are the same as those reported for ushkovite by Galliski & Hawthorne (2002), for paravauxite by Gatta *et al.* (2014) and for kummerite, $\text{Mn}^{2+}\text{Fe}^{3+}\text{Al}(\text{PO}_4)_2(\text{OH})_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$ by Grey *et al.* (2016). A full discussion of the hydrogen-bond network is given by Gatta *et al.* (2014).

The mean *M1*–O distance is only 2.11 Å, much shorter than the value of 2.20 Å for octahedrally coordinated Mn^{2+} –O calculated from the bond-valence parameters (Gagné & Hawthorne, 2015). Using the EMP-determined site-occupancy for *M1* of $\text{Zn}_{0.08}\text{Mg}_{0.08}\text{Mn}_{0.84}$, the BVS at *M1* was used to estimate the valency of the Mn, giving $0.60 \text{ Mn}^{2+} + 0.24 \text{ Mn}^{3+}$. The presence of some Mn^{3+} in laueite is not surprising, given the strong oxidizing conditions that prevailed, as evidenced by the ubiquitous presence of Mn^{3+} -containing mitridatite–robertsite

Table 5. Data collection and refinement conditions for (Zn + Mg)-bearing laueite and Zn-bearing earlshannonite.

	(Zn + Mg)-bearing laueite	Zn-bearing earlshannonite
Formula	$(\text{Zn}_{0.08}\text{Mg}_{0.08}\text{Mn}_{0.60}^{2+}\text{Mn}_{0.24}^{3+})_{\Sigma 1}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_{2.24}(\text{H}_2\text{O})_{7.86}$ MW = 533.6	$(\text{Fe}_{0.22}^{2+}\text{Mn}_{0.37}^{2+}\text{Zn}_{0.15}\text{Mg}_{0.03}\text{Fe}_{0.23}^{3+})_{\Sigma 1}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_{2.23}(\text{H}_2\text{O})_{3.77}$ MW = 463.7
Temperature	100 K	100 K
Wavelength	0.7107	0.7107
Crystal system/space group	Triclinic $P-1$	Monoclinic $P2_1/c$
Unit-cell dimensions	$a = 5.316(1) \text{ \AA}$, $b = 10.610(3) \text{ \AA}$, $c = 7.118(1) \text{ \AA}$ $\alpha = 107.33(3)^\circ$, $\beta = 111.33(3)^\circ$, $\gamma = 72.22(2)^\circ$ $V = 348.1(1) \text{ \AA}^3$, $Z = 1$	$a = 9.984(2) \text{ \AA}$, $b = 9.595(2) \text{ \AA}$, $c = 5.437(1) \text{ \AA}$ $\alpha = 90$, $\beta = 92.85(3)^\circ$, $\gamma = 90$ $V = 520.2(2) \text{ \AA}^3$, $Z = 2$
Density (calc.)	$2.54 \text{ g}\cdot\text{cm}^{-3}$	$2.96 \text{ g}\cdot\text{cm}^{-3}$
Absorption coefficient	3.28 mm^{-1}	4.55 mm^{-1}
Crystal size	$0.003 \times 0.003 \times 0.2 \text{ mm}^3$	$0.006 \times 0.009 \times 0.8 \text{ mm}^3$
Data collection resolution	0.70	0.70
Reflections collected	6107	9578
Unique reflections, R_{int}	1661, 0.018	1240, 0.042
Observed reflections, $I > 3\sigma(I)$	1602	1172
Parameters/restraints/constraints	138/13/20	106/7/22
R indices, observed reflections	$R_{\text{obs}} = 0.026$, $wR_{\text{obs}} = 0.039$	$R_{\text{obs}} = 0.042$, $wR_{\text{obs}} = 0.053$
R indices, all data	$R_{\text{obs}} = 0.026$, $wR_{\text{obs}} = 0.039$	$R_{\text{obs}} = 0.044$, $wR_{\text{obs}} = 0.053$
Largest difference peak and hole	+0.59 and $-0.42 \text{ e}\cdot\text{\AA}^{-3}$	+1.03 and $-0.97 \text{ e}\cdot\text{\AA}^{-3}$

Table 6. Refined coordinates and equivalent isotropic-displacement parameters ($\text{\AA}^2$), plus bond-valence sums (BVS) for (Zn + Mg)-bearing laueite.

	SOF	x	y	z	U_{iso}	BVS (ν)
Mn1	0.84	0	0	0	0.01222(14)	2.46
Mg1	0.08	0	0	0	0.01222(14)	1.93
Zn1	0.08	0	0	0	0.01222(14)	1.97
Fe2	1	0	0.5	0	0.00913(13)	3.14
Fe3	1	0	0.5	0.5	0.00958(13)	3.16
P1	1	0.34518(6)	0.67127(3)	0.92693(4)	0.00934(14)	5.01
O1	1	0.16762(19)	0.65544(10)	0.04137(13)	0.0113(3)	1.80
O2	1	0.30482(19)	0.57562(10)	0.71424(13)	0.0116(3)	1.83
O3	1	0.2687(2)	0.81893(10)	0.90391(14)	0.0126(3)	1.64
O4	1	0.34565(19)	0.36442(10)	0.95000(13)	0.0120(3)	1.70
Oh1	1	0.15740(19)	0.50547(11)	0.29734(13)	0.0119(3)	1.20
Ow1	1	0.2399(2)	0.30592(11)	0.54483(14)	0.0130(3)	0.38
Ow2	1	0.2415(2)	0.00438(12)	0.31619(16)	0.0201(4)	0.37
Ow3	1	0.2279(2)	0.10933(12)	0.95112(19)	0.0210(4)	0.42
Ow4	1	0.2635(2)	0.80253(12)	0.50828(15)	0.0182(4)	—
Hoh	1	0.330(4)	0.496(3)	0.323(4)	0.036(2)	
H1a	1	0.382(4)	0.288(3)	0.511(3)	0.036(2)	
H1b	1	0.276(5)	0.335(3)	0.673(3)	0.036(2)	
H2a	1	0.198(6)	0.0830(19)	0.398(4)	0.036(2)	
H2b	1	0.211(6)	$-0.058(2)$	0.353(4)	0.036(2)	
H3a	1	0.395(4)	0.114(2)	0.986(4)	0.036(2)	
H3b	1	0.121(4)	0.1883(19)	0.933(4)	0.036(2)	
H4a	1	0.199(5)	0.733(2)	0.435(3)	0.036(2)	
H4b	1	0.249(6)	0.819(3)	0.632(3)	0.036(2)	

$\text{Ca}_2(\text{Fe}_x^{3+}\text{Mn}_{1-x}^{3+})_3(\text{PO}_4)_3\text{O}_2(\text{H}_2\text{O})_3$, [where $x = 1$ for mitridatite and $x = 0$ for robertsite] shown under the laueite crystals in Fig. 3. The EMP analysis of the mitridatite gave (average of four, wt%) 13.3 CaO, 1.79 ZnO, 0.08 MgO, 2.20 Mn_2O_3 , 38.4 Fe_2O_3 , 31.3 P_2O_5 , total 87.1. Black globules of the Mn^{4+} -containing oxide-mineral chalcophanite, $\text{ZnMn}^{4+}_3\text{O}_7\cdot 3\text{H}_2\text{O}$, are also closely associated with the secondary phosphate minerals in the 67-m nodule.

The most compelling question arising from this study is why is the Mn replaced by an equi-atomic combination of Mg + Zn at the surface of the laueite crystals? There is only one crystallographic site available for divalent cations, M1 shown in Fig. 9, so ordering of the Zn and Mg is not possible, and X-ray diffraction studies gave no evidence for a superstructure in which ordering could occur. A possible explanation is that the $\text{Zn}_{0.5}\text{Mg}_{0.5}$

Table 7. Polyhedron bond-distances (Å) in (Zn + Mg)-bearing laueite and Zn-bearing earlshannonite.

(Zn + Mg)-bearing laueite		Zn-bearing earlshannonite	
M1–O3 × 2	2.110(2)	Fe1–O3 × 2	2.087(3)
M1–Ow2 × 2	2.142(1)	Fe1–Ow1 × 2	2.256(3)
M1–Ow3 × 2	2.083(2)	Fe1–Ow2 × 2	2.043(3)
Av.	2.112	Av.	2.129
Fe2–O1 × 2	2.004(1)	Fe2–O1	2.091(2)
Fe2–O4 × 2	2.032(1)	Fe2–O1	2.060(3)
Fe2–Oh1 × 2	1.962(1)	Fe2–O2	2.027(2)
Av.	1.999	Fe2–O4	1.987(2)
		Fe2–Oh1	1.975(3)
Fe3–O2 × 2	1.965(1)	Fe2–Oh1	1.994(2)
Fe3–Oh1 × 2	1.934(1)	Av.	2.022
Fe3–Ow1 × 2	2.112(2)		
Av.	2.004	P1–O1	1.567(3)
		P1–O2	1.561(3)
P1–O1	1.523(1)	P1–O3	1.534(2)
P1–O2	1.533(1)	P1–O4	1.530(2)
P1–O3	1.537(1)	Av.	1.548
P1–O4	1.543(1)		
Av.	1.534		

Table 8. Hydrogen bonds in (Zn–Mg)-bearing laueite and Zn-bearing earlshannonite.

<i>D–H...A</i>	<i>d</i> (<i>D–H</i>) (Å)	<i>d</i> (<i>H...A</i>) (Å)	<i>d</i> (<i>D...A</i>) (Å)	<i><</i> (<i>DHA</i>) (°)
(Zn + Mg)-bearing laueite				
Oh1–Hoh...O2	0.85(2)	1.94(2)	2.747(2)	159(2)
Ow1–Hw1A...O4	0.84(2)	1.82(2)	2.643(2)	168(3)
Ow1–Hw1B...Ow4	0.83(2)	1.87(2)	2.655(2)	158(3)
Ow2–Hw2A...Ow1	0.88(2)	2.33(2)	3.127(3)	151(3)
Ow2–Hw2B...Ow4	0.85(2)	2.00(3)	2.819(2)	161(2)
Ow3–Hw3A...O3	0.84(2)	1.94(2)	2.752(2)	162(2)
Ow3–Hw3B...O1	0.87(2)	1.90(2)	2.729(2)	158(3)
Ow4–Hw4A...Oh1	0.86(2)	2.36(2)	3.187(3)	162(2)
Ow4–Hw4B...O3	0.87(2)	1.90(2)	2.760(2)	168(2)
Zn-bearing earlshannonite				
Oh1–Hoh...O2	0.84(5)	2.12(6)	2.799(3)	138(5)
Ow1–Hw1A...O3	0.85(3)	1.94(4)	2.781(4)	169(5)
Ow1–Hw1B...O2	0.84(4)	2.03(4)	2.854(4)	168(5)
Ow2–Hw2A...O4	0.85(3)	1.93(3)	2.772(3)	169(5)
Ow2–Hw2B...Ow1	0.85(4)	1.89(4)	2.738(4)	171(6)

composition of the *M1* site is stabilised by configurational entropy. In a binary *AB* alloy with a random distribution of *A* and *B* over the lattice sites, the configurational entropy of mixing is $S = R[(1 - x_B)\ln(1 - x_B) + x_B\ln x_B]$. This function goes through a minimum at $x_A = x_B = 0.5$ and as a result, for an ideal solution the free energy is at a minimum at the $A_{0.5}B_{0.5}$ composition. In the laueite structure, as shown in Fig. 9, the interlayer *M1* octahedra, *M1* (Op)₂(H₂O)₄, are relatively unconstrained by their topology, involving *trans*-corner connections to Op of PO₄ groups, and having four equatorial H₂O. As a result, it would be expected that substitution of different cations in the *M1* sites would involve only small changes in enthalpy,

especially when the cations are of the same charge and similar size, as is the case for Mg and Zn. In this case the free energy would be determined predominantly by the configurational entropy and would thus be consistent with stability of the Zn_{0.5}Mg_{0.5} composition at *M1*. This explanation implies that the surface layer is an overgrowth rather than the result of a mineral replacement reaction ((Zn + Mg) replacing Mn in the crystal), because the latter is a ternary system and the configurational entropy stabilization is at a maximum at Mn_{0.33}Zn_{0.33}Mg_{0.33} in this case.

A limited search of the literature reveals that the situation with mid-range compositions prevailing is quite common. In an example relevant to laueite-group minerals, Matsubara (2000) reports six analyses of ferrous-rich ushkovite from Oshibedani, Kobe, Japan, in which the divalent cation ratios in *M1* range from Fe_{0.56}²⁺Mg_{0.43} to Fe_{0.43}²⁺Mg_{0.54} (minor Mn²⁺ incorporated with the Fe²⁺), giving a mean close to Fe_{0.5}²⁺Mg_{0.5}, analogous to Zn_{0.5}Mg_{0.5} studied here. A comprehensive review of the literature is warranted to determine the extent to which, and the structural conditions under which, configurational entropy influences site compositions.

4.4. Zn-bearing earlshannonite

Zn-bearing whitmoreite–earlshannonite solid-solution members, (Fe_x²⁺Mn_{1-x}²⁺)Fe₂³⁺(PO₄)₂(OH)₂(H₂O)₄, of the arthurite group are ubiquitous as close associates of (Zn + Mg)-bearing laueite on altered phosphophyllite rinds in the 67-m nodule. They occur in the form of orange-brown hemispherical mounds (Fig. 3), which are composed of radiating acicular crystals. The EMP analyses are reported in Table 3. The empirical formula, normalised to 2 P *apfu* and with all iron as Fe²⁺ is Fe_{2.45}Mn_{0.37}Zn_{0.15}Mg_{0.03}(PO₄)₂(OH)₂(H₂O)₄. A single-crystal structure refinement, to be reported below, gave almost equal amounts of Fe²⁺ and Fe³⁺ in the *M1* site based on BVS calculations. With significant Fe²⁺ in the *M1* site, it is reasonable to assume that the Mn is divalent. The resulting structural formula is: (Fe_{0.22}²⁺Mn_{0.37}²⁺Zn_{0.15}Mg_{0.03}Fe_{0.23}³⁺)_{Σ1.0}Fe₂³⁺(PO₄)₂(OH)_{2.23}(H₂O)_{3.77}. Based on Mn²⁺ being the dominant cation of dominant valency in the *M1* site (Hatert & Burke, 2008), the mineral is a Zn-bearing earlshannonite.

An unusual crystal-chemical aspect of the laueite/earlshannonite associations is that, whereas the laueite crystals have surface layers containing equal amounts of Zn + Mg, the earlshannonite crystals have significant surface Zn, but very little Mg. The EDS analyses of the surfaces of earlshannonite crystals commonly gave Zn > Mn, corresponding to a new arthurite-group species, with the surface phase only a few μm thick. The MgO in the interior of the crystals is an order-of-magnitude smaller than the ZnO content, see Table 3.

The crystal structure of earlshannonite has not been reported (Peacor *et al.*, 1984). Although the crystal structure of the isostructural whitmoreite has been refined, it was based on photographic film data with a relatively

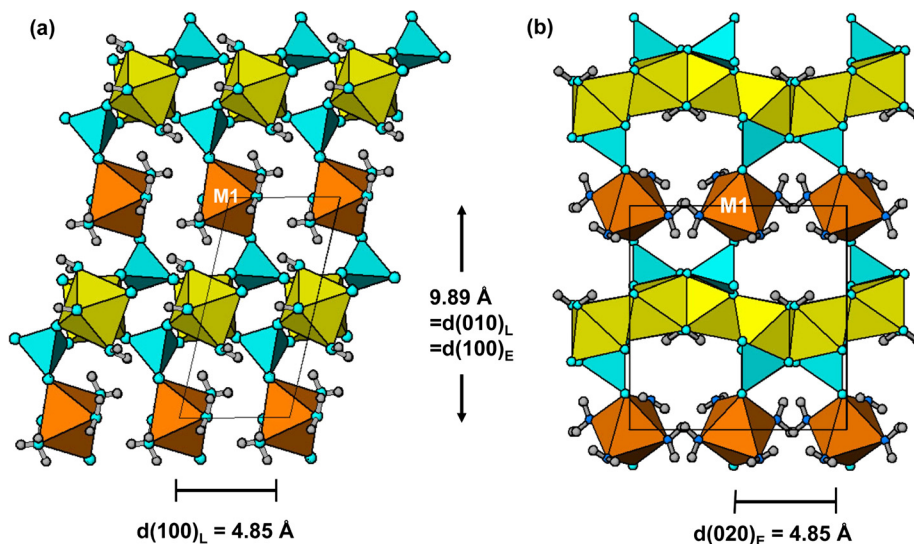


Fig. 9. [001] projections of the structures of (a) laueite and (b) earlshannonite, showing perfect matching of the dimensions within the (001) planes for the two structures, which is the basis for epitactic growth of earlshannonite on laueite shown in Fig. 10. (Online version in color)

Table 9. Atom coordinates and equivalent isotropic-displacement parameters ($\text{\AA}^2$), plus bond-valence sums (BVS) for Zn-bearing earlshannonite.

	SOF	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}	BVS (<i>vu</i>)
Fe1	0.45	0	0	0	0.0156(2)	2.26
Mn1	0.27	0	0	0	0.0156(2)	2.42
Zn1	0.25	0	0	0	0.0156(2)	1.93
Mg1	0.03	0	0	0	0.0156(2)	1.89
Fe2	1	0.45975(4)	0.13816(4)	0.33942(9)	0.00579(16)	2.97
P1	1	0.30158(7)	0.42598(8)	0.32789(16)	0.0068(2)	4.85
O1	1	0.3961(2)	0.4804(2)	0.1271(5)	0.0076(6)	2.00
O2	1	0.3568(2)	0.4793(2)	0.5845(5)	0.0087(6)	1.66
O3	1	0.1596(2)	0.4815(2)	0.2684(5)	0.0108(6)	1.65
O4	1	0.3035(2)	0.2666(2)	0.3198(5)	0.0086(6)	1.81
Oh1	1	0.5559(2)	0.2380(2)	0.0840(5)	0.0079(6)	1.09
Ow1	1	0.1298(2)	0.8999(3)	0.3022(6)	0.0193(8)	0.26
Ow2	1	0.0451(2)	0.1806(3)	0.1851(6)	0.0215(8)	0.45
Hoh	1	0.601(5)	0.192(6)	−0.013(9)	0.027(6)	
Hw2a	1	0.122(3)	0.206(5)	0.246(11)	0.027(6)	
Hw2b	1	−0.012(3)	0.245(4)	0.204(13)	0.027(6)	
Hw1a	1	0.130(4)	0.929(6)	0.450(5)	0.027(6)	
Hw1b	1	0.201(3)	0.924(6)	0.239(8)	0.027(6)	

high *R* factor and the H atoms were not located (Moore *et al.*, 1974). We collected synchrotron single-crystal XRD data for Zn-bearing earlshannonite and located the H atoms from a difference-Fourier map. The same refinement conditions were used as reported above for (Zn + Mg)-bearing laueite. Twinning by 180° rotation about *a** was incorporated and refined twin volumes were 0.580(6)/0.42. Data collection and refinement information is given in Table 5. Refined atom coordinates, equivalent isotropic-displacement parameters and bond-valence sums are reported in Table 9. Selected bond-distances and hydrogen bonds are reported along with those for (Zn + Mg)-bearing laueite in Tables 7 and 8, respectively. The hydrogen bonds are principally to phosphate oxygen atoms O2, O3 and O4,

which are all significantly deficient according to the BVS values in Table 9. The only other hydrogen bond is between the H₂O molecules Ow1 and Ow2, coordinated to M1. The same system of hydrogen bonds was reported by Kampf (2005) for the arthurite-group mineral cobaltarthurite, Co²⁺Fe³⁺(AsO₄)₂(OH)₂(H₂O)₄.

The BVS at the M2 site is 2.97 *vu*, consistent with Fe³⁺ at this site. In the refinement, the M1 site was assigned as 0.45 Fe + 0.27 Mn + 0.25 Zn + 0.03 Mg, based on the EMP analyses. The BVS values in Table 9 were used to determine the amounts of Fe³⁺ and Fe²⁺, giving 0.23 Fe³⁺ + 0.22 Fe²⁺, resulting in the structural formula reported in Table 5. The Zn-bearing earlshannonite is more resistant to oxidation than the co-existing (Zn + Mg)-bearing laueite, which

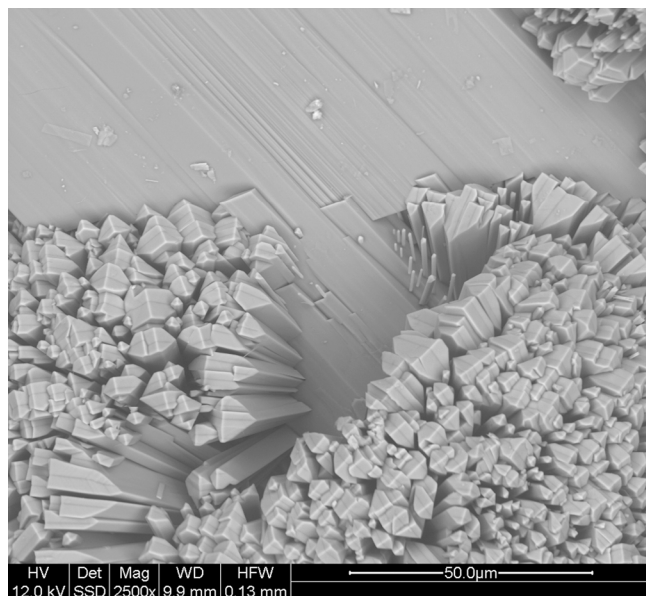


Fig. 10. SEM BSE image of Zn-bearing earlshannonite rods epitactic on (Zn + Mg)-bearing laueite.

contains Fe only as Fe^{3+} , and has some oxidation of the Mn^{2+} to Mn^{3+} .

Commonly, earlshannonite was observed to form epitactic growths on laueite, as shown in Fig. 10. A PXRD pattern of ground earlshannonite/laueite epitactic assemblages displayed perfect coincidence of $(0k0)_L$ with $(h00)_E$ and $(h00)_L$ with $(02k0)_E$ reflections. The structural basis for the epitaxy is shown by a comparison of the c axis projections of both structures in Fig. 9. From Rietveld refinement of the PXRD pattern, the layer separations given by $d(010)_L$ and $d(100)_E$ both equal 9.89 Å, and the intralayer separation of the $M1$ -centred octahedra, given by $d(100)_L$ and $d(020)_E$, both equal 4.85 Å.

5. Paragenetic considerations

Mücke (1981) has presented a comprehensive paragenesis scheme for those phosphate minerals known at the time at the Hagendorf-Süd pegmatite. He divides the parageneses into two subparageneses: his Table I concerns rock-bridgeite-free sub-parageneses and Table II concerns sub-parageneses involving rockbridgeite and zwieselite. Phosphophyllite plays a dominant role in paragenesis 1C in Table 1, through its decomposition, leaching and mineral-replacement reactions, which result in the formation of other secondary phosphates. Mücke (1981) proposed that phosphophyllite decomposes into laueite and whitmoreite. In the latter case, Mücke gave the stepwise-alteration reactions, involving substitution of Fe^{2+} for Zn, followed by hydrolysis and oxidation of two-thirds of the Fe^{2+} . Other minerals in paragenesis 1C that Mücke considered as being derived from phosphophyllite are whitmoreite, strunzite, stewartite, mitridatite, keckite and oxidized schoonerite-group minerals. There are



Fig. 11. Schoonerite-group mineral inclusions in phosphophyllite. FOV = 4 mm. Photo V. Betz. (Online version in color)

problems with Mücke's formula for keckite, as discussed by Hochleitner & Fehr (2010), and it is likely that the Zn-bearing jahnsite-(CaMnMn) described here equates to Mücke's keckite in paragenesis 1C. Similarly, Mücke's whitmoreite in paragenesis 1C equates to earlshannonite in the current study, because partial oxidation of the Fe^{2+} in our material results in Mn^{2+} being the dominant divalent-cation at the $M1$ site. Mücke noted that whitmoreite in paragenesis 1C was an oxidized variety, but did not provide chemical analyses.

As mentioned in section 3, oxidized schoonerite-group minerals are the most abundant of the secondary phosphates associated with altered phosphophyllite. It is possible that the oxidized schoonerite-group minerals and altered phosphophyllite are contemporaneous, with both being formed from reaction of triphylite with Zn-rich solutions. Indirect evidence for this comes from studies on unaltered phosphophyllite crystals from less-weathered locations in the mine. These show abundant inclusions of green (less-oxidized) schoonerite-group minerals in the transparent phosphophyllite crystals (Fig. 11). As seen in Fig. 11, an exposed schoonerite-type lath at the surface of the phosphophyllite crystal has undergone oxidation and has a similar red colour to schmidite in the 67-m nodule. Alteration and leaching of the relatively unstable phosphophyllite crystals would liberate the schoonerite-type crystals, and their oxidation and clumping together could explain the aggregates of red laths shown adjacent to heavily leached phosphophyllite in Fig. 2.

The next mineral in the paragenetic sequence seems to be Zn-rich jahnsite, from reaction of the leached phosphophyllite surface with Ca in solution. The jahnsite grows epitactically on the phosphophyllite surface and forms a resistant rind, which remains after the phosphophyllite has been removed by leaching, as shown in Fig. 2. The initial jahnsite crystals were probably more Fe^{2+} -rich than the high- Fe^{3+} species reported here, and so would have been close to mid-range members of the solid solution between jahnsite-(CaMnMn) and jahnsite-(CaMnFe). The epitactic jahnsite crystals, as shown in Fig. 5, are generally only visible on the underside of the

rind. They are usually covered with a layer of amorphous ferric phosphate, which we have equated to Zn-bearing santabarbaraite, and/or a thin layer of mitridatite. As seen from a comparison of the analyses in Tables 1 and 2, the amorphous phase has a composition similar to that of Zn-bearing jahnsite, if one allows for replacement of Mn in the jahnsite by Fe. The zoned-jahnsite regions show the same Mn-for-Fe replacement, so it is possible that the amorphous upper layer on the phosphophyllite rinds derives directly from the jahnsite by a mineral-replacement reaction.

Laueite and earlshannonite are younger minerals in the paragenetic sequence resulting from phosphophyllite alteration, since they are always observed as idiomorphic crystals on the surface of the phosphophyllite rind, either on the amorphous ferric-phosphate coating or on a thin layer of mitridatite. The new mineral zincostrunzite (Kampf *et al.*, 2017a) is also a relatively common mineral on the phosphophyllite rind. It is likely that leaching of the underlying jahnsite provided the Mg for the (Zn + Mg)-enriched surface phase on the laueite crystals. As noted by Mücke (1981), “Mg is only found in trace concentration in rare cases” at Hagendorf-Süd. The jahnsite in the surface rind on phosphophyllite contains a relatively high MgO content (0.8 wt%) and this decreases to 0.3 wt% in the overlying amorphous ferric phosphate on which the laueite crystals form.

A number of interesting paragenetic questions remain to be resolved. Does the (Zn + Mg)-enriched surface phase on the laueite crystals result from new growth as a result of changed ambient conditions? Why do the laueite crystals incorporate equal amounts of Zn and Mg at the surface, but the closely associated earlshannonite crystals incorporate predominantly Zn? Was there a change in the availability of Mg, with laueite forming first when it was readily available (from jahnsite leaching?) and earlshannonite forming later when the available Mg had been largely consumed? Or is it due to the different tolerances of the M1 site in the two structures? The M1 site has the same coordination, $M1Op_2(H_2O)_4$, and same topology (*trans*-connectivity between PO_4 groups of adjacent layers) in the two structures (Fig. 9). There are, however, subtle differences, which may affect the cations that can substitute at M1. In particular, laueite has zeolitic-type H_2O (Ow4 in Tables 6 and 8), which participates in a number of hydrogen bonds with the H_2O molecules coordinating M1, whereas zeolitic H_2O is absent in earlshannonite. Also, the mean M1–O bond-distance is longer in earlshannonite, which could give a greater strain contribution to the enthalpy of mixing with the incorporation of the smaller Mg compared with Zn, which could negate the 50/50 configurational-entropy contribution to the free energy discussed in section 4.3. Quantum mechanical calculations could contribute to understanding the different crystal-chemical behaviour of the two minerals. A question also remains about whether the amorphous ferric-phosphate coating in the phosphophyllite surface rind derives from breakdown of the underlying epitactic jahnsite crystals. It would be interesting to do

low-temperature hydrothermal-heating tests on the amorphous phase to see if it can be crystallised.

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