



## Article

# Plumboperloffite, $\text{PbMn}_2^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3(\text{OH})_3$ , a new member of the bjarebyite group from Wiperaminga Hill, South Australia, Australia

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### Abstract

Plumboperloffite,  $\text{PbMn}_2^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3(\text{OH})_3$ , is a new mineral and member of the bjarebyite group from Wiperaminga Hill West Quarry, Boolcoomatta Reserve, Olary Province, South Australia, Australia. The mineral was found in a single cavity in triplite–barbosolite matrix associated with fluorapatite, phosphosiderite, natrodufrénite and fluorite. The mineral forms intergrowths of subparallel, thin tabular to bladed crystals. Individual crystals are up to 40  $\mu\text{m}$  in length. Plumboperloffite is brownish orange in colour with a vitreous lustre. The mineral has brittle tenacity, an excellent cleavage on {100} and uneven fracture. The calculated density is 4.416  $\text{g}/\text{cm}^3$ . Plumboperloffite is biaxial (+),  $\alpha = 1.87(1)$ ,  $\beta = 1.88(1)$  and  $\gamma = 1.89(1)$  as measured in white light. The measured 2V is 88(1)°. Dispersion is apparently strong, based on extinction colours and the orientation is  $Y = \mathbf{b}$ . The pleochroism in shades of yellow brown is  $X < Z < Y$ . Electron microprobe analysis gave the empirical formula (based on 15 O apfu)  $(\text{Pb}_{0.92}\text{Ca}_{0.04}\text{Ba}_{0.01}\text{K}_{0.01})_{\Sigma 0.98}(\text{Mn}_{1.84}\text{Fe}_{0.13})_{\Sigma 1.97}(\text{Fe}_{1.97}\text{Al}_{0.03})_{\Sigma 2.00}(\text{P}_{3.01}\text{O}_{11.94})(\text{OH})_{\Sigma 3.06}$ . Plumboperloffite is monoclinic, space group  $P2_1/m$  with  $a = 9.1765(18)$ ,  $b = 12.340(3)$ ,  $c = 5.0092(10)$  Å,  $\beta = 101.01(3)^\circ$ ,  $V = 556.8(2)$  Å<sup>3</sup> and  $Z = 2$ . The crystal structure has been refined using X-ray single-crystal data to a final  $R_1 = 0.0207$  on the basis of 1417 reflections with  $F_o > 4\sigma(F_o)$ . The mineral is isostructural with members of the bjarebyite-group minerals.

**Keywords:** plumboperloffite; new mineral species; bjarebyite group; crystal structure; pegmatitic phosphate; Wiperaminga Hill West Quarry; Australia

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### Introduction

Bjarebyite-group minerals are secondary phosphates that occur primarily in granitic pegmatites, but have also been found in the oxidised zones of ore deposits. Bjarebyite was first described from the Palermo No.1 pegmatite, New Hampshire, USA by Moore *et al.* (1973) and its atomic structure was determined by Moore and Araki (1974). The bjarebyite group currently consists of seven International Mineralogical Association (IMA) approved minerals (Table 1). The minerals have the general formula  $\text{XM}_1\text{M}_2(\text{PO}_4)_3(\text{OH})_3$  where  $X = \text{Ba}, \text{Sr}, \text{Pb}$ ;  $\text{M}_1 = \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}$  and  $\text{M}_2 = \text{Al}$  or  $\text{Fe}^{3+}$ . Until the discovery of strontioferroperloffite (Elliott, 2019), all group members contained Ba as the dominant cation at the X site. The new mineral species, plumboperloffite, characterised and described in this paper, is the first member of the group with Pb dominant at the X site. The name is for the relationship to perloffite with Pb dominating the X site. The mineral and mineral name (symbol Pplf) have been approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification (IMA2020-007,

Elliott and Kampf, 2020). The type specimen is deposited in the South Australian Museum, Adelaide, South Australia, (Registration number G34868).

### Occurrence

Plumboperloffite was found on a specimen collected in 2018 from the dumps of the Wiperaminga Hill West Quarry, Boolcoomatta Reserve, Olary Province, South Australia, Australia (140°27'34"E, 31°57'42"S). Pegmatites at Wiperaminga Hill were exploited for feldspar, beryl and muscovite between 1957 and 1980 (Olliver and Steveson, 1982). Four pegmatites were worked in three workings on Wiperaminga Hill West and Wiperaminga Hill East. Recorded production is 31.7 tonnes of beryl and 2030 tonnes of feldspar. The pegmatites occur near the base of a prominent range of hills which comprise banded quartz–mica gneiss and schist of the Early to Middle Proterozoic age Willyama Complex. The metasediments have been granitised and in many places are intruded by granite and associated pegmatite and aplite bodies. The pegmatites are usually small lenticular bodies varying from 6 m to 30 m in length and from 1 m to 3 m in width (Hiern, 1966). The pegmatites are mineralogically zoned and comprise an outer border zone of fine- to medium-grained microcline, quartz, plagioclase and muscovite, an intermediate zone of coarse-grained

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**Table 1.** Comparison of related minerals.

Mineral name	plumboperloffite	strontioperloffite	bjarebyite	johntomaite	kulanite	perloffite	penikisite
Formula	$\text{PbMn}_2^+\text{Fe}_3^{3+}$ ( $\text{PO}_4$ ) <sub>3</sub> (OH) <sub>3</sub>	$\text{SrMn}_2^+\text{Fe}_3^{3+}$ ( $\text{PO}_4$ ) <sub>3</sub> (OH) <sub>3</sub>	$\text{BaMn}_2^+\text{Al}_2$ ( $\text{PO}_4$ ) <sub>3</sub> (OH) <sub>3</sub>	$\text{BaFe}_2^+\text{Fe}_3^{3+}$ ( $\text{PO}_4$ ) <sub>3</sub> (OH) <sub>3</sub>	$\text{BaFe}_2^+\text{Al}_2$ ( $\text{PO}_4$ ) <sub>3</sub> (OH) <sub>3</sub>	$\text{BaMn}_2^+\text{Fe}_2$ ( $\text{PO}_4$ ) <sub>3</sub> (OH) <sub>3</sub>	$\text{BaMg}_2\text{Al}_2$ ( $\text{PO}_4$ ) <sub>3</sub> (OH) <sub>3</sub>
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$
<i>a</i> (Å)	9.1765(18)	9.2195(18)	8.930(14)	9.199(9)	9.014(1)	9.223(5)	8.9577(4)
<i>b</i> (Å)	12.340(3)	12.410(3)	12.073(24)	12.359(8)	12.074(1)	12.422(8)	12.0150(5)
<i>c</i> (Å)	5.0092(10)	4.9990(10)	4.917(9)	5.004(2)	4.926(1)	4.995(2)	4.9079(2)
$\beta$ (°)	101.01(3)	100.09(3)	100.15(13)	100.19(6)	100.48(1)	100.39(4)	100.505(2)
<i>V</i> (Å <sup>3</sup> )	556.8(2)	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	2
Reference	This work	Elliott (2019)	Moore and Araki (1974)	Kolitsch et al. (2000)	Cooper and Hawthorne (1994)	Kampf (1977)	Bowman et al. (2013)

muscovite, quartz, microcline, plagioclase, beryl and apatite (and triplite), and an inner quartz core or cores (Lottermoser and Lu, 1997). The Wiperaminga Hill pegmatites belong to the beryl–columbite–phosphate rare-element type in the classification of Černý (1991). Phosphate minerals, dufrénite and florencite, were first reported from Wiperaminga Hill by King (1954), and Hiern (1966) reported apatite, triplite, dickinsonite and barbosalite. During a visit to the locality in 2018 by one of the authors (PE), masses of orange to dark brown triplite–zwieselite were found on the dumps of the eastern quarry. Secondary phosphate minerals have formed in seams and cavities in the triplite–zwieselite by hydrothermal alteration and weathering, in an oxidising, low-temperature, low-pH environment (Lottermoser and Lu, 1997). Plumboperloffite occurs in a single cavity in a matrix comprising triplite, barbosalite and minor quartz. Associated minerals are fluorapatite, phosphosiderite, natrodufrénite and fluorite.

### Physical and optical properties

Plumboperloffite occurs as thin tabular to bladed crystals, with a brownish-orange colour. Individual crystals are up to 40 µm in length (Fig. 1). The streak is pale orange and the mineral has a vitreous lustre. The hardness is estimated to be 4 based on the hardness of other bjarebyite-group minerals. The fracture is uneven, the tenacity is brittle and the mineral has an excellent



**Figure 1.** Orange crystals of plumboperloffite associated with natrodufrénite (black) and fluorite (white). The scale bar is 200 µm. South Australian Museum registration number G34868.

cleavage on {100}. Density was not determined owing to the small amount of material available. The calculated density is 4.416 g/cm<sup>3</sup> from the empirical formula. Plumboperloffite is optically biaxial (+) with indices of refraction  $\alpha = 1.87(1)$ ,  $\beta = 1.88(1)$  and  $\gamma = 1.89(1)$  measured in white light. The 2V measured directly by conoscopic observation is 88(1)°. The calculated 2V is 90.5°. Dispersion is apparently strong, based on extinction colours, but the sense could not be determined because of the indistinct conoscopic figure. The pleochroism in shades of yellow brown is  $X < Z < Y$ . The optical orientation is  $Y = \mathbf{b}$ . The optical orientation could not be completely determined because crystals are sub-parallel intergrowths and the refractive indices are high. The compatibility index  $1 - (K_p/K_c)$  is 0.03 (excellent) based upon the empirical formula, density calculated using the single-crystal cell and the measured indices of refraction (Mandarino, 1981).

### Chemical composition

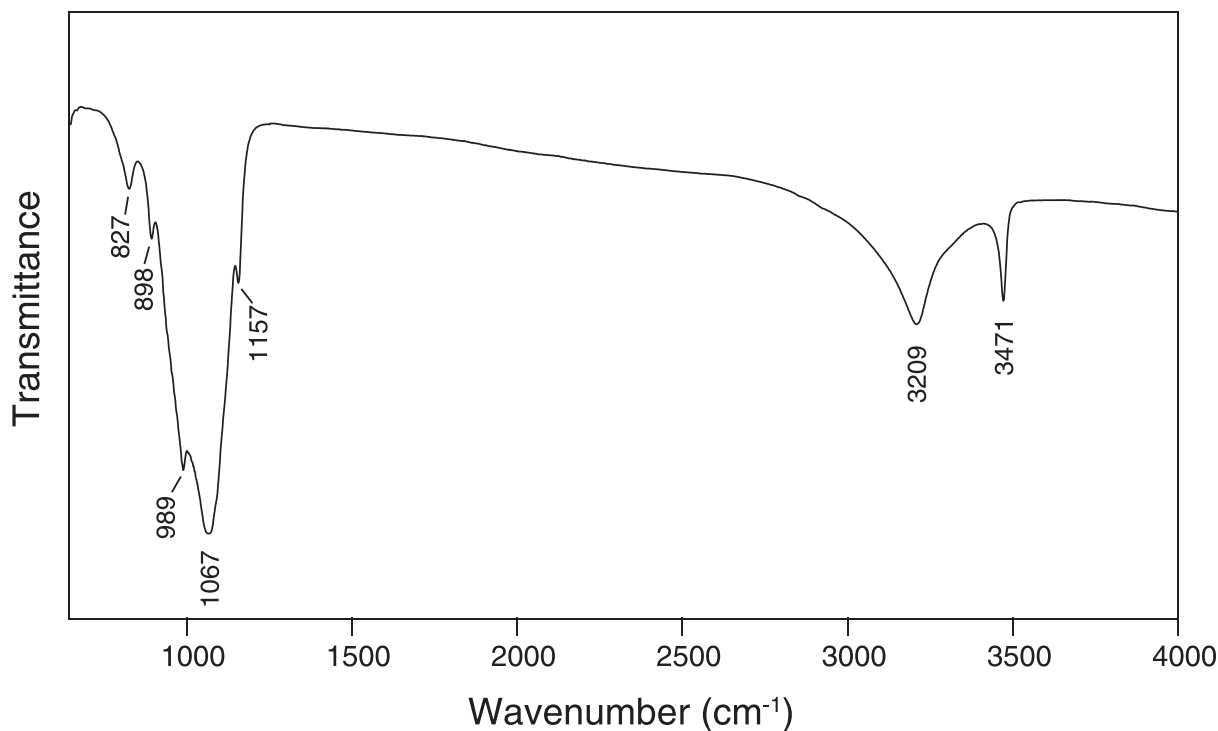
Analyses of plumboperloffite (12 spots) were performed with a Cameca SXFive electron microprobe (wavelength-dispersive spectroscopy mode, 20 kV, 20 nA and 5 µm beam diameter). Data were processed using the  $\varphi(\rho Z)$  correction procedure of Pouchou and Pichoir (1991). There was insufficient material for direct determination of H<sub>2</sub>O content so it was based on the crystal structure analysis. The results of the analyses are reported in Table 2. The empirical formula unit, based on 15 O atoms per formula unit (apfu) is  $(\text{Pb}_{0.92}\text{Ca}_{0.04}\text{Ba}_{0.01}\text{K}_{0.01})_{\Sigma 0.98}(\text{Mn}_{1.84}\text{Fe}_{0.13})_{\Sigma 1.97}(\text{Fe}_{1.97}\text{Al}_{0.03})_{\Sigma 2.00}(\text{P}_{3.01}\text{O}_{11.94})(\text{OH})_{\Sigma 3.06}$ . The ideal formula is  $\text{PbMn}_2^+\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_3$  which requires PbO 29.19, MnO 18.55, Fe<sub>2</sub>O<sub>3</sub> 20.87, P<sub>2</sub>O<sub>5</sub> 27.86, H<sub>2</sub>O 3.53, total 100.00 wt.%.

**Table 2.** Analytical data for plumboperloffite.

Constituent	Wt.%	Range	S.D.	Probe standard
PbO	26.60	25.82–27.44	0.48	galena
BaO	0.25	0.10–0.61	0.15	barite
CaO	0.28	0.08–0.86	0.25	plagioclase
K <sub>2</sub> O	0.23	0.11–0.39	0.09	sanidine
MnO	17.06	16.51–17.62	0.29	rhodonite
FeO*	1.23	0.78–2.09	0.41	almandine–pyrope
Fe <sub>2</sub> O <sub>3</sub> *	20.53	20.13–20.78	0.18	almandine–pyrope
Al <sub>2</sub> O <sub>3</sub>	0.18	0.01–0.50	0.14	almandine–pyrope
P <sub>2</sub> O <sub>5</sub>	27.98	27.79–28.58	0.23	apatite
H <sub>2</sub> O (calc)**	3.60			
Total	97.94			

\*FeO and Fe<sub>2</sub>O<sub>3</sub> calculated to give Fe<sup>3+</sup> + Al = 2.00

\*\*H<sub>2</sub>O calculated from the refined formula.



**Figure 2.** The Fourier-transform infrared spectrum of powdered plumboperloffite.

**Table 3.** Powder X-ray data ( $d$  in Å) for plumboperloffite.\*

$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$l_{\text{calc}}$	$hkl$	$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$l_{\text{calc}}$	$hkl$	$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$l_{\text{calc}}$	$hkl$
<b>25</b>	<b>9.029</b>	9.0076	39	1 0 0	9	2.1673	2.1643	3	2 5 0	7	1.6255	1.6262	12	4 4 1
12	6.196	6.1700	10	0 2 0										
<b>40</b>	<b>5.105</b>	5.0903	38	1 2 0	16	2.1233	2.1338	4	1 3 2	14	1.5937	1.6068	4	5 0 2
8	4.848	4.9170	19	0 0 1										
<b>30</b>	<b>4.583</b>	4.5677	32	0 1 1	25	<b>2.0669</b>	2.1154	5	4 2 0	15	1.5595	1.5872	6	1 6 2
		4.4010	11	1 1 1			8	3 0 2	9			4 4 2		
10	4.349	4.4010	11	1 1 1	29	<b>1.9919</b>	2.1099	8	3 0 2	23	<b>1.5273</b>	1.5837	9	4 4 2
5	4.027	4.0061	5	1 0 1			5	1 5 1	3			0 6 2		
9	3.770	3.7442	11	1 2 1	14	1.8806	2.0836	3	4 2 1	9	1.4978	1.5703	3	3 0 3
		3.6907	7	2 0 1			20	0 6 0	4			5 4 1		
20	3.657	3.6377	25	2 2 0	6	3.367	2.0516	5	2 5 1	23	<b>1.5273</b>	1.5590	4	5 4 1
6	3.553	3.5360	21	2 1 1			3	1 6 0	7			2 5 2		
18	3.367	3.3600	12	1 2 1	29	<b>1.9919</b>	2.0030	3	2 0 2	9	1.4639	1.5531	3	3 6 1
		3.1673	5	2 2 1			8	3 2 2	4			0 8 0		
<b>100</b>	<b>3.158</b>	3.1549	50	0 3 1	14	1.8806	1.9837	21	1 3 2	9	1.4978	1.5425	4	0 8 0
		3.0984	44	1 3 1			8	2 1 2	3			2 3 3		
18	3.064	3.0372	16	2 3 0	23	<b>1.5273</b>	1.9772	8	2 1 2	9	1.4978	1.5255	8	2 7 1
<b>42</b>	<b>2.950</b>	2.9556	36	2 1 1			16	4 3 1	6			0 3 3		
<b>23</b>	<b>2.898</b>	2.9186	39	1 4 0	6	1.8342	1.8974	3	0 6 1	6	1.4639	1.5202	10	3 7 0
		2.8699	28	1 3 1			4	3 4 1	6			6 0 1		
27	2.822	2.8222	27	2 2 2	14	1.8806	1.8721	11	2 4 2	9	1.4978	1.5132	5	1 2 3
		2.7470	3	2 3 1			6	3 5 1	3			4 1 2		
<b>58</b>	<b>2.738</b>	2.7422	52	3 1 1	9	1.8070	1.8255	4	1 4 2	6	1.4639	1.4967	3	5 3 2
		2.7300	28	2 2 1			12	5 0 0	11			3 7 1		
13	2.584	2.6998	32	3 2 0	4	1.7736	1.8015	12	5 0 0	6	1.4639	1.4728	3	3 6 2
		2.5808	16	1 4 1			3	5 1 0	3			1 4 3		
12	2.498	2.5452	6	2 4 0	7	1.7424	1.7680	10	4 2 2	5	1.4451	1.4547	4	4 1 3
		2.4959	16	1 0 2			4	3 0 2	3			2 0 3		
11	2.452	2.4585	12	0 0 2	7	1.6746	1.7416	8	3 4 2	5	1.4451	1.4511	5	2 4 3
		2.4464	7	1 1 2			5	3 1 2	4			1 8 1		
4	2.364	2.4111	5	0 1 2	4	1.7079	1.7286	5	3 1 2	6	1.4251	1.4326	3	0 7 2
		2.3692	3	3 0 1			5	4 3 2	3			4 3 2		
<b>30</b>	<b>2.205</b>	2.2153	8	4 1 0	26	<b>1.6519</b>	1.6685	6	1 5 2	14	1.3740	1.4251	7	6 3 1
		2.2057	5	0 5 1			4	0 7 1	3			2 7 2		
30	2.205	2.2005	5	2 2 2	26	<b>1.6519</b>	1.6542	5	5 3 1	14	1.3740	1.4063	3	6 0 2
		2.1861	22	1 5 1			6	4 5 1	4			2 8 1		
							1.6390	3	0 0 3			1.3720	4	3 8 0
												1.3650	3	4 4 2

\* Only calculated lines with  $l \geq 3$  are listed.  $l_{\text{calc}}$  values have been scaled so that the three lines contributing to the highest observed peak have a total intensity of 100; the strongest lines are in bold.

**Table 4.** Crystal data, data collection and refinement details.

<b>Crystal data</b>	
Formula	PbMn <sub>2</sub> <sup>2+</sup> Fe <sub>2</sub> <sup>3+</sup> (PO <sub>4</sub> ) <sub>3</sub> (OH) <sub>3</sub>
Space group	<i>P2<sub>1</sub>/m</i>
<i>a, b, c</i> (Å)	9.1765(18), 12.340(3), 5.0092(10)
$\beta$ (°)	101.01(3)
<i>V</i> (Å <sup>3</sup> ), <i>Z</i>	556.8(2), 2
<i>F</i> (000)	702.0
$\mu$ (mm <sup>-1</sup> )	20.344
Absorption correction	multi-scan, $T_{\min}, T_{\max} = 0.34, 0.43$
Crystal dimensions (μm)	0.25 × 0.20 × 0.05
<b>Data collection</b>	
Diffractometer	Dectris EigerX 16M
Temperature (K)	100
Radiation	Synchrotron, $\lambda = 0.710754$ Å
Crystal detector distance (mm)	108.033
$\theta$ range (°)	2.80–28.70
<i>h, k, l</i> ranges	–12 → 12, –16 → 16, –6 → 6
Total reflections measured	9136
Unique reflections	1417 ( $R_{\text{int}} = 0.0355$ )
<b>Refinement</b>	
Refinement on	$F^2$
$R_1$ for $F_0 > 4\sigma(F_0)$ .	2.07%
$wR_2^1$ for all $F_0^2$	7.23%
Reflections used $F_0 > 4\sigma(F_0)$	1417
Number of parameters refined	119
Goof	0.927
$(\Delta/\sigma)_{\text{max}}$	0.000
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e <sup>-</sup> /Å)	1.119, –2.248

$$^1wR_2 = \sum w(|F_0|^2 - |F_c|^2)^2 / \sum w|F_0|^2; w = 1/[\sigma^2(F_0^2) + (0.0646P)^2 + 2.08P]; P = ([\text{max of } (0 \text{ or } F_0^2) + 2F_c^2] / 3)$$

### Infrared spectroscopy

The infrared spectrum of plumboperloffite (Fig. 2) was recorded using a Nicolet 5700 FTIR spectrometer equipped with a Nicolet Continuum IR microscope and a diamond-anvil cell. Data were acquired from a powdered sample during 50 scans in the wavenumber range 4000 to 700 cm<sup>-1</sup>. The spectrum shows bands at 3471 cm<sup>-1</sup> and 3209 cm<sup>-1</sup> that correspond to O–H-stretching vibrations of OH groups forming weak hydrogen bonds (Libowitzky and Beran, 2004). The bands at 1157, 1067, 989 and 898 cm<sup>-1</sup> are assigned to  $\nu_3$  vibrations of the PO<sub>4</sub> tetrahedra and the band at 827 cm<sup>-1</sup> is assigned to the  $\nu_1$  vibration of the PO<sub>4</sub> tetrahedra. No absorption attributed to H–O–H bending vibrations was observed in the spectrum.

**Table 5.** Fractional atomic coordinates and displacement parameters for plumboperloffite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
X	0.53089(2)	3/4	0.81612(4)	0.01373(13)	0.01212(16)	0.02002(17)	0.00940(17)	0	0.00298(10)	0
M1	0.29861(6)	–0.10841(4)	0.21722(12)	0.00569(16)	0.0056(3)	0.0053(3)	0.0063(3)	0.00021(18)	0.0016(2)	0.00053(18)
M2	0.09489(6)	0.39784(4)	0.13454(11)	0.00540(15)	0.0048(3)	0.0068(3)	0.0049(3)	0.00017(16)	0.00149(19)	–0.00041(16)
P1	0.16275(14)	3/4	0.6835(3)	0.0038(2)	0.0041(5)	0.0049(5)	0.0027(6)	0	0.0010(4)	0
P2	0.33514(10)	0.44237(7)	0.71734(19)	0.0052(2)	0.0050(4)	0.0066(4)	0.0042(4)	0.0007(3)	0.0015(3)	0.0010(3)
O1	0.2878(4)	3/4	0.9401(8)	0.0064(7)	0.0072(16)	0.0076(16)	0.0040(17)	0	0.0004(13)	0
O2	0.2374(4)	3/4	0.4344(8)	0.0089(12)	0.0119(19)	0.0091(18)	0.008(2)	0	0.0084(14)	0
O3	0.0698(3)	0.6478(2)	0.6877(6)	0.0069(5)	0.0077(11)	0.0061(10)	0.0083(12)	–0.0016(9)	0.0053(10)	–0.0012(9)
O4	0.3775(3)	0.5521(2)	0.6183(6)	0.0095(5)	0.0103(12)	0.0096(12)	0.0089(13)	0.0041(10)	0.0025(10)	0.0004(10)
O5	0.2655(3)	0.4584(2)	0.9764(6)	0.0079(5)	0.0083(12)	0.0120(12)	0.0040(12)	–0.0014(9)	0.0022(10)	–0.0003(9)
O6	0.2256(3)	0.3832(2)	0.4964(6)	0.0103(5)	0.0101(12)	0.0134(12)	0.0063(13)	–0.0012(10)	–0.0010(10)	–0.0006(10)
O7	0.4718(3)	0.3689(2)	0.8075(6)	0.0086(5)	0.0051(12)	0.0102(12)	0.0099(13)	0.0031(10)	0.0000(10)	0.0019(9)
OH8	0.1341(5)	1/2	0.0026(9)	0.0096(8)	0.0123(18)	0.0087(17)	0.0075(18)	0	0.0015(15)	0
OH9	0.0617(3)	0.5601(2)	0.1952(6)	0.0066(5)	0.0070(11)	0.0086(12)	0.0039(12)	–0.0021(9)	0.0007(9)	0.0007(9)
H8	0.204(9)	1/2	–0.08(2)	0.032						
H9	0.053(8)	0.590(6)	0.334(10)	0.032						

### Crystallography

#### Powder X-ray diffraction

Powder X-ray diffraction data for plumboperloffite were obtained using a Rigaku R-Axis Rapid II curved-imaging-plate microdiffractometer, with monochromatised MoK $\alpha$  radiation (50 kV and 40 mA). A Gandolfi-like motion on the  $\varphi$  and  $\omega$  axes was used to randomise the sample. Observed *d* values and intensities were derived by profile fitting using JADE 2010 software (Materials Data, Inc.). Data (in Å for MoK $\alpha$ ) are given in Table 3. Unit-cell parameters refined from the powder data using JADE 2010 with whole-pattern fitting are  $a = 9.17(2)$ ,  $b = 12.41(2)$ ,  $c = 5.02(2)$  Å,  $\beta = 100.84(5)^\circ$  and  $V = 561(3)$  Å<sup>3</sup>.

#### Single-crystal X-ray diffraction

The single-crystal X-ray diffraction experiment was carried out on the micro-focus macromolecular MX2 beamline at the Australian Synchrotron, part of ANSTO (Aragao *et al.*, 2018). A crystal was attached to a MiTeGen polymer loop and X-ray diffraction data were collected at 100 K using a Dectris EigerX 16M detector and monochromatic radiation with a wavelength of 0.710754 Å. The intensity data sets were processed using XDS (Kabsch, 2010) without scaling and with absorption correction and scaling performed using SADABS (Bruker, 2001). Crystal data and experimental details are reported in Table 4.

#### Structure refinement

The structure was solved in space group *P2<sub>1</sub>/m* using SHELXT (Sheldrick, 2015a) as implemented in the WinGX suite (Farrugia, 2012). SHELXL-2018 (Sheldrick, 2015b) was used for the refinement of the structure. Following the solution of the structure, the atom coordinates were transformed to correspond to those in the structure of perloffite (Elliott and Willis, 2011). Difference-Fourier syntheses then located all H atom positions. The H sites were refined with soft restraints on the O–H distances of 0.85(3) Å for the O–H groups and 0.90(3) Å. The final cycle of the refinement converged to  $R_1 = 0.0207$ . Final atom coordinates and anisotropic-displacement parameters are listed in Table 5, selected interatomic distances and framework angles are given in Table 6, and bond-valence values, calculated using the parameters of Gagné and Hawthorne (2015) are given in Table 7.

**Table 6.** Selected interatomic distances (Å), angles (°) and hydrogen bonds for plumboperloffite.

X-O7	2.392(3) × 2	M2-O3	1.977(3)	
X-O1	2.427(4)	M2-O6	1.982(3)	
X-O4	2.897(3) × 2	M2-OH8	1.996(2)	
X-O2	2.992(3)	M2-O5	2.028(3)	
X-O8	3.034(4)	M2-OH9	2.039(3)	
X-O5	3.232(3) × 2	M2-OH9	2.057(3)	
X-O6	3.388(3) × 2	<M-O>	2.013	
X-O7	3.447(3) × 2	P1-O3	1.525(3) × 2	
<X-O>	3.012	P1-O2	1.534(4)	
		P1-O1	1.551(4)	
		<P-O>	1.534	
X-O4	2.119(3)	P2-O4	1.518(3)	
X-O7	2.153(3)	P2-O6	1.531(3)	
X-O2	2.187(2)	P2-O7	1.544(3)	
X-O5	2.198(3)	P2-O5	1.565(3)	
X-O1	2.222(2)	<P-O>	1.540	
X-OH9	2.236(3)			
<M-O>	2.186			
<b>Hydrogen bonds</b>				
D-H...A	D-H	H...A	D...A	∠D-H...A
OH8-H8...O6	0.81(3)	2.73(6)	3.263(5)	124(6)
OH9-H9...O3	0.81(3)	1.89(3)	2.682(4)	168(8)

**Table 7.** Bond-valence\* analysis for plumboperloffite.

	X	M1	M2	P1	P2	H1	H2	Sum
O1	0.41	0.31		1.20				1.93
O2	0.11	0.34		1.26				1.71
O3			0.56	1.28 <sup>x21</sup>		0.21		2.05
O4	0.14 <sup>x21</sup>	0.40			1.30			2.00
O5	0.07	0.33	0.48		1.17			2.05
O6	0.05		0.55		1.26	0.03		1.89
O7	0.44 <sup>x21</sup>	0.41			1.22			2.03
	0.04 <sup>x21</sup>							
OH8	0.10		0.53 <sup>x2→</sup>			0.97		2.14
OH9		0.30	0.47				0.79	2.01
			0.45					
Sum	2.10	2.05	3.04	5.02	4.95	1.00	1.00	

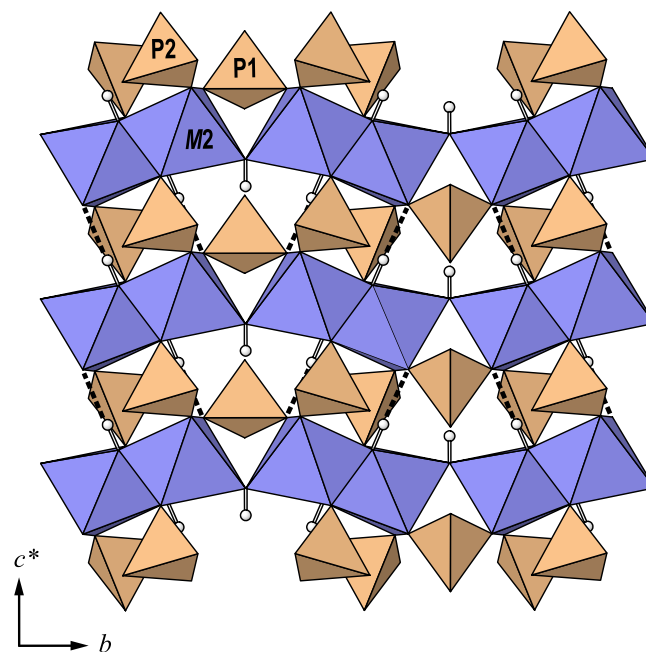
\*Bond-valence parameters used are from Gagné and Hawthorne (2015). Bond-valences for the X, M1 and M2 sites are based on the refined occupancy.

The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

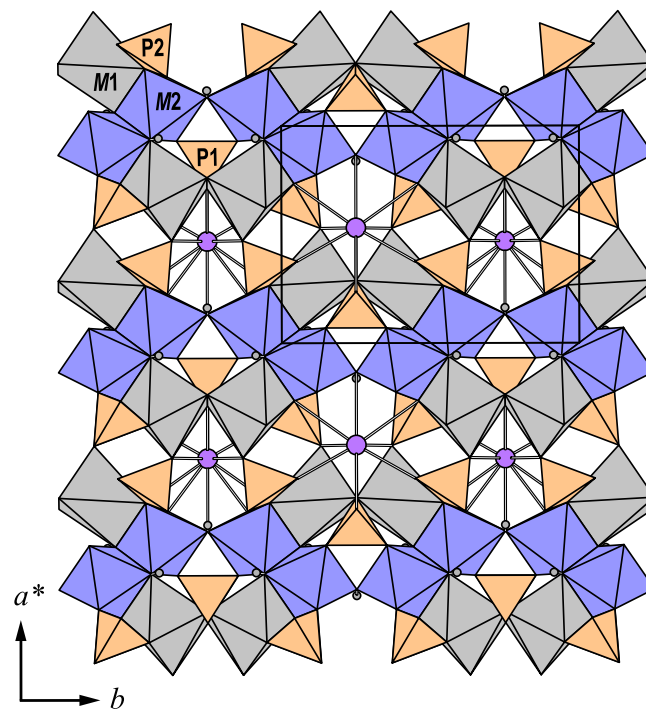
### Structure description

Plumboperloffite is isostructural with minerals of the bjarebyite group. The structure contains one X site (occupied by Pb and minor Ca, Ba and K), one M1 site (occupied by Mn<sup>2+</sup> and minor Fe<sup>2+</sup>), one M2 site, (occupied by Fe<sup>3+</sup> and minor Al) and two P sites. The M1 and M2 sites were refined with full occupancy of Mn and Fe, respectively.

[M<sub>2</sub>O<sub>3</sub>(OH)<sub>3</sub>] octahedra share edges to form [M<sub>2</sub>O<sub>6</sub>(OH)<sub>4</sub>] dimers which corner-link to form (M<sub>2</sub>Φ<sub>9</sub>) chains along the **b**-direction (Fig. 3). Octahedra that share corners are also linked by P1O<sub>4</sub> tetrahedra. The chains are decorated by P2O<sub>4</sub> tetrahedra, which link between chains in the **c**-direction via the O5 and O6 anions. Chains are linked in the **a**-direction via [M1O<sub>5</sub>(OH)] octahedra, which share an edge with [M<sub>2</sub><sup>3+</sup>O<sub>3</sub>(OH)<sub>3</sub>] octahedra and corners with P1O<sub>4</sub> and P2O<sub>4</sub> tetrahedra (Fig. 4). The X site

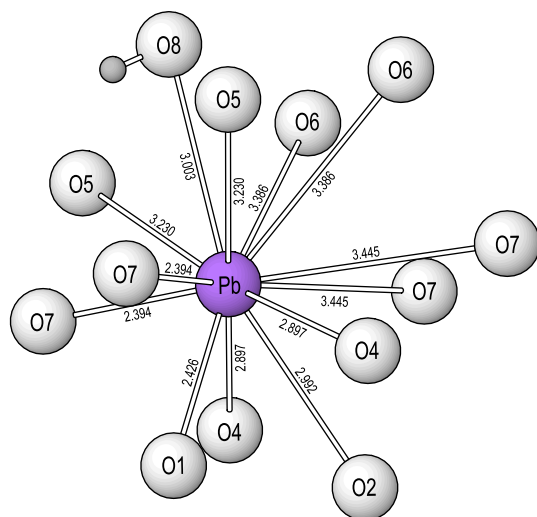


**Figure 3.** The crystal structure of plumboperloffite projected on (100). Hydrogen atoms are grey spheres. Hydrogen bonds are indicated by dotted lines. Structure drawings were completed using ATOMS (Shape Software, Kingsport, Tennessee, USA).



**Figure 4.** The crystal structure of plumboperloffite projected onto (001). The X positions are shown as purple spheres. The unit cell is outlined.

occupies channels parallel to [001] and also provides linkage between chains in the **a**-direction. The X site exhibits a lop-sided coordination (Fig. 5) with three very short bonds to O1 and O7, four medium length bonds to O2, O4 and OH8, and six very long bonds to O5, O6 and O7. This coordination is distinct from the more regular coordination of the X site in the structures of other bjarebyite-group minerals and is attributable to the



**Figure 5.** The Pb coordination in plumboperloffite showing Pb–O bond lengths (in Å).

accommodation of the stereoactive  $6s^2$  electron lone pair on  $Pb^{2+}$ . Coordination of the M1 and M2 sites is similar to the sites in the structures of other bjarebyite-group minerals. The  $M1O_6$  octahedron is strongly distorted with bond angles in the range 86.35 to 109.53°. The  $M2O_6$  octahedron is relatively undistorted with bond angles in the range 86.77 to 96.22°.

The hydrogen bonding scheme for plumboperloffite given in Table 6, is the same as reported in previous studies on bjarebyite-group minerals (e.g. Cooper and Hawthorne, 1994; Elliott, 2019). The H9 atom associated with OH9 hydrogen bonds to O3 with a donor–acceptor distance of  $H9\cdots O3 = 1.89(3)$  Å and an  $OH9-H2\cdots O3$  angle of 168(8)°, an arrangement typical of strong hydrogen bonding (Libowitzky and Beran, 2004). The H8 atom provides a weak hydrogen bond to O6 with a donor–acceptor distance of  $H8\cdots O6 = 2.73(2)$  Å and an  $OH8-H8\cdots O6$  angle of 124(6)°.

**Supplementary material.** The supplementary material for this article can be found at <https://doi.org/10.1180/mgm.2023.97>.

**Competing interests.** The authors declare none.

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