

Penriceite, $[\text{Mg}(\text{H}_2\text{O})_6][\text{Na}(\text{H}_2\text{O})_2\text{Al}_3(\text{PO}_4)_2\text{F}_6]\cdot\text{H}_2\text{O}$, the F-analogue of aldermanite, from the Penrice marble quarry, South Australia

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Abstract

Penriceite, $[\text{Mg}(\text{H}_2\text{O})_6][\text{Na}(\text{H}_2\text{O})_2\text{Al}_3(\text{PO}_4)_2\text{F}_6]\cdot\text{H}_2\text{O}$, a new secondary phosphate mineral from the Penrice marble quarry, South Australia, is the fluorine analogue of aldermanite. It occurs as rod-like aggregates of platy crystals, with the platelets up to 100 μm across but only 1–2 μm thick. It is associated with angastonite, minyulite, perhamite, crandallite, quartz and goethite. The calculated density is 2.12 $\text{g}\cdot\text{cm}^{-3}$. Optically the crystals are biaxial (+) with $\alpha = 1.502(2)$, $\beta = 1.503(2)$, $\gamma = \text{n.d.}$ (due to extreme thinness of the crystals). The measured 2V is in the range 10 to 20°. The orientation is $X = \text{b}$, $Y \approx \text{c}$, $Z \approx \text{a}^*$. Electron microprobe analyses give the empirical formula based on 23 anions as $\text{Na}_{0.85}\text{K}_{0.05}\text{Ca}_{0.17}\text{Mg}_{1.35}\text{Al}_{2.68}\text{P}_{2.04}\text{H}_{20.38}(\text{F}_{3.42}\text{O}_{19.58})$. Penriceite is monoclinic, space group $P2_1/c$ (#14), with $a = 13.478(3)$ Å, $b = 9.971(2)$ Å, $c = 6.999(1)$ Å, $\beta = 97.20(3)^\circ$, $V = 933.2(3)$ Å³, $Z = 2$. The crystal structure was refined using single-crystal synchrotron X-ray diffraction data to $wR_{\text{obs}} = 0.088$ for 1660 independent reflections. Penriceite is isostructural with aldermanite, $[\text{Mg}(\text{H}_2\text{O})_6][\text{Na}(\text{H}_2\text{O})_2\text{Al}_3(\text{PO}_4)_2(\text{OH},\text{F})_6]\cdot\text{H}_2\text{O}$, and differs only in having F dominant over OH in the univalent anion sites.

KEYWORDS: penriceite, Penrice marble quarry, Kapunda, South Australia

Introduction

For more than a century the phosphate rock deposits in the Kapunda–Angaston region of South Australia (Fig. 1) have played a significant role in Australia's mineral heritage, both economically and as a repository of a diverse range of secondary phosphate minerals of interest to collectors and mineralogists. Specimens of fluellite, minyulite and wavellite from these deposits are equal to or better than those from other world localities in terms of size and crystal perfection. Commercial mining of the phosphate rock for superphosphate production commenced in the early 1900s at several deposits in the region, including at Moculta (Klemm's quarry), St. John's, St. Kitt's and Tom's quarries (Johns, 1976; Elliott et al., 2014) and was relatively large-scale up until 1919 when higher-quality (low Al, Fe) ore from Nauru and Christmas Island became available. However, small-scale mining continued sporadically at the Kapunda–Angaston deposits until the 1990s with mining at Tom's quarry still ongoing today. The latter deposit is the type locality for three secondary phosphate minerals: peisleyite, $\text{Na}_2\text{Al}_9[(\text{P},\text{S})\text{O}_4]_8(\text{OH})_6\cdot 28\text{H}_2\text{O}$ (Pilkington et al., 1982; Mills et al., 2011), kapundaite, $(\text{Na},\text{Ca})_2\text{Fe}^{3+}_4(\text{PO}_4)_4(\text{OH})_3\cdot 5\text{H}_2\text{O}$ (Mills et al., 2010) and jahnsite-(CaFeMg), $\text{CaFe}^{2+}\text{Mg}_2\text{Fe}^{3+}_2(\text{PO}_4)_4(\text{OH})_2\cdot 8\text{H}_2\text{O}$ (Elliott, 2016). Klemm's quarry, Moculta, is the type locality for aldermanite, $[\text{Mg}(\text{H}_2\text{O})_6][\text{Na}(\text{H}_2\text{O})_2\text{Al}_3(\text{PO}_4)_2(\text{OH},\text{F})_6]\cdot\text{H}_2\text{O}$ (Harrowfield et al., 1981;

Elliott et al., 2021) while the Penrice marble quarry is the type locality for angastonite, $\text{CaMgAl}_2(\text{PO}_4)_2(\text{OH})_4\cdot 7\text{H}_2\text{O}$ (Mills et al., 2008). A common feature of these secondary phosphate minerals is that they are usually extremely fine-grained and intergrown with other secondary minerals on a scale of a few micrometres. The application of high-resolution microscopic techniques and synchrotron X-ray diffraction studies, that were not available when the minerals were first characterized, has led to the re-definition of the formulae and the crystallography of both peisleyite (Mills et al., 2011) and aldermanite (Elliott et al., 2021).

Aldermanite was first described by Harrowfield et al. (1981) as a Mg–Al-phosphate with the formula $\text{Mg}_5\text{Al}_{12}(\text{PO}_4)_8(\text{OH})_{22}\cdot 32\text{H}_2\text{O}$. The minute, talc-like crystals had a thickness of only 0.1–0.2 μm and were unsuitable for single-crystal diffraction analysis. The authors obtained an orthorhombic unit cell from analysis of the powder X-ray diffraction (XRD) data. Elliott et al. (2021) obtained an aldermanite specimen from Tom's quarry that had better-developed crystals and they collected single-crystal XRD data that enabled the structure to be determined and the formula to be revised to $[\text{Mg}(\text{H}_2\text{O})_6][\text{Na}(\text{H}_2\text{O})_2\text{Al}_3(\text{PO}_4)_2(\text{OH},\text{F})_6]\cdot\text{H}_2\text{O}$. Aldermanite has a monoclinic structure, built from layers of corner-connected $[\text{Al}(\text{OH}_4)\text{O}_2]$ octahedra and PO_4 tetrahedra, with hydrated magnesium ions, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and water molecules packing between the layers and holding them together by hydrogen bonding. The structure is closely related to that for natrowalentaite from the Griffins Find gold deposit, Western Australia (Grey et al., 2019).

In ongoing studies of secondary aluminium phosphate minerals from the Kapunda–Angaston rock phosphate deposits, we identified pseudohexagonal platelets resembling aldermanite in specimens from the Penrice marble quarry. Electron microprobe analyses conducted on the crystals confirmed a similar composition to that for

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aldermanite, but with F dominant over OH, and with higher levels of sodium and magnesium but lower aluminium. Single-crystal synchrotron XRD data was collected for the mineral and the crystal structure was refined, confirming the close relationship to aldermanite. A new mineral proposal to the Commission for New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) has been approved (IMA2021-068), with the mineral being named penriceite, after the locality. The holotype specimen is housed in the mineralogical collections of the Museum of South Australia, catalogue number G32227. A co-type used for the optical measurements is in the collections of the Natural History Museum of Los Angeles County, catalogue number 76158.

Occurrence

The type locality for penriceite is the Penrice marble quarry (34°28'54" S, 139°2'48" E), located 2 km north of Angaston in the northern Mount Lofty Ranges, South Australia (Fig. 1). The specimens studied were collected by Mr Vince Peisley in 1988–89. Phosphate-rich areas in a gossanous zone consisting of limonitic and manganiferous clay-rich rocks were located within the marble. Penriceite occurs as characteristic rod-like aggregates (Fig. 2) of platy crystals. Associated minerals are angastonite, minyulite, perhamite, crandallite and fluorapatite. Penriceite has crystallized from groundwaters at ambient temperatures and the phosphorus derived by leaching of weakly phosphatic limestones or low-grade primary phosphorites during the late Neogene and the Quaternary (Johns, 1976; Elliott et al., 2014). The phosphate zone that produced the specimens studied here was removed during mining for marble and limestone, and

no specimens have been collected since the 1980s. Many of the specimens collected at the Penrice quarry by Vince Peisley have been deposited at Museums Victoria and the South Australian Museum and they have provided material for the characterization of the new type minerals penriceite and angastonite (Mills et al., 2008).

Appearance and Properties

Penriceite occurs as platy crystals with pseudo-hexagonal outline, up to ~100 µm across but only 1 to 2 µm thick (Fig. 3). Platelets identical in appearance from the Penrice quarry were described as angastonite by Mills et al. (2008) (their figure 4) but we have subsequently confirmed, from electron microprobe analyses (EMPA) and powder X-ray diffraction (PXRD), that angastonite is the anhydrous matrix phase on which penriceite platelets occur, as shown in Figure 4 here. The platelets are colourless but appear white when clustered together. They have a vitreous lustre and exhibit good cleavage on {100}. The density could not be measured due to the difficulty of obtaining a large-enough sample free from other minerals. The calculated density is 2.12 g·cm⁻³ for the empirical formula.

Penriceite crystals are biaxial (+), with $\alpha = 1.502(2)$, $\beta = 1.503(2)$, $\gamma = \text{n.d.}$ (white light). The measured 2V is in the range 10 to 20°, estimated from conoscopic observation of relatively diffuse interference figures. The orientation is $X = \mathbf{b}$, $Y \approx \mathbf{c}$, $Z \approx \mathbf{a}^*$ ($\mathbf{a}^* = \mathbf{a}$ -axis vector in reciprocal-space. Equal to $\mathbf{a} \cos(\beta)$ where β is the monoclinic angle). No dispersion or pleochroism was observed. The extreme thinness of the blades made the measurement of γ impossible.

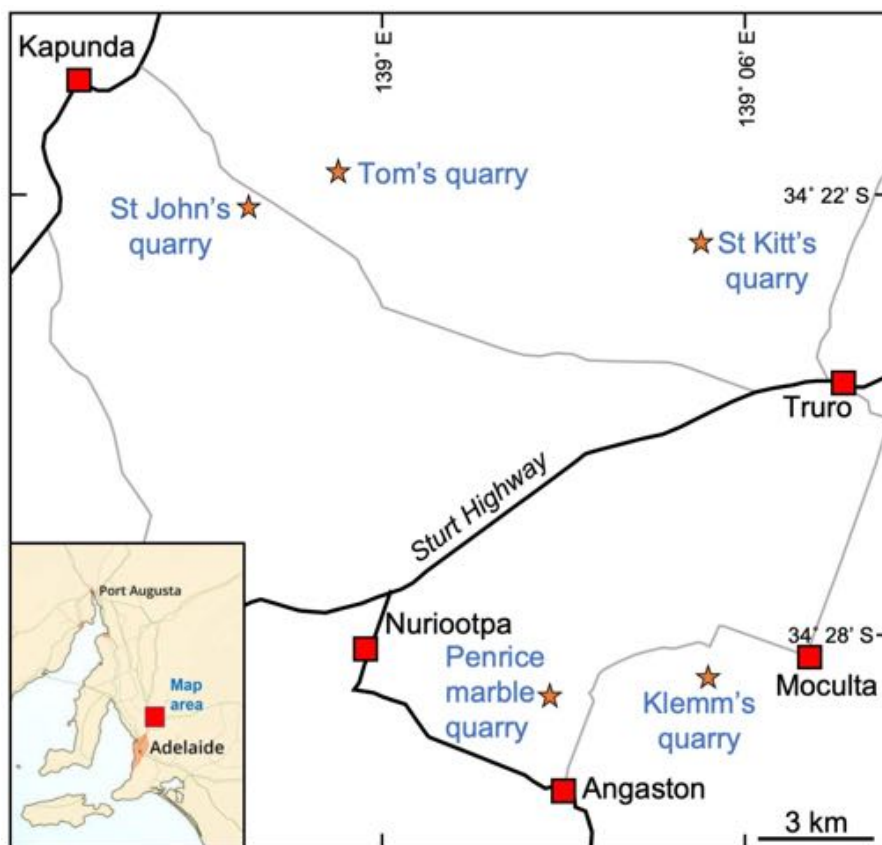


Figure 1 Location of the Kapunda–Angaston phosphate deposits



Figure 2 Rod-like aggregates of penriceite crystals. The field of view is 2.5 mm across. Photo Peter Elliott.

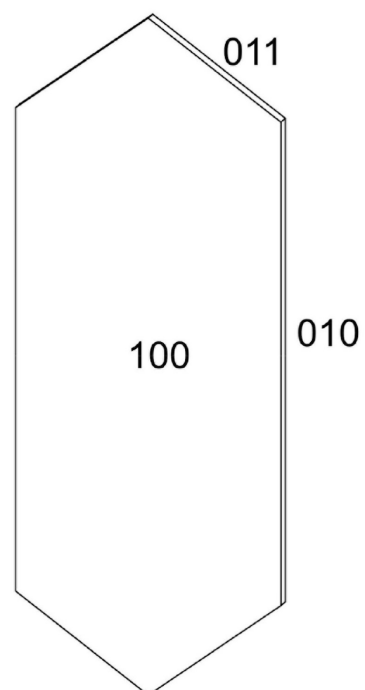
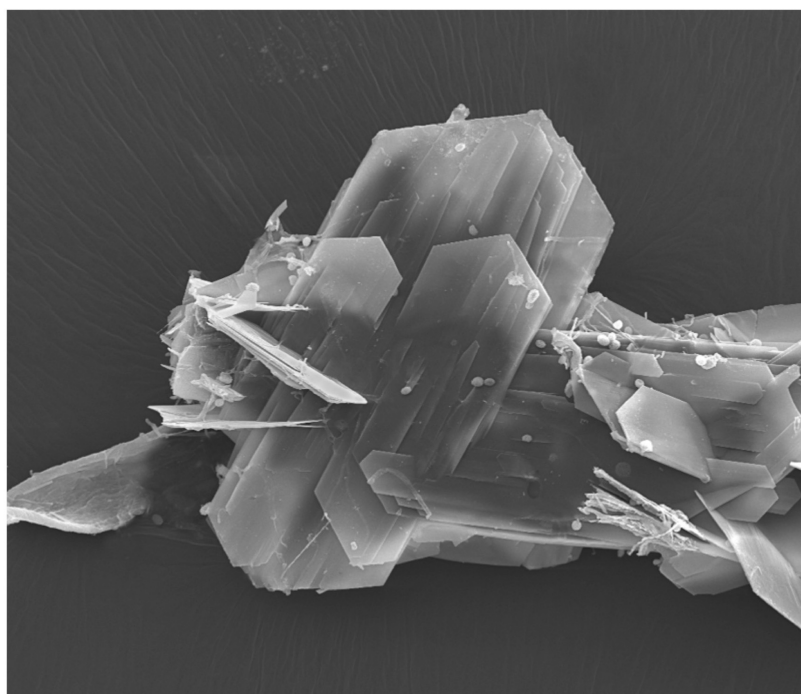


Figure 3 Scanning electron microscope (SEM) image of bladed crystals of penriceite (field of view is 0.025 mm across) and clinographic projection showing crystal forms.

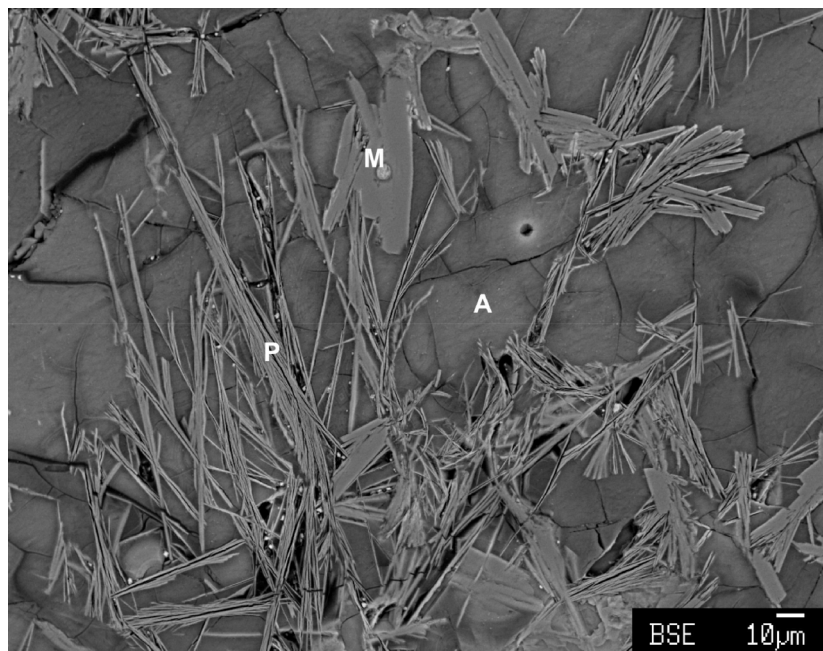


Figure 4 Back-scattered electron image of penriceite crystals (P) associated with angastonite (A) and minyulite (M). Image Matt Glenn.

Infrared spectroscopy

The infrared spectrum, 700 to 4000 cm^{-1} , is shown in Figure 5. The O-H stretch region comprises a broad envelope of bands, with a maximum at 3300 cm^{-1} and shoulders at 3015, 3460 and 3590 cm^{-1} . According to Libowitzky (1999), these bands correspond to H-bonded O...O distances in the range 2.6 to 3.0 Å, representing a wide range of H-bonding from strong to very weak. In penriceite the majority of the univalent anion sites are occupied by F rather than OH, so the O-H stretching vibrations are due mainly to H_2O molecules, both coordinated and H-bonded. The H-O-H bending mode band is at 1660 cm^{-1} with a shoulder at 1630 cm^{-1} . A split band at 1440/1475 cm^{-1} is most likely due to carbonate. Similar doublets are reported in carbonate-substituted fluorapatite and plumbogummite, where CO_3 substitutes for PO_4 (Grey et al., 2011). The P-O stretching bands form an envelope with a maximum at 1032 cm^{-1} and with shoulders at 975, 1058, 1120, 1170 and 1220 cm^{-1} . Penriceite has the same topology of PO_4 tetrahedra sharing three basal anions with Al-centred octahedra as in crandallite, and the analysis of the IR spectrum of crandallite (Frost et al., 2011) assisted in the assignment of the P-O stretching bands. The bands at 975 and 1032 cm^{-1} correspond to symmetric P-O stretching modes of PO_4 and the bands at 1058, 1120 and 1170 cm^{-1} are the antisymmetric stretching modes of PO_4 (and possibly also $\text{PO}_3(\text{OH})$). A well-defined weak peak at 1220 cm^{-1} could also be an antisymmetric stretching mode. Frost et al. (2011) show a similar peak at 1223 cm^{-1} in the IR spectrum for crandallite from the Jenolan Caves, New South Wales, but they did not assign it.

Chemical composition

Crystals of penriceite in the Museum of South Australia specimen G32227 (Fig. 4) were analysed using wavelength-dispersive spectrometry on a JEOL JXA 8500F Hyperprobe operated at an accelerating voltage of 15 kV and a beam

current of 2.6 nA. The beam was defocused to between 5 and 10 μm , depending on the size of the crystal aggregates. Analytical results are given in Table 1. There was insufficient material for direct determination of H_2O , so it was based upon the ideal formula with 2OH and 9 H_2O . A specimen of the type aldermanite, catalogue number M34778 from Museums Victoria, was analysed under the same conditions and the results are given in Table 1. The empirical formula based on 23 anions is $\text{Na}_{0.85}\text{K}_{0.05}\text{Ca}_{0.17}\text{Mg}_{1.35}\text{Al}_{2.68}\text{P}_{2.04}\text{H}_{20.38}(\text{F}_{3.42}\text{O}_{19.58})$. The simplified formula is $(\text{Na,K,Ca})\text{Mg}(\text{Al,Mg})_3(\text{PO}_4)_2(\text{F,OH,H}_2\text{O})_6 \cdot 9\text{H}_2\text{O}$. The end-member formula is $\text{NaMgAl}_3(\text{PO}_4)_2\text{F}_6 \cdot 9\text{H}_2\text{O}$. Expressed in terms of the structure the end-member formula is $[\text{Mg}(\text{H}_2\text{O})_6][(\text{Na}(\text{H}_2\text{O})_2\text{Al}_3(\text{PO}_4)_2\text{F}_6)] \cdot \text{H}_2\text{O}$, which requires Na₂O 5.22, MgO 6.78, Al₂O₃ 25.7, P₂O₅ 23.9, F 19.2, H₂O 27.3, -O=F -8.1, total 100 wt%.

X-ray crystallography

Powder diffraction

Platelet crystals of penriceite were carefully separated from the substrate, ground and dispersed on a silicon disc for a powder XRD data collect. A pattern was obtained at room temperature using a Panalytical Empyrean diffractometer employing $\text{CoK}\alpha$ radiation (1 h collect, step size = 0.02°). The paucity of material and structural damage due to grinding the platelets restricted the resolution to $d = 2.0$ Å for the measurement of peaks above the background. Measured d values and intensities derived by profile refinement using FULLPROF (Rodriguez-Carvajal, 1990) are given in Table 2. Monoclinic unit cell parameters refined from the powder data are: $a = 13.516(2)$ Å, $b = 9.979(2)$ Å, $c = 7.0180(10)$ Å, $\beta = 97.17(2)^\circ$, $V = 939.2(3)$ Å³, $Z = 2$. Systematic absences correspond to the space group $P2_1/c$ (#14).

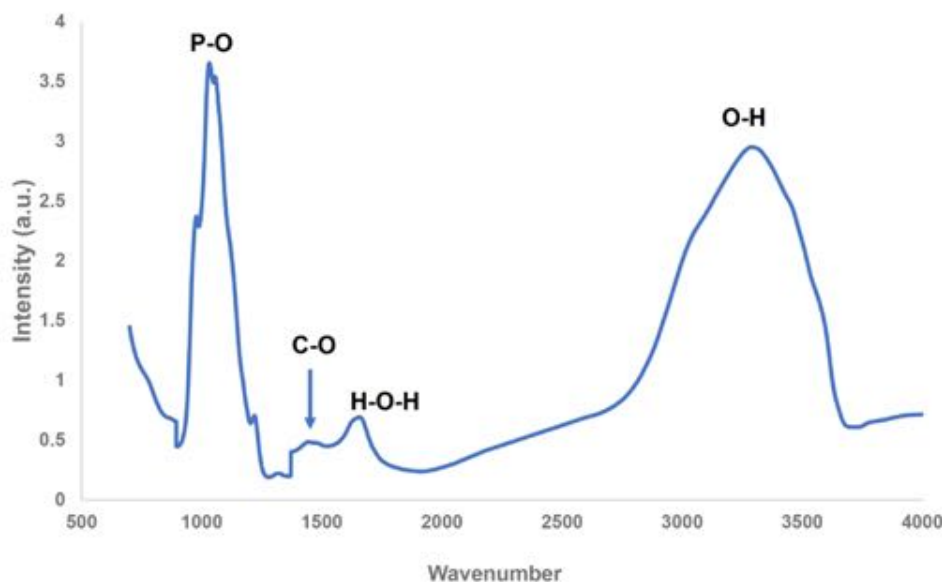


Figure 5 Infrared spectrum for penriceite.

Table 1 Electron microprobe analyses (wt%)

Constituent	Penriceite (av. of 7)			Type aldermanite (av. of 14)		Standard
	Mean	Range	SD	Mean	SD	
Na ₂ O	4.39	3.33-5.17	0.79	2.67	0.43	albite
K ₂ O	0.32	0.08-0.71	0.29	0.17	0.04	adularite
CaO	1.58	0.72-2.38	0.56	1.45	0.20	apatite
MgO	9.10	8.17-10.4	0.86	7.50	0.30	spinel
Al ₂ O ₃	22.7	19.1-24.5	2.04	24.3	0.76	berlinite
P ₂ O ₅	24.0	21.2-26.3	1.70	24.1	0.60	berlinite
F	10.8	9.71-12.61	1.11	8.73	1.02	CaF ₂
-O=F	-4.56			-3.66		
H ₂ O	30.5			32.5		
Total	98.83			97.76		

Single-crystal study

A platelet measuring $0.050 \times 0.040 \times 0.002$ mm was used for a data collection 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 $0.7109 \text{ \AA}$. The crystal was maintained at 100 K in an open-flow nitrogen cryostream. Refined unit cell parameters are: $a = 13.478(3) \text{ \AA}$, $b = 9.971(2) \text{ \AA}$, $c = 6.999(1) \text{ \AA}$, $\beta = 97.20(3)^\circ$, $V = 933.2(3) \text{ \AA}^3$.

Refinement of the crystal structure was initiated using the published coordinates for aldermanite in space group $P2_1/c$ (Elliott et al., 2021), with F replacing OH in the three univalent anion sites. Application of TWINROT in WinGX (Farrugia, 1999) indicated twinning by 180° rotation about a^* , as found also for aldermanite. Refinement using JANA2006 (Petříček et al., 2014) with anisotropic

displacement parameters for the heteropolyhedral atoms and isotropic displacement parameters for the interlayer atoms converged at $wR_{\text{obs}} = 0.084$ for 1312 observed reflections with $I > 3\sigma(I)$ and $wR_{\text{obs}} = 0.088$ for all 1660 independent reflections. The relatively high R factors ($R_{\text{merge}} = 0.082$) are due to the poor diffracting quality of penriceite crystals, which have thicknesses of only $\sim 2 \text{ \mu m}$, composed of sub- μm thick platelets in subparallel orientation (Fig. 3). Nevertheless, the refinement gave a crystallochemically sensible model with bond distances in the ranges normally reported for the constituent atoms. The refined coordinates, equivalent isotropic displacement parameters and bond valence sum (BVS) values (Gagné and Hawthorne, 2015) are reported in Table 3. Although H atoms were not located in the structure refinement, the BVS values in Table 3 confirm the presence of seven independent H_2O molecules. Polyhedral bond distances are reported in Table 4.

Table 2 Powder X-ray diffraction data (*d* in Å) for penriceite

<i>I</i> _{obs}	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>
100	13.39	13.41	1 0 0
30	8.000	8.006	1 1 0
12	5.718	5.711	0 1 1
26	5.562	5.566	2 1 0
3	4.988	4.989	0 2 0
2	3.480	3.482	0 0 2
2	3.353	3.357, 3.353	3 1 1, 4 0 0
2	3.330	3.329	3 2 0
4	3.284	3.287, 3.283	0 1 2, -1 1 2
1	3.176	3.178	4 1 0
2	3.103	3.109, 3.100	1 1 2, -2 1 2
5	3.004	3.001	0 3 1
16	2.855	2.855, 2.853	0 2 2, -1 2 2
4	2.815	2.823, 2.811	2 1 2, -3 1 2
15	2.782	2.783	4 2 0
4	2.731	2.736, 2.730	1 2 2, -2 2 2
4	2.670	2.669	3 3 0
2	2.590	2.590	5 1 0
1	2.529	2.529	-5 1 1
1	2.404	2.404	-1 3 2
2	2.087	2.088	5 3 0
1	2.040	2.044, 2.039	1 2 3, 6 2 0
1	2.028	2.028	0 4 2

Table 4 Polyhedral bond lengths [Å] for penriceite

Al1-O2	x2	1.859(4)	Al2-O3	1.937(9)
Al1-F2	x2	1.898(3)	Al2-O4	1.871(9)
Al1-F3	x2	1.852(2)	Al2-Oh1	1.798(8)
Av.		1.870	Al2-Oh1	1.963(8)
			Al2-Oh2	1.866(8)
P1-O1		1.519(3)	Al2-Oh3	1.916(8)
P1-O2		1.553(4)	Av.	1.892
P1-O3		1.557(3)		
P1-O4		1.552(4)	Mg1-Ow2	2.032(7)
Av.		1.545	Mg1-Ow3	2.070(7)
			Mg1-Ow4	2.084(11)
Na-F1	x2	2.491(3)	Mg1-Ow5	2.085(11)
Na-F2	x2	2.500(3)	Mg1-Ow6	1.950(12)
Na-F3	x2	2.547(3)	Mg1-Ow7	2.070(11)
Na-Ow1	x2	2.393(5)	Av.	2.049
Av.		2.483		

Table 3 Atom coordinates, equivalent isotropic displacement parameters (Å²) and bond-valence sums (BVS) for penriceite

	Site	Occup.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	BVS*
Na	2a	1	0	0	0	0.0399(8)	1.09
Mg1	4e	0.5	0.4383(2)	0.4040(3)	0.6111(5)	0.0255(7)	2.17
Al1	2c	1	0	0.5	0	0.0138(4)	2.91
Al2	4e	1	0.12811(9)	0.74926(11)	0.78133(17)	0.0118(3)	2.73
P1	4e	1	0.22925(9)	0.53170(10)	0.05207(16)	0.0189(3)	4.90
O1	4e	1	0.3209(2)	0.4418(3)	0.0717(5)	0.0211(8)	1.30
O2	4e	1	0.1328(3)	0.4449(3)	0.0275(5)	0.0234(9)	1.76
O3	4e	1	0.2302(3)	0.6215(3)	0.2343(4)	0.0204(9)	1.64
O4	4e	1	0.2314(3)	0.6242(4)	0.8743(5)	0.0259(10)	1.68
F1*	4e	1	0.1294(2)	0.8203(2)	0.0266(3)	0.0195(7)	0.91
F2*	4e	1	-0.0255(3)	0.3729(3)	0.1898(4)	0.0279(9)	0.90
F3*	4e	1	0.0278(2)	0.6256(2)	0.1943(4)	0.0227(8)	0.93
Ow1	4e	1	0.1301(4)	0.1648(5)	0.0327(7)	0.0455(7)	0.19
Ow2	4e	0.75	0.3041(5)	0.4993(7)	0.5692(11)	0.0455(7)	0.26
Ow3	4e	0.75	0.5639(5)	0.2829(7)	0.6542(10)	0.0455(7)	0.23
Ow4	4e	0.5	0.4752(7)	0.5150(10)	0.8621(16)	0.0455(7)	0.34
Ow5	4e	0.5	0.3916(8)	0.2823(11)	0.3744(16)	0.0455(7)	0.42
Ow6	4e	0.5	0.3772(8)	0.2805(11)	0.7782(16)	0.0455(7)	0.50
Ow7	4e	0.5	0.4926(8)	0.4647(10)	0.5593(15)	0.0455(7)	0.35

* site occupancies of 0.67F+0.33OH used for BVS calculations

Discussion

Description of the crystal structure

An [001] projection of the crystal structure of penriceite, showing location of the cations and the fluorine sites, is shown in Figure 6. As described for aldermanite (Elliott et al., 2021), the structure of penriceite is composed of sawtooth-shaped layers of corner-connected $[\text{AlF}_4\text{O}_2]$ octahedra, decorated with corner-connected PO_4 tetrahedra, and with $\text{Mg}(\text{H}_2\text{O})_6$ octahedra and H_2O molecules located between the layers. The corner-connected octahedra form 6-membered rings that are centred by 8-coordinated sodium and have a topology identical to a 3-octahedra-wide {110} slice of the pyrochlore structure. The connectivity between the octahedra and tetrahedra, with each tetrahedron sharing three basal anions with three octahedra, is identical to that in crandallite (Blount, 1974). The heteropolyhedral layers conform to the symmetry of space group $P2_1/c$, whereas the interlayer $\text{Mg}(\text{H}_2\text{O})_6$ octahedra are disordered over sites with 50% occupancy. Ordering of the magnesium and associated H_2O is possible in the sub-group $P2_1$ of space group $P2_1/c$, as described for aldermanite (Elliott et al., 2021). The two independent $\text{Mg}(\text{H}_2\text{O})_6$ octahedra in $P2_1$ are shown in different colours in Figure 6. The empirical formula is consistent with minor substitution of magnesium for aluminium in the octahedra. The BVS values in Table 3 indicate that this substitution occurs preferentially in the Al2 site. Charge balance is at least partially restored by minor substitution of calcium for sodium. This is analogous to the correlated Mg/Al and Ca/Na substitutions in the rhombohedral pyrochlore structure of coussellite, $\text{CaNa}_3\text{AlMg}_3\text{F}_{14}$ (Mumme et al., 2010; renamed to fluornatrocoussellite by Atencio et al., 2017).

The properties of penriceite and its OH-analogue, aldermanite, are compared in Table 5. The properties are

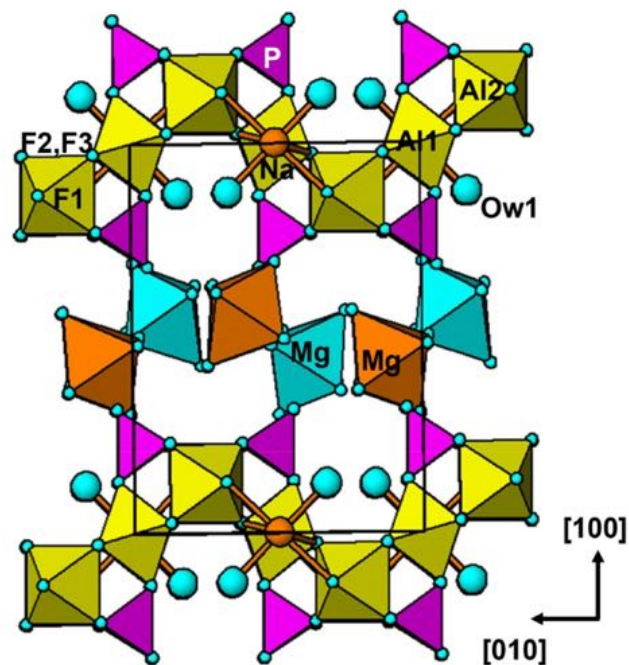


Figure 6 [001] projection of the structure of penriceite.

very similar, as expected when the compositions are so closely related, except for a higher fluorine content for penriceite shown in Table 1. The results in Table 1 and in Elliott et al. (2021) indicate that there is very little substitution of magnesium for aluminium in aldermanite. The penriceite structure is closely related to those of walentaite group minerals (Grey et al., 2020) that have the same sawtooth heteropolyhedral layers and interlayer hydrated cations, as described by Elliott et al. (2021).

Table 5 Comparison of properties for penriceite and aldermanite

	Penriceite	Aldermanite*
Ideal end-member formula	$\text{NaMgAl}_3(\text{PO}_4)_2\text{F}_6 \cdot 9\text{H}_2\text{O}$	$\text{NaMgAl}_3(\text{PO}_4)_2(\text{OH})_6 \cdot 9\text{H}_2\text{O}$
Symmetry	Monoclinic, space group $P2_1/c$	Monoclinic, space group $P2_1/c$
a (Å)	13.478(3)	13.524(3)
b (Å)	9.971(2)	9.958(2)
c (Å)	6.9990(10)	7.0130(10)
β (°)	97.20(3)	97.40(3)
Volume (Å ³), Z	933.2(3), 2	936.6(3), 2
Refractive index	Biaxial (+), $\alpha = 1.502(2)$, $\beta = 1.503(2)$, $\gamma = \text{n.d.}$	Only one RI measured, 1.500(5)
Strongest lines in PXRD	13.39, (100), (100)	13.40, (100)
d , (l), (hkl)	8.000, (30), (110)	7.98, (80)
	5.562, (26), (210)	5.55, (60)
	5.718, (12), (011)	5.70, (30)
		4.96, (30)
	2.855, (16), (022)	2.841, (50)
	2.782, (15), (420)	

* RI and PXRD for aldermanite from Harrowfield et al. (1981)

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References

- Atencio D, Andrade MB, Neto ACB and Pereira VP, 2017. Ralstonite renamed hydrokenoralstonite, coulsellite renamed fluornatrocoulsellite, and their incorporation into the pyrochlore supergroup: *The Canadian Mineralogist*, v. 55, p. 115–120.
- Blount AM, 1974. The crystal structure of crandallite: *American Mineralogist*, v. 59, p. 41–47.
- Elliott P, 2016. Jahnsite-(CaFeMg), a new mineral from Tom's quarry, South Australia: description and crystal structure: *European Journal of Mineralogy*, v. 28, p. 991–996.
- Elliott P, Grey IE and Willis AC, 2021. Redefinition of the formula for aldermanite, $[\text{Mg}(\text{H}_2\text{O})_6][\text{Na}(\text{H}_2\text{O})_2\text{Al}_3(\text{PO}_4)_3(\text{OH},\text{F})_6]\cdot\text{H}_2\text{O}$, and its crystal structure: *Mineralogical Magazine*, v. 85, p. 348–353.
- Elliott P, Peisley V and Mills SJ, 2014. The phosphate deposits of South Australia: *Australian Journal of Mineralogy*, v. 17, p. 3–32.
- Farrugia LJ, 1999. WinGX suite for small-molecule single-crystal crystallography: *Journal of Applied Crystallography*, v. 32, p. 837–838.
- Frost R, Xi Y, Palmer S and Pogson R, 2011. Vibrational spectroscopic analysis of the mineral crandallite $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5\cdot(\text{H}_2\text{O})$ from the Jenolan caves, Australia: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, v. 82, p. 461–466.
- Gagné OC and Hawthorne FC, 2015. Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen: *Acta Crystallographica*, v. B71, p. 562–578.
- Grey IE, Hochleitner R, Rewitzer C, Riboldi-Tunnicliffe A, Kampf AR, MacRae CM, Mumme WG, Kaliwoda M, Friis H and Martin CU, 2020. The walentaite group and the description of a new member, alcantarillaite, from the Alcantarilla mine, Belalcázar, Córdoba, Andalusia, Spain: *Mineralogical Magazine*, v. 84, p. 412–419.
- Grey IE, Mumme WG, Kampf AR, MacRae CM and Wilson NC, 2019. Natrowalentaite, a new mineral from the Griffins Find gold deposit, Western Australia: *Australian Journal of Mineralogy*, v. 20, p. 7–15.
- Grey IE, Shanks FL, Wilson NC, Mumme WG and Birch WD, 2011. Carbon incorporation in plumbogummite-group minerals: *Mineralogical Magazine*, v. 75, p. 145–158.
- Harrowfield IR, Segnit ER and Watts JA, 1981. Aldermanite, a new magnesium aluminium phosphate: *Mineralogical Magazine*, v. 44, p. 59–62.
- Johns RK, 1976. Phosphate, South Australia. In *Economic geology of Australia and Papua New Guinea*, 4, *Industrial minerals and rocks*, CL Knight, Editor, p. 282–285. Australasian Institute of Mining and Metallurgy, Monograph Series, 8.
- Libowitzky E, 1999. Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals: *Monatshefte für Chemie*, v. 130, p. 1047–1059.
- Mills SJ, Birch WD, Kampf AR, Christy AG, Pluth JJ, Pring A, Raudsepp M and Chen Yu-S, 2010. Kapundaite, a new phosphate species from Tom's quarry, South Australia: description and structural relationship to melonjosephite: *American Mineralogist*, v. 95, p. 754–760.
- Mills SJ, Groat LA, Wilson SA, Birch WD, Whitfield PS and Raudsepp M, 2008. Angastonite, $\text{CaMgAl}_2(\text{PO}_4)_2(\text{OH})_4\cdot 7\text{H}_2\text{O}$: a new phosphate mineral from Angaston, South Australia: *Mineralogical Magazine*, v. 72, p. 1011–1020.
- Mills SJ, Ma C and Birch WD, 2011. A contribution to understanding the complex nature of peisleyite: *Mineralogical Magazine*, v. 75, p. 2733–2737.
- Mumme WG, Grey IE, Birch WD, Pring A, Bougerol C and Wilson NC, 2010. Coulsellite, $\text{CaNa}_3\text{AlMg}_3\text{F}_{14}$, a rhombohedral pyrochlore with a 1:3 ordering of both A and B sites, from the Cleveland Mine, Tasmania, Australia: *American Mineralogist*, v. 95, p. 736–740.
- Petříček V, Dušek M and Palatinus L, 2014. Crystallographic Computing System JANA2006: General features: *Zeitschrift für Kristallographie*, v. 229, p. 345–352.
- Pilkington ES, Segnit ER and Watts JA, 1982. Peisleyite, a new sodium aluminium sulphate phosphate: *Mineralogical Magazine*, v. 46, p. 449–452.
- Rodriguez-Carvajal J, 1990. FULLPROF: A Program for Rietveld refinement and Pattern Matching Analysis, in *Satellite meeting on powder diffraction of the Fifteenth General Assembly and International Congress of Crystallography*, Toulouse, France, 16–19 July 1990.

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