

# Aluminium-bearing strunzite derived from jahnsite at the Hagendorf-Süd pegmatite, Germany

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## ABSTRACT

Aluminium-bearing strunzite,  $[\text{Mn}_{0.65}\text{Fe}_{0.26}\text{Zn}_{0.08}\text{Mg}_{0.01}]^{2+}[\text{Fe}_{1.50}\text{Al}_{0.50}]^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , occurs as fibrous aggregates in a crystallographically oriented association with jahnsite on altered zwieselite samples from the phosphate pegmatite at Hagendorf Süd, Bavaria, Germany. Synchrotron X-ray data were collected from a 3  $\mu\text{m}$  diameter fibre and refined in space group  $P\bar{1}$  to  $R_1 = 0.054$  for 1484 observed reflections. The refinement confirmed the results of chemical analyses which showed that one quarter of the trivalent iron in the strunzite crystals is replaced by aluminium. The paragenesis revealed by scanning electron microscopy, in combination with chemical analyses and a crystal-chemical comparison of the strunzite and jahnsite structures, are consistent with strunzite being formed from jahnsite by selective leaching of (100) metal–phosphate layers containing large divalent Ca and Mn atoms.

**KEYWORDS:** Al-bearing strunzite, strunzite paragenesis, strunzite structure refinement, Hagendorf Süd secondary phosphates.

## Introduction

STRUNZITE, ideally  $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , is a relatively rare secondary phosphate mineral found in altered granitic pegmatites (Moore, 1965; Viana and Prado, 2007; Dill *et al.*, 2008). It is a late-stage product in the supergene alteration of primary phosphate minerals such as triphylite, zwieselite and apatite via intermediate phosphates including rockbridgeite, mitridatite, vivianite, whitmoreite and jahnsite (Mücke, 1981; Keller and Von Knorring, 1989; Dill *et al.*, 2008).

The presence of Al from the breakdown of aluminosilicates in contact with solutions rich in phosphate is a common feature of secondary pegmatite phosphate alteration (Fransolet, 1980; Keller and von Knorring, 1989; Dill *et al.*, 2008).

The feldspar pegmatite at Hagendorf Süd, Bavaria, contains a large number of secondary Al-phosphates including eosphorite, kingsmoun-tite, paravauxite, fluellite, morinite, variscite, scorzalite, kastningite, nordgauite, whiteite and wavellite as well as Al-bearing secondary Fe–Mn phosphates including keckite, rockbridgeite and jahnsite (Mücke, 1981; Dill *et al.*, 2008; Grey *et al.*, 2010; Birch *et al.*, 2011). Strunzite is relatively widespread at Hagendorf Süd, and has been found (by E.K.) between the 45 and 84 m levels in the Cornelia mine open cut. It is particularly common between 60 and 67 m.

Dill *et al.* (2008) listed “Al-strunzite” as one of the phosphate minerals from the Hagendorf pegmatite province, but provided no details of its composition or occurrence. A few occurrences of fibrous Al-bearing strunzite in close association with Al-bearing jahnsite have been found in a continuing study of secondary phosphate minerals from the Cornelia mine open cut (Grey *et al.*,

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2010; Birch *et al.*, 2011). We have characterized both minerals by electron microprobe analysis and refined the structure of the strunzite from single-crystal synchrotron X-ray diffraction data. We report here the results of these studies together with an analysis of the crystal-chemical relationships between the two minerals, which provides evidence for formation of the strunzite by crystallographically controlled leaching of the jahnsite.

## Experimental

Hand specimens containing strunzite associated with jahnsite on altered zwieselite were collected by one of us (E.K.) from the 67 m level of the Cornelia mine open cut. The strunzite occurs as sheaves of ultrathin white to yellowish fibres; the jahnsite occurs as transparent tabular crystals which are commonly corroded. Samples were mounted in epoxy blocks, polished and carbon-coated for scanning electron microscopy and electron microprobe (EMP) analyses by wavelength dispersive spectrometry on a JEOL JXA 8500F Hyperprobe operating at an accelerating voltage of 12 kV and a beam current of 11 nA. The beam was defocused to a 1  $\mu\text{m}$  spot size. The analytical standards used were  $\text{CaSiO}_3$  for Ca;  $\text{AlPO}_4$  for Al, P;  $\text{MgAl}_2\text{O}_4$  for Mg; hematite for Fe;  $\text{MnSiO}_3$  for Mn, ZnS for Zn and albite for Na. The EMP results are given in Table 1. All EMP data were corrected using a  $\phi(\rho z)$  matrix correction (Armstrong, 1988).

A needle-shaped crystal of strunzite, 80  $\mu\text{m}$  long and  $\sim 3$   $\mu\text{m}$  in diameter, was used for X-ray data collection on the macromolecular beam line MX2 at the Australian Synchrotron. Data were

collected at room temperature using an ADSC Quantum 315r detector and monochromatic radiation with a wavelength of 0.71000  $\text{\AA}$ . A  $\phi$  scan was employed with frame widths of  $2^\circ$  and a counting time per frame of 2 s. The intensity datasets were processed to produce data files which were analysed in *WinGX* (Farrugia, 1999). The refinement was made using *SHELXL-97* (Sheldrick, 2008).

The published atom coordinates and metal atom site assignments for strunzite (Fanfani *et al.*, 1978) were used as the initial model for refinement in space group  $P\bar{1}$ . The scattering curve for Mn was used for the Mn site, which also contains minor Fe, Mg and Zn. Refinement with isotropic displacement parameters, and with refinement of Al/Fe occupancy in the two independent trivalent Fe sites converged to  $R_1 = 0.08$ . Hydrogen atoms associated with hydroxyl and water groups were located in difference-Fourier maps. They were refined with soft restraints on the O–H and H–H distances of O–H = 0.80(4)  $\text{\AA}$  and H–H = 1.25(8)  $\text{\AA}$ . These restrained O–H distances are consistent with distances reported in previous X-ray refinements (e.g. Harte *et al.*, 2005). A common isotropic displacement parameter was refined for the hydrogen atoms. The final refinement, incorporating anisotropic displacement parameters for all non-H atoms, converged to  $R_1 = 0.054$  for 1481 observed reflections with  $F > 4\sigma(F)$ . Further details of the refinement are summarized in Table 2. Refined atom coordinates and equivalent isotropic displacement parameters are reported in Table 3. Tables of anisotropic displacement parameters and observed and calculated structure factors have been deposited with the Principal

TABLE 1. Electron microprobe analyses of Al-bearing strunzite and jahnsite from Hagendorf Sd.

	Strunzite (9 analyses)		Jahnsite (7 analyses)	
	Range (wt.%)	Mean (wt.%)	Range (wt.%)	Mean (wt.%)
CaO	0–0.12	0.05	5.22–6.39	5.48
Na <sub>2</sub> O	0–0.02	0.01	0.11–0.24	0.15
MnO	9.01–10.90	10.29	14.09–19.25	17.20
Fe <sub>2</sub> O <sub>3</sub>	29.19–34.48	31.25	16.87–21.02	18.97
Al <sub>2</sub> O <sub>3</sub>	5.39–6.25	5.74	1.71–3.93	2.91
MgO	0–0.09	0.09	0.75–1.17	0.92
ZnO	1.33–1.61	1.39	1.67–2.40	2.07
P <sub>2</sub> O <sub>5</sub>	29.90–32.61	31.07	31.69–33.96	32.69
Total	76.60–84.30	79.89	78.07–83.35	80.39

TABLE 2. Data collection and structure refinement details for Al-bearing strunzite.

<b>Crystal data</b>	
Unit cell: $a, b, c$ (Å)	10.277(1), 9.826(1), 7.205(1)
Unit cell: $\alpha, \beta, \gamma$ (°)	90.077(4), 98.865(4), 118.442(4)
Volume (Å <sup>3</sup> )	629.8(1)
Z	2
Space group	$P\bar{1}$
Calculated density (g cm <sup>-3</sup> )	2.54
Formula from refinement	MnFe <sub>1.44</sub> Al <sub>0.56</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> ·6H <sub>2</sub> O
Formula weight	970.0
<b>Data collection</b>	
Temperature (K)	293
Wavelength (Å)	0.7100
Crystal size (mm)	0.003 diameter × 0.08 long
Collection mode	$\phi$ scan, 360°, $\Delta\Phi = 0.02^\circ$
Count time per frame (s)	2
2 $\theta_{\max}$ (°)	50
No. of unique reflections	2024
No. of reflections, $I > 2\sigma(I)$	1484
Absorption coefficient (mm <sup>-1</sup> )	3.19
<b>Refinement</b>	
Data/restraints/parameters	2024/20/235
Goodness-of-fit	0.892
Final $R$ indices ( $F > 4\sigma(F)$ )	$R_1 = 0.054, wR_2 = 0.128$
Final $R$ indices (all data)	$R_1 = 0.078, wR_2 = 0.145$
Largest diff. peak and hole (e Å <sup>-3</sup> )	-0.68, +1.06

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## Results and discussion

### *Electron probe microanalysis and paragenesis*

The EMP analyses of the strunzite and associated jahnsite crystals are reported in Table 1. Both phases show relatively high compositional homogeneity between different regions, with no strong inter-element correlations. Weak positive correlations between the Mn, Al and Fe analyses appear to reflect variable analytical totals, possibly due to varying water loss resulting from heating by the electron beam. The jahnsite is Al-bearing and its composition is close to that we have previously reported for jahnsite-(CaMnMn) in contact with zwieselite-triplite and with nordgaultite in samples from the Cornelia mine open cut (Grey *et al.*, 2010). Mücke (1981) reported Al-bearing keckite, CaMn<sub>2</sub>(Fe,Al)<sub>3</sub>(OH)<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>· $x$ H<sub>2</sub>O, associated with strunzite in altered zwieselite

secondary phosphate assemblages at Hagendorf. According to recent studies, however, keckite can be mistaken for jahnsite-(CaMnFe) or jahnsite-(CaMnMn) (Hochleitner and Fehr, 2010; Kampf *et al.*, 2008).

The strunzite analyses are similar to those reported by Frondel (1958), but with one quarter of the Fe replaced by Al, giving a formula Mn<sub>0.65</sub>Fe<sub>1.76</sub>Al<sub>0.50</sub>Zn<sub>0.08</sub>Mg<sub>0.01</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O. For comparison, the ideal strunzite formula is MnFe<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O, and the formula from the structure refinement is MnFe<sub>1.44</sub>Al<sub>0.56</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O. The analyses reported in Table 1 show that strunzite and jahnsite have similar Fe/Al ratios but the amount of these trivalent elements in strunzite is about double that in jahnsite. We propose that this chemical relationship is due to the strunzite being formed from jahnsite by selective leaching of divalent phosphate components, thereby enriching the trivalent element concentrations.

This type of paragenesis is supported by the spatial relationship between the two phases,

TABLE 3. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for Al-bearing strunzite;  $U_{\text{eq}}$  is one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$ ( $\text{\AA}^2$ )
Mn	5002(1)	3289(1)	2497(2)	18(1)
Fe(1)*	9694(1)	2439(1)	1384(2)	12(1)
Fe(2)*	301(1)	7741(1)	3618(2)	13(1)
P(1)	8132(2)	4666(2)	584(3)	12(1)
P(2)	1869(2)	1527(2)	4415(3)	13(1)
O(1)	6474(6)	4022(7)	635(8)	25(1)
O(2)	8417(6)	3304(6)	214(8)	23(1)
O(3)	9097(6)	5559(6)	2471(7)	16(1)
O(4)	8496(6)	5706(6)	8944(7)	19(1)
O(5)	901(6)	1456(6)	2512(7)	16(1)
O(6)	1564(6)	-122(6)	4777(8)	21(1)
O(7)	3515(6)	2515(6)	4379(8)	24(1)
O(8)	1529(6)	2226(6)	6036(8)	19(1)
OH1	9615(6)	3094(6)	3917(8)	19(1)
OH2	384(6)	8474(6)	1084(8)	20(1)
Ow1	3087(7)	2407(7)	120(9)	27(1)
Ow2	6922(7)	4330(6)	4882(9)	25(1)
Ow3	4997(7)	5511(7)	2502(9)	29(1)
Ow4	5032(11)	1024(9)	2504(15)	59(2)
Ow5	2317(7)	7766(7)	3361(9)	27(1)
Ow6	-2319(7)	456(6)	1652(9)	24(1)
HOH1	9460(120)	3800(90)	3840(150)	39(8)
HOH2	360(120)	9270(70)	1220(150)	39(8)
H1A	3110(120)	2770(110)	-910(80)	39(8)
H1B	2500(100)	2500(120)	570(130)	39(8)
H2A	6770(110)	4720(110)	5770(110)	39(8)
H2B	7680(70)	4900(90)	4590(140)	39(8)
H3A	5540(90)	6240(80)	3290(110)	39(8)
H3B	4260(70)	5070(100)	2950(140)	39(8)
H4A	4920(120)	1110(120)	1400(60)	39(8)
H4B	4290(80)	380(100)	2800(140)	39(8)
H5A	2130(120)	7360(110)	2290(70)	39(8)
H5B	2420(120)	7140(100)	4000(110)	39(8)
H6A	-1950(120)	290(110)	2600(80)	39(8)
H6B	-2450(120)	-270(90)	970(110)	39(8)

\* Refined site occupancies for Fe(1) and Fe(2) are both 0.72(1)Fe + 0.28(1)Al.

which is shown in the photomicrographs in Fig. 1. The tabular jahnsite crystals are heavily corroded, and Fig. 1a shows the transformation of the ends of the crystals into fibrous strunzite. The axes of the strunzite fibres are parallel to the long dimension of the jahnsite crystal. Precession single-crystal XRD studies on excavated grains showed that the fibre axis of the strunzite,  $c$ , and the axis corresponding to the long dimension of the jahnsite crystals,  $b$ , are crystallographically equivalent  $7.2 \text{ \AA}$  axes, corresponding to the repeat distance of chains of corner-connected Fe-centred

octahedra that are common to both minerals. An advanced stage of the breakdown of jahnsite to fibrous strunzite is shown in Fig. 1b. The transformation of jahnsite into strunzite is explained in the following sections by comparing their crystal structures.

#### Strunzite crystal structure

The only published crystal-structure analysis of strunzite is due to Fanfani *et al.* (1978). They studied fibrous strunzite from the Big Chief mine,

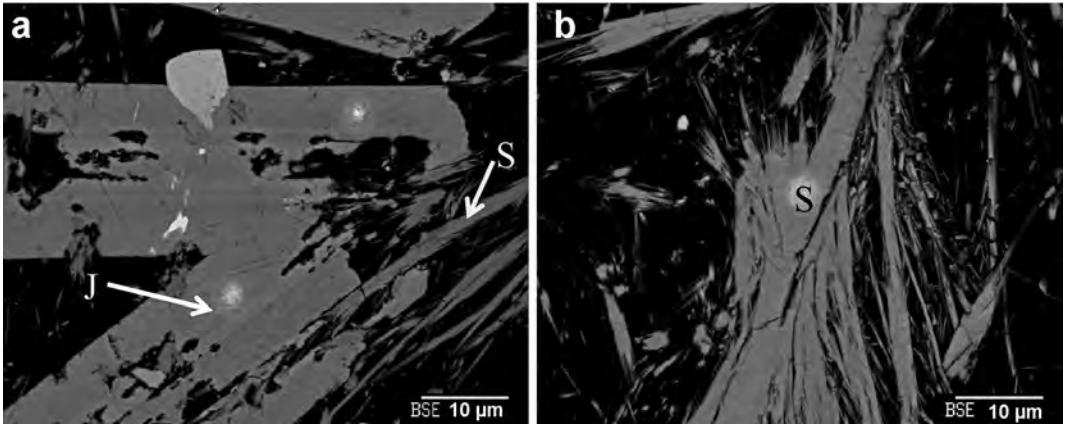


FIG. 1. (a) An SEM image showing jahnsite (J) associated with Al-bearing strunzite (S). (b) An SEM image showing the development of strunzite fibres from jahnsite.

Dakota, and noted problems due to the poor quality of the data. Anisotropic refinement gave non-positive displacement parameters for some oxygen atoms, and the H atoms were not located. Our synchrotron analysis produced good quality data, albeit of very low intensity due to the tiny crystal diameter, and anisotropic refinement gave reasonable displacement parameters for all non-H atoms. In addition the H atoms were located, allowing the H-bonding scheme to be determined.

In their review of the crystal chemistry of phosphate minerals, Huminicki and Hawthorne (2002) included strunzite in the subgroup of infinite sheets of  $\text{PO}_4$  tetrahedra and  $\text{M}\Phi_6$  octahedra ( $\Phi = \text{O}, \text{OH}, \text{H}_2\text{O}, \text{F}$ ). The sheets consist of  $7.2 \text{ \AA}$  chains of Fe-centred octahedra, *trans*-corner-linked through OH along [001], and interconnected via corner-sharing with  $\text{PO}_4$  tetrahedra along [010] to form (100) sheets. The sheets are interconnected along [100] by corner-

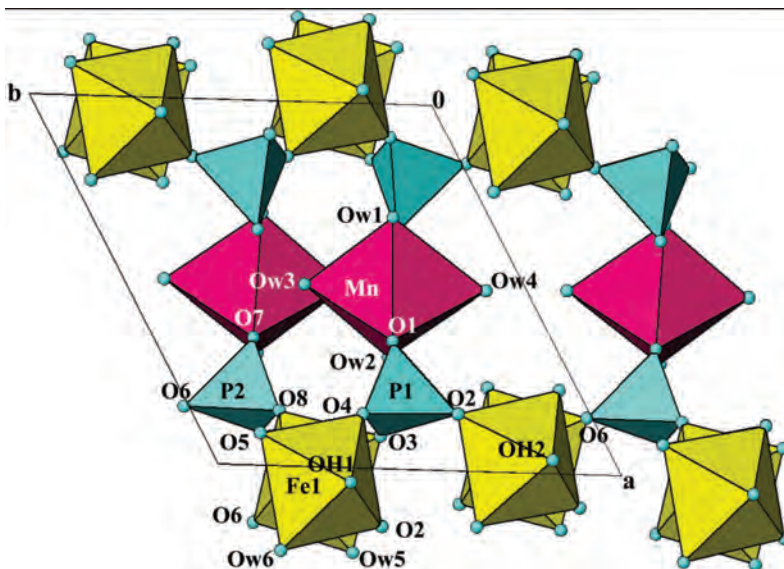


FIG. 2. Polyhedral representation of the strunzite structure, projected along [001].

sharing of the tetrahedra with  $\text{MnO}_2(\text{H}_2\text{O})_4$  octahedra, as illustrated in Fig. 2. The Fe-centred octahedra have the composition  $\text{FeO}_3(\text{OH})_2(\text{H}_2\text{O})$ . The occupancy of the Fe sites obtained from the structure refinement is 0.72(1) Fe + 0.28(1) Al. This compares well with the results from the microprobe analyses, which produce a formula  $[\text{Mn}_{0.65}\text{Fe}_{0.26}\text{Zn}_{0.08}\text{Mg}_{0.01}]^{2+}[\text{Fe}_{1.50}\text{Al}_{0.50}]^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , after appropriate assignment of the elements into the  $\text{M}^{2+}$  and  $\text{M}^{3+}$  sites. In particular,  $0.75\text{Fe}^{3+} + 0.25\text{Al}^{3+}$  are present in the Fe sites. The partial occupation of the Fe sites by Al results in shorter M–O bonds (with a mean distance of 1.987(6) Å) than those reported for strunzite (2.01(1) Å), although the difference is barely significant within the associated errors. In general, the bond lengths in Table 4 closely match those reported by Fanfani *et al.* (1978). The long M–Ow distances for both the Fe and Mn sites (Table 4) are notable.

Hydrogen bonds with O–O distances <3 Å are listed in Table 5. Most of the assignments agree with those proposed by Fanfani *et al.* (1978) from bond-valence considerations. The majority of the stronger H-bonds lie close to (100) planes, as shown in Fig. 3. The strongest H-bonds are between Ow and O of adjacent intrachain octahedra. In jahnsite and related minerals such

pairs of anions (Ow6 and O6, Ow5 and O2) form the edges of  $\text{PO}_4$  tetrahedra, giving four bridging intrachain tetrahedra per octahedron, compared to only two in strunzite.

#### *Jahnsite to strunzite transformation*

The general formula for jahnsite-group minerals can be written  $\text{XM}(1)\text{M}(2)_2\text{Fe}_2(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . The dominant elements in the first three sites are added as a suffix to produce species names of the form jahnsite-(XM(1)M(2)) (Moore and Ito, 1978). Generally these elements are divalent and are listed in order of decreasing ionic radius. Using this nomenclature, the original jahnsite described by Moore (1974) is jahnsite-(CaMnMg). Recently, a new variation involving monovalent Na in the X site and trivalent Fe in M(1) site has been reported (Kampf *et al.*, 2008).

The structure of jahnsite was first determined by Moore and Araki (1974). A view of the structure in projection along the 7.2 Å *b* axis is shown in Fig. 4*a*. It consists of [010] chains of *trans*-corner-connected Fe-centred octahedra,  $\text{FeO}_4(\text{OH})_2$ , that are decorated by bridging  $\text{PO}_4$  tetrahedra to give columns of composition  $\text{Fe}(\text{PO}_4)_2(\text{OH})$ . The columns connect along [100] with [010] chains of edge-shared  $\text{XO}_6$  and  $\text{M}(1)\text{O}_6$  octahedra to form (001) sheets. These

TABLE 4. Selected bond lengths (Å) for Al-bearing strunzite.

Mn–O(1)	2.049(6)		
Mn–O(7)	2.071(6)		
Mn–Ow3	2.185(6)		
Mn–Ow1	2.211(6)		
Mn–Ow2	2.219(6)		
Mn–Ow4	2.240(7)		
<Mn–O>	<b>2.162</b>		
Fe(1)–O(4)	1.936(5)	Fe(2)–O(8)	1.951(5)
Fe(1)–OH1	1.961(5)	Fe(2)–O(6)	1.964(5)
Fe(1)–OH2	1.964(5)	Fe(2)–OH2	1.963(6)
Fe(1)–O(2)	1.968(5)	Fe(2)–OH1	1.964(6)
Fe(1)–O(5)	1.992(5)	Fe(2)–O(3)	1.991(5)
Fe(1)–Ow6	2.097(6)	Fe(2)–Ow5	2.097(6)
<Fe(1)–O>	<b>1.986</b>	<Fe(2)–O>	<b>1.988</b>
P(1)–O(1)	1.516(6)	P(2)–O(7)	1.501(6)
P(1)–O(3)	1.534(5)	P(2)–O(8)	1.520(6)
P(1)–O(2)	1.532(5)	P(2)–O(6)	1.528(5)
P(1)–O(4)	1.534(6)	P(2)–O(5)	1.545(5)
<P(1)–O>	<b>1.529</b>	<P(2)–O>	<b>1.524</b>

TABLE 5. Hydrogen bond lengths and angles ( $\text{\AA}$  and  $^\circ$ ) for Al-bearing strunzite.

D—H...A	D—H	H...A	D...A	$\angle(\text{DHA})$
OH1—HOH1...O(3)	0.79(4)	2.14(6)	2.880(7)	156(10)
OH2—HOH2...O(5) <sup>i</sup>	0.80(4)	2.12(6)	2.875(7)	158(10)
Ow1—H1B...O(5)	0.77(4)	2.19(6)	2.844(9)	142(9)
Ow1—H1A...Ow3 <sup>ii</sup>	0.82(4)	2.35(8)	2.992(10)	135(9)
Ow2—H2B...O(3)	0.78(4)	2.16(6)	2.846(9)	148(10)
Ow2—H2A...Ow3 <sup>iii</sup>	0.82(4)	2.28(6)	2.986(10)	144(9)
Ow3—H3A...O(7) <sup>iii</sup>	0.82(4)	1.90(5)	2.693(8)	162(10)
Ow3—H3B...Ow2 <sup>iii</sup>	0.79(4)	2.35(7)	2.985(10)	138(9)
Ow5—H5A...O(2) <sup>ii</sup>	0.82(4)	1.82(4)	2.636(8)	170(10)
Ow5—H5B...Ow2 <sup>iii</sup>	0.81(4)	1.98(5)	2.773(8)	164(11)
Ow6—H6A...O(6) <sup>iv</sup>	0.79(4)	1.89(5)	2.638(8)	158(10)
Ow6—H6B...Ow1 <sup>v</sup>	0.81(4)	2.00(5)	2.781(8)	163(10)

Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $-x+1, -y+1, -z$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $-x, -y, -z+1$ ; (v)  $-x, -y, -z$ .

sheets connect along [001] by corner-sharing of the  $\text{PO}_4$  tetrahedra with  $\text{M}(2)\text{O}_2(\text{H}_2\text{O})_4$  octahedra.

An alternative description of the structure in terms of (100) polyhedral sheets emphasizes the separation of large weakly bonded X and M(1) atoms from small tightly bonded trivalent Fe atoms in alternate (100) layers. The two types of layers are shown in Fig. 4a. Removal of the planes containing X and M(1) and associated  $\text{PO}_4$

and  $\text{M}(2)\Phi_6$  polyhedra gives the residual polyhedral layers shown in Fig. 4b. Breaking one quarter of the intrachain bridging  $\text{PO}_4$  links (which are replaced by  $\text{H}_2\text{O}$ ) and then connecting the layers by corner-sharing between  $\text{PO}_4$  and  $\text{Fe}\Phi_6$  (indicated by the arrows in Fig. 4b) generates the strunzite structure (cf. Fig. 2). These structural considerations suggest that strunzite could form from jahnsite by selective

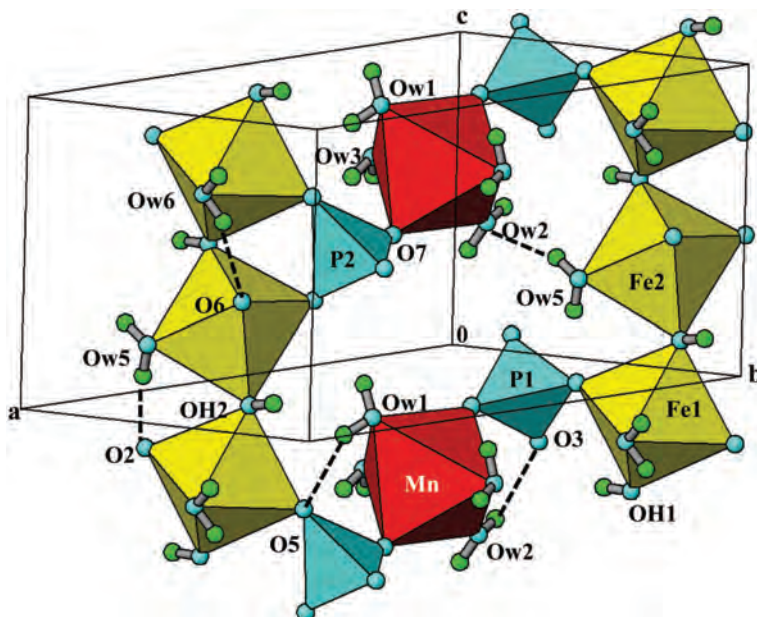


FIG. 3. An (010) slice through the strunzite structure, showing the H-bonding arrangement.

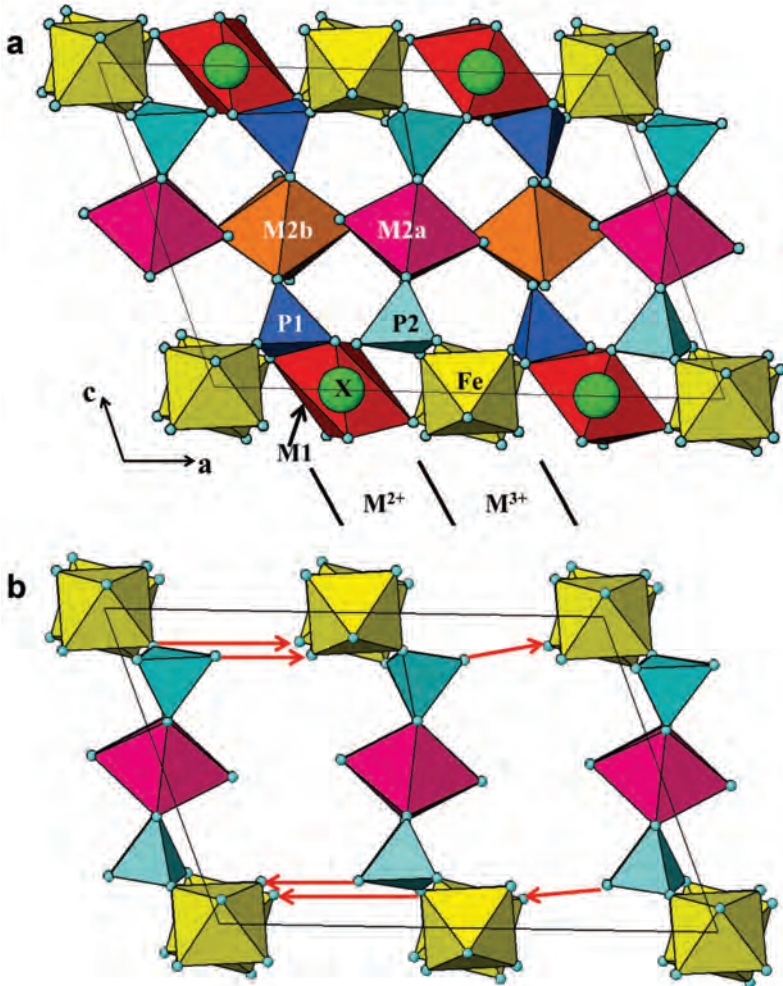
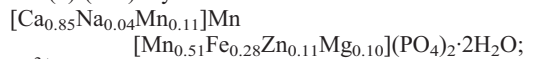


FIG. 4. (a) Projection of jahnsite structure along [010]. (b) Jahnsite after the removal of (010) layers of XM(1)P(1)M(2b) polyhedra. The arrows show the interlayer corner-sharing connections that are required to generate the strunzite structure.

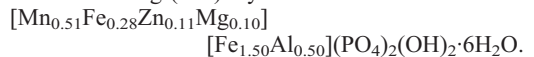
leaching of (100) layers containing the large divalent X and M(1) atoms.

Supporting evidence for this mechanism is provided by the EMP analyses of the two coexisting phases. The jahnsite formula, calculated from the results in Table 1 is  $[\text{Ca}_{0.85}\text{Na}_{0.04}\text{Mn}_{0.11}]\text{Mn}[\text{Mn}_{1.02}\text{Fe}_{0.56}\text{Zn}_{0.22}\text{Mg}_{0.20}][\text{Fe}_{1.50}\text{Al}_{0.50}](\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , where the atoms are assigned to the X, M(1), M(2) and Fe(/Al) sites in order of decreasing size. The M(2) and  $\text{PO}_4$  sites in alternate (100) layers are crystallographically independent, so the composition can be separated into two layers as follows:

XM(1) (100) layer:



$\text{Fe}^{3+}$ -containing (100) layer:



For comparison the Al-bearing strunzite formula from the EMP analyses in Table 1 is



There is a close match between the Al-bearing strunzite formula and that of the second jahnsite



(100) layer, particularly in the level of Al substitution in the Fe sites, which is consistent with the strunzite being derived from the jahnsite by leaching of the XM(1)-containing (100) layers. An extension of this type of mechanism to the leaching of whiteite, the Al analogue of jahnsite, would predict the formation of an Al-dominant strunzite. Whiteite-(CaMnMn) is present in secondary phosphate assemblages at Hagendorf Süd (Chernyateieva *et al.*, 2010; Grey *et al.*, 2010), but despite extensive investigation we have not yet located any associated Al-dominant strunzite-type phase.

## Conclusions

Aluminium-bearing strunzite and jahnsite are found in close association at the 67 m level of the Cornelia mine open cut at Hagendorf Süd. Their crystallographically oriented spatial relationship and respective morphologies (corroded tabular jahnsite grading into fibrous strunzite) are consistent with strunzite being derived from jahnsite by supergene alteration reactions. A comparative study of the two minerals reveals a close structural relationship: the jahnsite structure contains (100) layers with a strunzite-type structure and composition, alternating with (100) layers containing larger divalent atoms. There is a close chemical match between the composition of the strunzite-like layers in jahnsite and the associated strunzite crystals. This leads to a proposed paragenetic mechanism involving the selective leaching of the (100) layers containing large divalent metal atoms, followed by linkage of the residual strunzite-like layers. If such a mechanism was also applicable to whiteite it would produce a new Al-dominant analogue of strunzite.

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Table D1. Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for Al-bearing strunzite.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Mn	15(1)	16(1)	24(1)	-1(1)	1(1)	9(1)
Fe(1)	13(1)	9(1)	14(1)	-3(1)	-4(1)	8(1)
Fe(2)	15(1)	8(1)	16(1)	-4(1)	-4(1)	8(1)
P(1)	12(1)	8(1)	17(1)	-2(1)	-1(1)	6(1)
P(2)	13(1)	10(1)	16(1)	-1(1)	-3(1)	7(1)
O(1)	16(3)	35(3)	20(3)	0(2)	0(2)	9(3)
O(2)	31(3)	20(3)	21(3)	-7(2)	-10(2)	19(3)
O(3)	21(3)	15(2)	16(3)	-2(2)	0(2)	12(2)
O(4)	24(3)	15(3)	15(3)	1(2)	-3(2)	10(2)
O(5)	14(3)	15(2)	19(3)	-2(2)	-5(2)	9(2)
O(6)	29(3)	19(3)	19(3)	1(2)	-5(2)	19(2)
O(7)	16(3)	29(3)	20(3)	-4(2)	-1(2)	6(3)
O(8)	12(3)	17(3)	25(3)	-4(2)	-4(2)	7(2)
OH1	25(3)	19(3)	20(3)	-3(2)	-4(2)	18(2)
OH2	29(3)	10(2)	23(3)	-5(2)	-6(2)	13(2)
Ow1	26(3)	30(3)	30(4)	-4(3)	1(3)	20(3)
Ow2	21(3)	18(3)	30(4)	-1(2)	0(3)	7(2)
Ow3	35(4)	20(3)	28(4)	-5(3)	-7(3)	14(3)
Ow4	68(6)	28(4)	87(7)	0(4)	7(5)	29(4)
Ow	30(3)	30(3)	28(4)	-3(3)	-2(3)	22(3)
Ow	28(3)	18(3)	22(4)	-3(2)	-5(3)	12(3)

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 OH1 0.025(3) 0.019(3) 0.020(3) -0.003(2) -0.004(2) 0.018(2)  
 OH2 0.029(3) 0.010(2) 0.023(3) -0.005(2) -0.006(2) 0.013(2)  
 OW1 0.026(3) 0.030(3) 0.030(4) -0.004(3) 0.001(3) 0.020(3)  
 OW2 0.021(3) 0.018(3) 0.030(4) -0.001(2) 0.000(3) 0.007(2)  
 OW3 0.035(4) 0.020(3) 0.028(4) -0.005(3) -0.007(3) 0.014(3)  
 OW4 0.068(6) 0.028(4) 0.087(7) 0.000(4) 0.007(5) 0.029(4)  
 OW5 0.030(3) 0.030(3) 0.028(4) -0.003(3) -0.002(3) 0.022(3)  
 OW6 0.028(3) 0.018(3) 0.022(4) -0.003(2) -0.005(3) 0.012(3)

\_geom\_special\_details

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All esds (except the esd in the dihedral angle between two l.s. planes)  
 are estimated using the full covariance matrix. The cell esds are taken  
 into account individually in the estimation of esds in distances, angles  
 and torsion angles; correlations between esds in cell parameters are only  
 used when they are defined by crystal symmetry. An approximate (isotropic)  
 treatment of cell esds is used for estimating esds involving l.s. planes.

;

loop\_

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Mn1 OW2 2.219(6) . ?  
Mn1 OW4 2.240(7) . ?  
Fe1 O4 1.936(5) 2\_766 ?  
Fe1 OH2 1.964(5) 2\_665 ?  
Fe1 OH1 1.961(5) . ?  
Fe1 O2 1.968(5) . ?  
Fe1 O5 1.992(5) 1\_655 ?  
Fe1 OW6 2.097(6) 1\_655 ?  
Fe2 O8 1.951(5) 2\_566 ?  
Fe2 O6 1.964(5) 1\_565 ?  
Fe2 OH1 1.964(6) 2\_666 ?  
Fe2 OH2 1.963(6) . ?  
Fe2 O3 1.991(5) 1\_455 ?  
Fe2 OW5 2.097(6) . ?  
P1 O1 1.516(6) . ?  
P1 O3 1.534(5) . ?  
P1 O2 1.532(5) . ?  
P1 O4 1.534(6) 1\_554 ?  
P2 O7 1.501(6) . ?  
P2 O8 1.520(6) . ?  
P2 O6 1.528(5) . ?  
P2 O5 1.545(5) . ?  
O3 Al2 1.991(5) 1\_655 ?  
O3 Fe2 1.991(5) 1\_655 ?  
O4 P1 1.534(6) 1\_556 ?  
O4 Fe1 1.936(5) 2\_766 ?  
O4 Al1 1.936(5) 2\_766 ?  
O5 Al1 1.992(5) 1\_455 ?  
O5 Fe1 1.992(5) 1\_455 ?  
O6 Al2 1.964(5) 1\_545 ?  
O6 Fe2 1.964(5) 1\_545 ?  
O8 Al2 1.951(5) 2\_566 ?  
O8 Fe2 1.951(5) 2\_566 ?  
OH1 Al2 1.964(6) 2\_666 ?  
OH1 Fe2 1.964(6) 2\_666 ?  
OH1 HOH1 0.79(4) . ?  
OH2 Al1 1.964(5) 2\_665 ?  
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OW1 H1B 0.77(4) . ?  
OW2 H2A 0.82(4) . ?  
OW2 H2B 0.78(4) . ?  
OW3 H3A 0.82(4) . ?  
OW3 H3B 0.79(4) . ?  
OW4 H4A 0.79(4) . ?  
OW4 H4B 0.79(4) . ?  
OW5 H5A 0.82(4) . ?  
OW5 H5B 0.81(4) . ?  
OW6 Al1 2.097(6) 1\_455 ?  
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OW6 H6B 0.81(4) . ?

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OW3 Mn1 OW1 88.1(2) . . ?
O1 Mn1 OW2 89.9(2) . . ?
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OW1 Mn1 OW2 176.0(2) . . ?
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OW3 Mn1 OW4 179.4(3) . . ?
OW1 Mn1 OW4 92.4(3) . . ?
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O4 Fe1 OH2 89.8(2) 2_766 2_665 ?
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OH1 Fe1 O2 91.4(2) . . ?
O4 Fe1 O5 90.8(2) 2_766 1_655 ?
OH2 Fe1 O5 87.6(2) 2_665 1_655 ?
OH1 Fe1 O5 89.9(2) . 1_655 ?
O2 Fe1 O5 177.0(2) . 1_655 ?
O4 Fe1 OW6 177.6(2) 2_766 1_655 ?
OH2 Fe1 OW6 89.4(2) 2_665 1_655 ?
OH1 Fe1 OW6 84.2(2) . 1_655 ?
O2 Fe1 OW6 86.1(2) . 1_655 ?
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O8 Fe2 OH1 89.6(2) 2_566 2_666 ?
O6 Fe2 OH1 91.2(2) 1_565 2_666 ?
O8 Fe2 OH2 97.2(2) 2_566 . ?
O6 Fe2 OH2 91.1(2) 1_565 . ?
OH1 Fe2 OH2 172.8(2) 2_666 . ?
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O6 Fe2 O3 177.5(2) 1_565 1_455 ?
OH1 Fe2 O3 87.9(2) 2_666 1_455 ?
OH2 Fe2 O3 89.6(2) . 1_455 ?
O8 Fe2 OW5 177.4(2) 2_566 . ?
O6 Fe2 OW5 86.2(2) 1_565 . ?
OH1 Fe2 OW5 89.0(2) 2_666 . ?
OH2 Fe2 OW5 84.3(3) . . ?
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O3 P1 O4 111.9(3) . 1_554 ?
O2 P1 O4 109.4(3) . 1_554 ?
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O7 P2 O8 106.6(3) . . ?  
O7 P2 O6 108.5(3) . . ?  
O8 P2 O6 110.0(3) . . ?  
O7 P2 O5 111.3(3) . . ?  
O8 P2 O5 112.0(3) . . ?  
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Al2 O6 Fe2 0.00(11) 1\_545 1\_545 ?  
P2 O7 Mn1 140.5(4) . . ?  
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Al1 OH2 Fe1 0.00(7) 2\_665 2\_665 ?  
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Mn1 OW1 H1B 101(8) . . ?  
H1A OW1 H1B 107(8) . . ?  
Mn1 OW2 H2A 115(7) . . ?  
Mn1 OW2 H2B 114(8) . . ?  
H2A OW2 H2B 111(8) . . ?  
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Mn1 OW3 H3B 85(8) . . ?  
H3A OW3 H3B 102(8) . . ?  
Mn1 OW4 H4A 80(8) . . ?  
Mn1 OW4 H4B 109(8) . . ?  
H4A OW4 H4B 112(9) . . ?  
Fe2 OW5 H5A 102(7) . . ?  
Fe2 OW5 H5B 110(8) . . ?  
H5A OW5 H5B 102(7) . . ?  
Al1 OW6 Fe1 0.00(13) 1\_455 1\_455 ?  
Al1 OW6 H6A 92(8) 1\_455 . ?  
Fe1 OW6 H6A 92(8) 1\_455 . ?  
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H6A OW6 H6B 100(7) . . ?

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OW1 H1B O5 0.77(4) 2.19(6) 2.844(9) 142(9) .  
OW1 H1A OW3 0.82(4) 2.35(8) 2.992(10) 135(9) 2\_665  
OW2 H2B O3 0.78(4) 2.16(6) 2.846(9) 148(10) .  
OW2 H2A OW3 0.82(4) 2.28(6) 2.985(10) 144(9) 2\_666  
OW3 H3A O7 0.82(4) 1.90(5) 2.693(8) 162(10) 2\_666  
OW3 H3B OW2 0.79(4) 2.35(7) 2.985(10) 138(9) 2\_666  
OW4 H4A O1 0.79(4) 2.64(10) 3.026(11) 112(9) .  
OW5 H5A O2 0.82(4) 1.82(4) 2.636(8) 170(10) 2\_665  
OW5 H5B OW2 0.81(4) 1.98(5) 2.773(8) 164(11) 2\_666  
OW6 H6A O6 0.79(4) 1.89(5) 2.638(8) 158(10) 2\_556  
OW6 H6B OW1 0.81(4) 2.00(5) 2.781(8) 163(10) 2

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