

Strontioperloffite, $\text{SrMn}_2^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3(\text{OH})_3$, a new bjarebyite-group mineral from the Spring Creek mine, South Australia, Australia

PETER ELLIOTT^{1,2,*}

¹Department of Earth Sciences, School of Physical Sciences, The University of Adelaide, Adelaide, South Australia 5005, Australia

*Corresponding author, e-mail: peter.elliott@adelaide.edu.au

²South Australian Museum, North Terrace, Adelaide, South Australia 5000, Australia

Abstract: Strontioperloffite, $\text{SrMn}_2^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3(\text{OH})_3$, is a new bjarebyite-group mineral from the Spring Creek copper mine, near Wilmington, South Australia, Australia. It occurs as tabular to bladed crystals up to 0.4 mm in size. Associated minerals are copper, cuprite, mitridatite and rhodochrosite. The colour is dark brownish orange and the streak is pale orange. The lustre is vitreous and crystals are translucent. Cleavage is excellent parallel to {100}. Calculated density is 3.89 g/cm³. The mineral is biaxial (–), with $\alpha = 1.805(4)$, $\beta = 1.820(4)$, $\gamma = 1.829(4)$. The calculated $2V$ is 75.0°. Chemical analysis by electron microprobe gave P₂O₅ 31.90, As₂O₅ 0.10, Fe₂O₃ 23.62, Al₂O₃ 0.17, FeO 1.55, MnO 19.41, CaO 0.38, SrO 8.90, BaO 8.65, H₂O_{calc} 4.08, total 98.81 wt%. The empirical formula based on 15 oxygen atoms is $(\text{Sr}_{0.57}\text{Ba}_{0.38}\text{Na}_{0.01})_{\Sigma 0.96}(\text{Mn}_{1.83}^{2+}\text{Fe}_{0.14}^{2+}\text{Ca}_{0.05})_{\Sigma 2.02}(\text{Fe}_{1.98}^{3+}\text{Al}_{0.02})_{\Sigma 2.00}(\text{P}_{3.00}\text{As}_{0.01})_{\Sigma 3.01}\text{O}_{11.98}(\text{OH})_{3.02}$. The ideal formula is $\text{SrMn}_2^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3(\text{OH})_3$. The mineral is monoclinic, $P2_1/m$, with $a = 9.1830(18)$, $b = 12.349(3)$, $c = 5.0081(10)$ Å, $\beta = 100.23(3)^\circ$, $V = 558.91(19)$ Å³ and $Z = 2$. The strongest eight X-ray powder-diffraction lines [d in Å(I)(hkl)] are: 9.055(32)(100), 5.122(23)(120), 3.158(100)(031, 22 $\bar{1}$), 3.106(53)(040), 2.985(20)(211), 2.938(22)(140, 310), 2.892(20)(131) and 1.921(53)(222, 350). Strontioperloffite is isostructural with members of the bjarebyite group. The crystal structure was solved from single-crystal X-ray diffraction data using synchrotron radiation and refined to $R1 = 4.10\%$ on the basis of 1620 unique reflections with $F_o > 4\sigma(F_o)$.

Key-words: strontioperloffite; new mineral; phosphate; bjarebyite group; crystal structure; Spring Creek Mine; South Australia; synchrotron.

1. Introduction

Strontioperloffite is the sixth member of the bjarebyite group of minerals, which have general formula $XM_1M_2(\text{PO}_4)_3(\text{OH})_3$ where: $X = \text{Ba}, \text{Sr}$, $M_1 = \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}$ and $M_2 = \text{Al}, \text{Fe}^{3+}$. The specimen containing the mineral was collected from the dumps of the Spring Creek copper mine, near Wilmington, South Australia in the mid-1980s. Two other bjarebyite-group minerals also occur at the locality, perloffite (Birch & Mumme, 1988; Beyer & Elliott, 1996; Elliott & Willis, 2011) and johntomaite (Kolitsch *et al.*, 2000), for which the mine is the type locality. The mine is well known for its diverse suite of secondary copper and phosphate minerals (Beyer & Elliott, 1996; Kolitsch *et al.*, 1999b) and is the type locality for bariosincosite (Pring *et al.*, 1999) and springcreekite (Kolitsch *et al.*, 1999a). The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2015-023). The holotype specimen is deposited in the South Australian Museum, Adelaide, South Australia (Registration Number G34219).

2. Occurrence

The Spring Creek Mine, situated ~10 km south of Wilmington and on the eastern flank of Mt Remarkable, at the southern end of the Flinders Ranges, South Australia, was discovered in 1860 (Austin, 1863) and was worked intermittently until 1918. The geological sequence in the area is part of the Adelaide System of late Proterozoic age (Binks *et al.*, 1968). The mine is located between quartzite of the Rhynie Sandstone and slate of the Tindelpina Shale immediately south of an east–west fault. The copper mineralization lies as two intersection lodes in the fault zone. The lodes are up to 2.4 m wide with shoots of ore that pitch to the south. Mineralization occurs in a heavily brecciated, hydrothermal vein containing native copper, cuprite and minor chalcocite, chalcopyrite, covellite and pyrite. Secondary minerals occur in small cavities in quartz veins and have crystallised from low-temperature hydrothermal solutions. On the holotype specimen, strontioperloffite occurs in cavities in a matrix of quartz and minor goethite. Species that occur in association with strontioperloffite are copper, cuprite, mitridatite and rhodochrosite.



Fig. 1. Group of strontioferrolophite crystals, 0.5 mm across, on quartz.

3. Appearance, physical and optical properties

Strontioferrolophite is found as tabular to bladed crystals, which occur as individual crystals and as hemispherical aggregates of crystals to 0.5 mm in size (Fig. 1). Crystals are up to 0.4 mm in length and are flattened on {001}. Crystal forms are major {001}, with minor $\{\bar{1}01\}$, {021} and $\{\bar{1}31\}$ (Fig. 2). Crystals are dark brownish orange in colour and are translucent with a vitreous lustre. The streak is pale orange. The mineral is nonfluorescent. The Mohs hardness is 4.5. Crystals are brittle with one excellent cleavage parallel to {100}. Fracture is uneven. Crystals sink very slowly in the heaviest liquid that was available, diluted Clerici solution ($d = 3.80 \text{ g/cm}^3$). The calculated density is 3.89 g/cm^3 based on the empirical formula. Optically, strontioferrolophite is biaxial (-), with $\alpha = 1.805(4)$, $\beta = 1.820(4)$, $\gamma = 1.829(4)$ measured in white light. Conoscopic observation was not possible, however, the calculated $2V$ is 75.0° .

4. Chemical analysis

Chemical data for strontioferrolophite were obtained using a Cameca SXFive electron microprobe operating in wavelength dispersive mode at an accelerating potential of 20 kV, a sample current of 20 nA and a 5 μm beam diameter. The standards used are as follows: barite (Ba $K\alpha$), albite (Na $K\alpha$), almandine (Fe $K\alpha$, Al $K\alpha$), rhodonite (Mn $K\alpha$), celestite (Sr $K\alpha$), gallium arsenide (As $K\alpha$) and hydroxylapatite (Ca $K\alpha$, P $K\alpha$). No additional element with atomic number ≥ 9 was detected in amounts $>0.05 \text{ wt}\%$ oxide. Data were reduced using the $\phi(\rho Z)$ method of Pouchou & Pichoir (1985). Analytical results are given in Table 1. The empirical formula based on 15 oxygen atoms is $(\text{Sr}_{0.57}\text{Ba}_{0.38}\text{Na}_{0.01})_{\Sigma 0.96}(\text{Mn}_{1.83}^{2+}\text{Fe}_{0.14}^{2+}\text{Ca}_{0.05})_{\Sigma 2.02}(\text{Fe}_{1.98}^{3+}\text{Al}_{0.02})_{\Sigma 2.00}(\text{P}_{3.00}\text{As}_{0.01})_{\Sigma 3.01}\text{O}_{11.98}(\text{OH})_{3.02}$. The ideal formula is $\text{SrMn}_2^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3(\text{OH})_3$.

5. Infrared spectroscopy

An infrared absorption spectrum of strontioferrolophite was obtained using a Nicolet 5700 FTIR spectrometer equipped

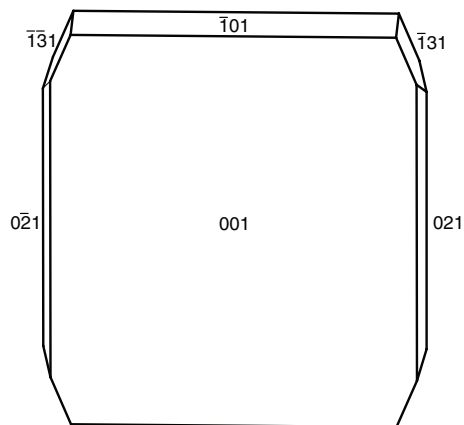


Fig. 2. Crystal drawing of strontioferrolophite. Drawing produced using SHAPE (Shape Software, 2005).

Table 1. Compositional data for strontioferrolophite.

Oxide	Wt%	Range	SD	Probe standard
P ₂ O ₅	31.90	31.30–33.31	0.58	Hydroxylapatite
As ₂ O ₅	0.10	0.02–0.18	0.05	Gallium arsenide
Fe ₂ O ₃ *	23.62	23.42–24.17	0.21	Almandine
Al ₂ O ₃	0.17	0.15–0.22	0.02	Almandine
FeO*	1.55	0.61–2.27	0.44	Almandine
MnO	19.41	19.09–19.79	0.25	Rhodonite
CaO	0.38	0.32–0.52	0.06	Hydroxylapatite
SrO	8.90	8.05–9.61	0.53	Celestite
BaO	8.65	7.85–9.71	0.62	Barite
NaO	0.05	0.03–0.10	0.02	Albite
H ₂ O**	4.08			
Total	98.81			

Note: Number of analyses = 13. SD = standard deviation.*FeO and Fe₂O₃ calculated to give Fe³⁺ + Al = 2.00;

**H₂O calculated from structural data.

with a Nicolet Continuum IR microscope and a diamond-anvil cell. A powdered crystal aggregate was used to record a spectrum in the range 4000–650 cm^{-1} (Fig. 3). The spectrum shows two distinct bands in the OH-stretching region. A broad band 3495–2740 cm^{-1} centred around 3160 cm^{-1} and a sharp band at 3565 cm^{-1} can be attributed to ν O–H stretching vibrations. Based on the correlation relation of Libowitzky (1999) the observed O–H stretching frequencies suggest O...O distances of ~ 2.68 and 3.03 Å which are indicative of strong and weak hydrogen bonds respectively, consistent with distances of 2.650 and 3.329 Å obtained from the crystal structure refinement. Bands at 1030 cm^{-1} with shoulders at 1198, 1165, 1030 and 945 cm^{-1} and the weaker band at 1200 cm^{-1} are assigned to PO₄ ν_3 antisymmetric stretching vibrations. The band at 665 cm^{-1} may be attributed to PO₄ ν_4 vibrations.

6. X-ray crystallography

Powder X-ray diffraction (Table 2) data were collected using a Rigaku Hiflux Homelab diffractometer (Cu $K\alpha$

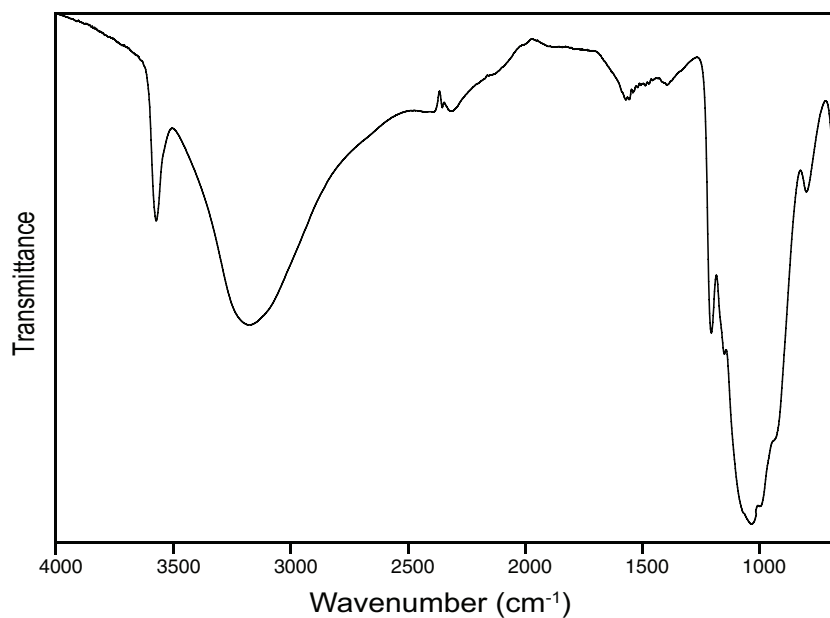


Fig. 3. The FT-IR spectrum of powdered strontioperloffite. Note: The band at 2315 cm^{-1} is due to atmospheric CO_2 .

Table 2. X-ray powder diffraction data for strontioperloffite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	h	k	l	I_{obs}	d_{obs}	I_{calc}	d_{calc}	h	k	l
32	9.055	20	9.056	1	0	0			{ 6	2.465	0	0	2
2	7.309	4	7.321	1	1	0	9	2.465	{ 8	2.464	1	4	1
2	6.210	4	6.219	0	2	0	1	2.374	5	2.373	2	4	$\bar{1}$
23	5.122	29	5.126	1	2	0	2	2.323	5	2.323	3	3	$\bar{1}$
4	4.927	7	4.929	0	0	1			{ 5	2.227	4	1	0
19	4.682	24	4.691	1	0	$\bar{1}$	3	2.230	{ 2	2.211	4	0	$\bar{1}$
13	4.576	{ 11	4.582	0	1	1			{ 9	2.198	1	5	$\bar{1}$
		{ 4	4.528	2	0	0	6	2.194	{ 5	2.195	2	2	$\bar{2}$
2	4.397	7	4.389	1	1	$\bar{1}$	2	2.138	3	2.139	1	2	2
3	4.115	4	4.040	1	0	1	1	2.118	1	2.118	1	5	1
3	3.865	4	3.863	0	2	1	2	2.092	11	2.083	4	2	$\bar{1}$
4	3.764	{ 6	3.769	1	3	0			{ 6	2.070	3	1	$\bar{2}$
		{ 4	3.745	1	2	$\bar{1}$	6	2.069	{ 6	2.073	3	3	1
		{ 5	3.673	2	0	$\bar{1}$			4	2.060	2	5	$\bar{1}$
6	3.666	{ 12	3.661	2	2	0	1	2.041	2	2.042	2	3	$\bar{2}$
4	3.527	8	3.523	2	1	$\bar{1}$	1	2.020	1	2.020	2	0	2
3	3.391	4	3.388	1	2	1	3	1.994	7	1.989	3	2	$\bar{2}$
100	3.158	{ 40	3.173	0	3	1	1	1.952	1	1.951	4	3	$\bar{1}$
		{ 100	3.163	2	2	$\bar{1}$			{ 69	1.921	2	2	2
53	3.106	88	3.109	0	4	0	53	1.921	{ 5	1.920	3	5	0
10	3.060	18	3.058	2	3	0	1	1.896	2	1.896	1	6	$\bar{1}$
20	2.985	39	2.985	2	1	1	1	1.868	1	1.873	2	4	$\bar{2}$
22	2.938	{ 22	2.941	1	4	0	1	1.837	1	1.837	4	0	$\bar{2}$
		{ 20	2.934	3	1	0	2	1.814	2	1.816	2	3	2
20	2.892	29	2.893	1	3	1	1	1.758	1	1.761	1	5	$\bar{2}$
19	2.749	{ 9	2.757	2	2	1	1	1.718	1	1.719	2	6	1
		{ 15	2.749	2	3	$\bar{1}$	1	1.691	1	1.694	2	4	2
	2.735	28	2.736	3	1	$\bar{1}$	1	1.665	1	1.667	3	6	$\bar{1}$
12	2.715	17	2.716	3	2	0	9	1.638	13	1.640	2	0	$\bar{3}$
4	2.587	8	2.592	1	4	$\bar{1}$	1	1.607	1	1.611	5	0	1
1	2.564	4	2.563	2	4	0	1	1.584	1	1.586	0	6	2
11	2.491	19	2.492	1	0	$\bar{2}$							

Note: I_{calc} calculated with programme Rietica (Hunter, 1998).

Table 3. Crystal data, data collection and refinement details.

Crystal data	
Structural formula	(Sr _{0.60} Ba _{0.38} Na _{0.02})(Mn _{1.86} ²⁺ Fe _{0.10} ²⁺ Ca _{0.00})(Fe _{1.98} ³⁺ Al _{0.02})(P _{3.00} As _{0.01})O ₁₂ (OH) ₃
Space group	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.1830(18), 12.349(3), 5.0081(10)
β (°)	100.23(3)
<i>V</i> (Å ³), <i>Z</i>	558.91(19), 2
<i>F</i> (000)	628.2
μ (mm ⁻¹)	9.40
Absorption correction	Multi-scan
Crystal dimensions (mm)	0.035 × 0.020 × 0.008
Data collection	
Diffractometer	ADSC Quantum 315r
Temperature (K)	293
Wavelength	Mo <i>K</i> α, λ = 0.71080 Å
θ range (°)	2.25–30.05
Detector distance (mm)	89.9
Rotation axes, width (°)	φ; 1
Total no. of frames	360
Collection time per frame (s)	1
<i>h</i> , <i>k</i> , <i>l</i> ranges	$\bar{1}2 \rightarrow 12$, $\bar{1}7 \rightarrow 17$, $\bar{7} \rightarrow 7$
Total reflections measured	10 687
Data completeness (%)	96.2
Unique reflections	1639 (<i>R</i> _{int} = 0.0393)
Refinement	
Refinement on	<i>F</i> ²
<i>R</i> ₁ [*] for <i>F</i> _o > 4σ(<i>F</i> _o)	4.10%
<i>wR</i> ₂ [†] for all <i>F</i> _o ²	14.83%
Reflections used <i>F</i> _o > 4σ(<i>F</i> _o)	1639
Number of parameters refined	119
Extinction factor	0.158(12)
Δρ _{min} , Δρ _{max} (e/Å ³)	1.642, −1.405
Goof	0.950

$$*R1 = \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$†wR2 = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2)^{1/2};$$

$$w = 1/[\sigma^2(F_o^2) + (0.042 P)^2 + 12.60 P];$$

$$P = (\max \text{ of } (0 \text{ or } F_o^2)) + 2 F_o^2 / 3.$$

X-radiation, λ = 1.540598 Å). Calculated intensities were obtained from the structural model. Unit-cell parameters refined using the Le Bail profile-fitting method (Le Bail *et al.*, 1988; Hunter, 1998) starting from the unit-cell parameters determined from single-crystal techniques are *a* = 9.202(3), *b* = 12.442(3), *c* = 5.008(1) Å, β = 100.15(2)°, *V* = 564.32(3) Å³.

A 0.035 × 0.020 × 0.008 crystal fragment was used for data collection 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 0.71080 Å. A φ scan was employed, with frame widths of 1° and a counting time of 1 s per frame. The data were integrated using XDS (Kabsch, 2010). Absorption correction was carried out with SADABS (Bruker, 2001). Details of data collection and refinement are given in Table 3. Structure refinement (SHELXL, Sheldrick, 2015) was initiated in space group *P*2₁/*m* using the atom positions for bjarebyite (Moore & Araki, 1974) and the

structure was refined by full-matrix least-squares to an *R*1 index of 4.34%. The two hydrogen atom sites associated with the OH groups were identified in difference-Fourier maps and were inserted into the refinement with the O–H distances restrained to 0.95(2) Å. Refinement of all parameters converged to a final *R* index of 4.10% for anisotropic-displacement parameters for all non H atoms. Refined atom coordinates and anisotropic-displacement parameters are listed in Table 4, selected interatomic distances are given in Table 5, and bond valences are given in Table 6.

7. Structure description

Strontioperloffite is isostructural with minerals of the bjarebyite group (Table 7). The structure, shown in Fig. 4, contains one *X* site (occupied by Sr, Ba and minor Na), one *M*1 site (occupied by Mn²⁺, Fe²⁺ and minor Ca), one *M*2 site, (occupied by Fe³⁺ and minor Al), two P sites. [M₂O₃(OH)₃] octahedra share OH9–OH9 edges to form [M₂O₆(OH)₄] dimers which corner-link to form [M₂O₆(OH)₃] chains along the **b**-direction (Fig. 4). The octahedra that share corners are also linked by P1O₄ tetrahedra. The chains are decorated by P2O₄ tetrahedra, which link between chains in the **c**-direction. Chains link in the **a**-direction via [M1O₅(OH)] octahedra, which share an edge with [M₂³⁺O₃(OH)₃] octahedra and corners with P1O₄ and P2O₄ tetrahedra (Fig. 5).

The *X* site coordinated by ten O atoms and one OH group occupies channels parallel to [001] and provides linkage between chains in the **a**-direction. The refined site-scattering located at the *X* site, 44.84(8) electrons, implies an occupancy of Sr_{0.62}Ba_{0.38}, which is consistent with the chemical analysis. The <*X*–O> distance of 2.908 Å is greater than that calculated for this occupancy (2.830 Å; Shannon, 1976) and the site has a deficient bond valence sum (Table 6). The equivalent sites in the structures of perloffite and johntomaite have an <*X*–O> distance near that expected for full occupancy of site by Ba (2.953 and 2.939 respectively Å). The <*X*–O> distances in the structures of bjarebyite (Moore & Araki 1974; Rotiroti *et al.*, 2016), kulanite (Cooper & Hawthorne, 1994) and penikisite (Bowman *et al.*, 2013) (2.874, 2.887 and 2.876 Å respectively) are less than expected for the occupancy of site by Ba and the sites have bond valence sums greater than the ideal. The difference in the size of the *X* site in these structures can be attributed to the difference in size of Fe³⁺, which occupies the *M*2 site in perloffite, johntomaite and strontioperloffite, and Al, which occupies the *M*2 site in bjarebyite, kulanite and penikisite. The difference in the size of the *X* sites is most pronounced along the **b**-direction. The (M₂φ₉) chains, which share edges with the *X* site, have a shorter repeat along the **b**-direction when the *M*2 site is occupied by Al and a longer repeat when occupied by Fe³⁺. Hence, occupancy of the *M*2 site has a significant effect on the <*X*–O> distance.

Coordination of the *M*1 and *M*2 sites is similar to the sites in the structures of other bjarebyite group minerals. The M1O₆ octahedron is strongly distorted, whereas the M2O₆ octahedron is relatively undistorted. The *M*1 site has a

Table 4. Atomic fractional coordinates and displacement parameters (\AA^2) for strontioferroite.

	<i>x</i>	<i>y</i>	<i>z</i>	U^{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
X^a	0.54362(6)	0.75	0.74599(11)	0.0160(3)	0.0136(3)	0.0203(4)	0.0134(3)	0	0.0003(2)	0
$M1^b$	0.29762(9)	-0.10879(6)	0.20357(15)	0.0127(3)	0.0118(4)	0.0127(4)	0.0133(4)	0.0004(2)	0.0013(3)	0.0002(2)
$M2^c$	0.09407(8)	0.39843(6)	0.13251(14)	0.0120(3)	0.0111(4)	0.0136(4)	0.0109(4)	0.0002(2)	0.0013(3)	-0.0004(2)
P1	0.1626(2)	0.75	0.6796(4)	0.0114(4)	0.0100(7)	0.0140(8)	0.0100(7)	0	0.0012(6)	0
P2	0.33912(14)	0.44189(11)	0.7095(2)	0.0122(3)	0.0109(5)	0.0150(6)	0.0106(6)	0.0003(4)	0.0014(4)	0.0002(4)
O1	0.2807(6)	0.75	0.9374(11)	0.0170(10)	0.015(2)	0.023(3)	0.012(2)	0	0.0002(18)	0
O2	0.2410(6)	0.75	0.4342(10)	0.0120(9)	0.015(2)	0.010(2)	0.010(2)	0	0.0003(17)	0
O3	0.0646(4)	0.6487(3)	0.6753(7)	0.0141(7)	0.0133(15)	0.0153(17)	0.0140(15)	0.0001(13)	0.0029(13)	-0.0018(13)
O4	0.3784(4)	0.5538(3)	0.6128(8)	0.0165(7)	0.0164(17)	0.0174(18)	0.0161(16)	0.0048(13)	0.0039(14)	-0.0002(14)
O5	0.2635(4)	0.4568(3)	0.9636(8)	0.0161(7)	0.0140(16)	0.0180(18)	0.0171(17)	-0.0002(14)	0.0052(13)	-0.0016(14)
O6	0.2348(5)	0.3812(3)	0.4813(8)	0.0183(8)	0.0206(18)	0.0188(18)	0.0133(16)	-0.0012(14)	-0.0030(14)	0.0022(15)
O7	0.4744(4)	0.3681(3)	0.7988(8)	0.0162(7)	0.0120(16)	0.0140(17)	0.0223(17)	0.0022(14)	0.0025(13)	0.0015(13)
OH8	0.1369(7)	0.25	0.0025(12)	0.0159(10)	0.021(3)	0.009(2)	0.019(2)	0	0.006(2)	0
OH9	0.0629(4)	0.5601(3)	0.1928(7)	0.0130(7)	0.0131(15)	0.0136(17)	0.0116(15)	-0.0017(12)	0.0000(12)	-0.0019(13)
H8	0.127(18)	0.25	-0.189(10)	0.04(2)						
H9	0.053(12)	0.584(9)	0.364(13)	0.04(2)						

Note: The anisotropic displacement factors (U^{ij}) are defined as $\exp[-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 j U_{ij} a_i^* a_j^* h_i h_j]$.

^aRefined occupancy Sr_{0.60}, Ba_{0.38}, Na_{0.02};

^bRefined occupancy Mn_{0.93}²⁺, Fe_{0.05}²⁺, Ca_{0.02};

^cRefined occupancy Fe_{0.99}³⁺, Al_{0.01}.

Table 5. Selected interatomic distances (\AA) and hydrogen bonds for strontioferroite.

<i>X</i>	O7 (×2)	2.736(4)	<i>M2</i>	O3	1.971(4)		
	O1	2.751(6)		O6	1.991(4)		
	O4 (×2)	2.874(4)		O8	2.007(2)		
	O2	2.936(5)		O5	2.031(4)		
	O6 (×2)	2.980(4)		O9	2.040(4)		
	O8	2.980(6)		O9	2.047(4)		
	O7 (×2)	3.072(4)		< <i>M-O</i> >	2.015		
	< <i>X-O</i> >	2.908					
	<i>M1</i>	O7		2.115(4)	<i>P1</i>	O2	1.531(6)
		O4		2.161(4)		O1	1.531(6)
O1		2.184(3)	O3 (×2)	1.539(4)			
O2		2.204(3)	< <i>P-O</i> >	1.535			
O5		2.221(4)					
O9		2.229(4)	<i>P2</i>	O4	1.529(4)		
< <i>M-O</i> >		2.186		O7	1.542(4)		
				O6	1.548(4)		
			O5	1.565(4)			
			< <i>P-O</i> >	1.546			

Hydrogen bonds

<i>D-H...A</i>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	$\angle D-H...A$
OH8-H8...O6 ⁱ	0.95(2)	2.63(2)	3.329(4)	130.9(4)
OH8-	0.95(2)	2.63(2)	3.329(4)	130.9(4)
OH8...O6 ⁱⁱ				
OH9-	0.93(2)	1.74(2)	2.650(4)	167.3(4)
OH9...O3 ⁱⁱⁱ				

Symmetry codes: (i) $x + 1, y, z + 1$; (ii) $x, -y + 1/2, z - 1$; (iii) $x, y, z - 1$.

refined site-scattering value of 24.96 *epfu* and is occupied by predominantly Mn²⁺ with minor Fe²⁺ and Ca. Chemical analyses of minerals in the perloffite-johntomaite series from the Spring Creek mine show Ca contents of up to 0.80 *apfu*. The analyses, plus crystal structure refinements, show that Ca is incorporated into the *M1* site in these

Table 6. Bond-valence* analysis for strontioferroite.

	<i>X</i>	<i>M1</i>	<i>M2</i>	<i>P1</i>	<i>P2</i>	<i>H1</i>	<i>H2</i>	Sum
<i>O1</i>	0.22	0.35		1.26				2.18
		0.35 →						
<i>O2</i>	0.14	0.33 × 2 →		1.26				2.06
<i>O3</i>			0.57	1.24 × 2 ↓			0.22	2.03
<i>O4</i>	0.17 × 2 ↓	0.36			1.27			1.80
<i>O5</i>		0.32	0.48		1.16			1.96
<i>O6</i>	0.13 × 2 ↓		0.54		1.21	0.05		1.93
<i>O7</i>	0.23 × 2 ↓	0.41			1.23			1.98
	0.11 × 2 ↓							
OH8	0.13		0.51 × 2 →			0.95		2.10
OH9		0.31	0.46				0.78	2.02
			0.47					
Sum	1.77	2.08	3.03	5.00	4.87	1.00	1.00	

*Bond-valence parameters used are from Gagné & Hawthorne (2015). Bond-valences for the *X*, *M1* and *M2* sites are based on the refined occupancy.

minerals. Results will be published in a separate paper. The site is coordinated by five O atoms shared with PO₄ tetrahedra and one OH group. The <*M1-O*> distance of 2.186 \AA is consistent with the corresponding distance in the structures of other bjarebyite group minerals: perloffite, johntomaite and bjarebyite. This distance is shorter in the structures of kulanite and penikisite due to the occupancy of the site by significant Mg. The *M2* site is coordinated by four O atoms shared with PO₄ tetrahedra and two OH groups. Refined site-scattering (24.96 *epfu*), bond distances (Table 5) and the bond-valence sum at the site (Table 6) indicate that the site is occupied by Fe³⁺ and minor Al. As expected, the <*M2-O*> distances are smaller in bjarebyite, kulanite and penikisite as the smaller Al cation is accommodated in the *M2* site in these structures.

Table 7. Comparison of related minerals.

Mineral	Strontioferloffite	Bjarebyite	Johntomaite	Kulanite	Perloffite	Penikisite
Formula	(Sr, Ba)Mn ₂ ²⁺ Fe ₂ ³⁺ (PO ₄) ₃ (OH) ₃	(Ba, Sr)(Mn, Fe, Mg) ₂ Al ₂ (PO ₄) ₃ (OH) ₃	Ba(Fe, Ca, Mn) ₂ Fe ₂ (PO ₄) ₃ (OH) ₃	Ba(Fe, Mn, Mg) ₂ Al ₂ (PO ₄) ₃ (OH) ₃	Ba(Mn, Fe) ₂ Fe ₂ (PO ₄) ₃ (OH) ₃	BaMg ₂ Al ₂ (PO ₄) ₃ (OH) ₃
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> (Å)	9.2195(18)	8.930(14)	9.199(9)	9.014(1)	9.223(5)	8.9577(4)
<i>b</i> (Å)	12.410(3)	12.073(24)	12.359(8)	12.074(1)	12.422(8)	12.0150(5)
<i>c</i> (Å)	4.9990(10)	4.917(9)	5.004(2)	4.926(1)	4.995(2)	4.9079(2)
β (°)	100.09(3)	100.15(13)	100.19(6)	100.48(1)	100.39(4)	100.505(2)
<i>V</i> (Å ³)	563.12(19)	521.8	559.9(5)	527.1(1)	562.9(5)	519.37
<i>Z</i>	2	2	2	2	2	2
Reference	this work	Moore & Araki (1974)	Kolitsch <i>et al.</i> (2000)	Cooper & Hawthorne (1994)	Kampf (1977)	Bowman <i>et al.</i> (2013)

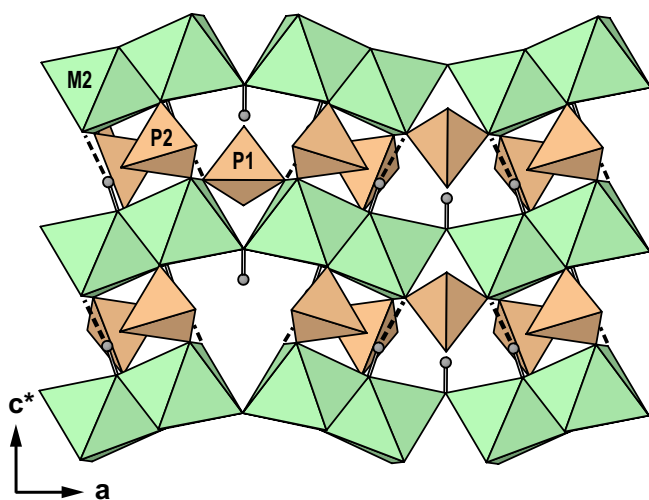


Fig. 4. The crystal structure of strontioferloffite projected onto (100). Hydrogen atoms are grey spheres. Hydrogen bonds are indicated by dotted lines. All structure drawings were completed with ATOMS (Shape Software, 1997).

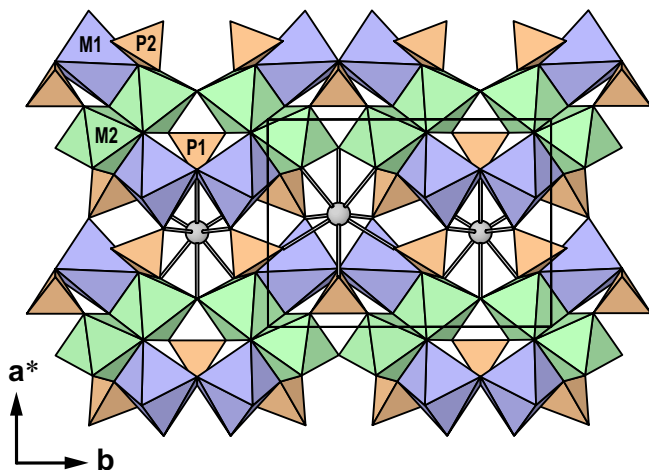


Fig. 5. The crystal structure of strontioferloffite projected onto (001). The X positions are shown as grey spheres.

There are two hydrogen atoms in the structure; both were located in electron density maps. The H9 atom associated with OH9 hydrogen-bonds to O3 with a donor-acceptor

distance of H9...O3 = 1.74(2) Å and an OH9–H9...O3 angle of 167(4)°, an arrangement typical of strong hydrogen bonding. The H8 atom provides a weak hydrogen-bond to O6 with a donor-acceptor distance of H8...O6 = 2.63(2) Å and an OH8–H8...O6 angle of 130.9(4)°.

Acknowledgements: The author thanks Ben Wade of Adelaide Microscopy, The University of Adelaide for assistance with the microprobe analysis. The infrared spectrum was obtained with the assistance of the Forensic Science Centre, Adelaide. Reviewers Taras Panikorovskii and Anthony Kampf are thanked for their constructive comments on the manuscript. The author acknowledges access to the Macromolecular beam line MX2 at the Australian Synchrotron, for collection of single-crystal X-ray data.

References

- Austin, J.B. (1863): The Mines of South Australia. Platts, Wigg, Dehane, Howell, Rigby and Mullet, Adelaide, 27–28.
- Beyer, B.D. & Elliott, P. (1996): Minerals from the Spring Creek mine, near Wilmington, South Australia. *Aust. J. Mineral.*, **2**, 57–70.
- Binks, P.J., Forbes, B.G., Mirams, R.C. (1968): Orroroo sheet, S 54-1, South Australia 1:250,000 geological map series. Geological Survey of South Australia, Adelaide.
- Birch, B. & Mumme, W.G. (1988): Hentschelite and perloffite from the Spring Creek Copper Mine, South Australia. *Mineral. Mag.*, **52**, 408–411.
- Bowman, M.G., Downs, R.T., Yang, H. (2013): Penikisite, BaMg₂Al₂(PO₄)₃(OH)₃, isostructural with bjarebyite. *Acta Cryst.*, **E69**, i4–i5.
- Bruker (2001): SADABS. Bruker AXS Inc., Madison, Wisconsin.
- Cooper, M. & Hawthorne, F.C. (1994): Refinement of the crystal structure of kulanite. *Can. Mineral.*, **32**, 15–19.
- Elliott, P. & Willis, A.C. (2011): The crystal structure of perloffite. *Mineral. Mag.*, **75**, 317–325.
- Gagné, O.C. & Hawthorne, F.C. (2015): Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Cryst.*, **B71**, 562–578.
- Hunter, B.A. (1998): Rietica – A visual rietveld program. *Comm. Powder Diffr. Newsletter*, **20**, 21.
- Kabsch, W. (2010): XDS. *Acta Cryst.*, **D66**, 125–132.
- Kampf, A.R., (1977): A new mineral: perloffite, the Fe³⁺ analogue of bjarebyite. *Mineralogical Record*, **8**, 112, 114.

- Kolitsch, U., Taylor, M.R., Fallon, G., Pring, A. (1999a): Springcreekite, $\text{BaV}_3^{3+}(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_5$, a new member of the crandallite group, from the Spring Creek mine, South Australia: the first natural V^{3+} -member of the alunite family and its crystal structure. *N. Jb. Mineral. Mh.*, **1999**, 529–544.
- Kolitsch, U., Pring, A., Elliott, P. (1999b): An update on the mineralogy of the Spring Creek mine, South Australia, including the new species springcreekite, bariosincosite and tomaite. *Aust. J. Mineral.*, **5**, 55–62.
- Kolitsch, U., Pring, A., Tiekink, E.R.T. (2000): Johntomaite, a new member of the bjarebyite group of barium phosphates: description and structure refinement. *Mineral. Petrol.*, **70**, 1–14.
- Le Bail, A., Duroy, H., Fourquet, J.L. (1988): Ab-initio structure determination of LiSbWO_6 by X-ray powder diffraction. *Mater. Res. Bull.*, **23**, 447–452.
- Libowitzky, E. (1999): Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatsh. Chem.*, **130**, 1047–1059.
- Moore, P.B. & Araki, T. (1974): Bjarebyite, $\text{Ba}(\text{Mn}, \text{Fe})_2^{2+}\text{Al}_2(\text{OH})_3[\text{PO}_4]_3$: Its atomic arrangement. *Am. Mineral.*, **59**, 567–572.
- Pouchou, J.L. & Pichoir, F. (1985): “PAP” ϕ (ρZ) procedure for improved quantitative microanalysis. in “Microbeam Analysis”. Armstrong, J.T., ed. San Francisco Press, California, 104–106.
- Pring, A., Kolitsch, U., Birch, W.D., Beyer, B.D., Elliott, P., Ayyappan, P., Ramanan, A. (1999): Bariosincosite, a new hydrated barium vanadium phosphate, from the Spring Creek Mine, South Australia. *Mineral. Mag.*, **63**, 735–741.
- Rotiroli, N., Vignola, P., Bersani, D., Simmons, W.B., Falster, A.U., Whitmore, R.W., Nizamoff, J.W., Lotti, P., Risplendente, A., Pavese, A. (2016): On the crystal-chemistry of bjarebyite, $\text{BaMn}_2^{2+}\text{Al}_2(\text{PO}_4)_3(\text{OH})_3$, from the Palermo #1 pegmatite, Grafton County, New Hampshire. *Can. Mineral.*, **54**, 1033–1041.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751–767.
- Shape Software (1997): ATOMS for Windows and Macintosh V 4.0, Kingsport, Tennessee, USA.
- (2005): *SHAPE for Windows, version 7.1*, Kingsport, Tennessee, USA.
- Sheldrick, G.M. (2015): Crystal structure refinement with SHELXL. *Acta Cryst.*, **C71**, 3–8.

Received 25 July 2018

Modified version received 10 September 2018

Accepted 12 September 2018