Mineralogical Magazine (2022), **86**, 525–530
doi:10.1180/mgm.2022.2

Article

Special Issue dedicated to Peter Williams

Reaphookhillite, $MgZn_2(PO_4)_2{\cdot}4H_2O$, the Mg analogue of parahopeite from Reaphook Hill, South Australia

Peter Elliott[1,2]*

[1]Department of Earth Sciences, School of Physical Sciences, The University of Adelaide, Adelaide, South Australia 5005, Australia; and [2]South Australian Museum, North Terrace, Adelaide, South Australia 5000, Australia

ABSTRACT

Reaphookhillite, ideally $MgZn_2(PO_4)_2{\cdot}4H_2O$, is a new phosphate mineral from Reaphook Hill, Flinders Ranges, South Australia, Australia. Reaphookhillite occurs as colourless, bladed to thin tabular crystals to 0.6 mm across. Cleavage is perfect parallel to {010}. The mineral occur as overgrowths on parahopeite crystals and is associated with scholzite, leucophosphite and chalcophanite. The calculated density is 3.09 g/cm^3 from the empirical formula. Reaphookhillite is optically biaxial (+), $\alpha = 1.583(3)$, $\beta = 1.596(3)$, $\gamma = 1.611(3)$ and $2V_{calc} = 88.7°$. Electron microprobe analyses gave ZnO 41.57, MgO 7.96, MnO 0.40, P_2O_5 33.72, $H_2O_{(calc)}$ 16.92, total 100.57 wt.%. The empirical formula, based on 12 O apfu, is $Mg_{0.83}Zn_{2.16}Mn^{2+}_{0.02}(PO_4)_{2.01}{\cdot}3.97H_2O$. Reaphookhillite is triclinic, $P\bar{1}$, with the unit-cell parameters of $a = 5.7588(12)$, $b = 7.5341(15)$ $c = 5.2786(11)$ Å, $\alpha = 93.44(3)$, $\beta = 91.27(3)$, $\gamma = 91.30(3)°$, $V = 228.49(8)$ Å^3 and $Z = 1$. The strongest eight lines in the powder X-ray diffraction pattern are [d_{obs} in Å (I) (hkl)] 7.577 (100) (010); 4.461 (24) $(01\bar{1})$; 4.461 (24) $(01\bar{1})$; 3.771 (14) (020); 3.158 (13) $(02\bar{1})$; 2.982 (32) (021); 2.880 (27) (200); 2.775 (14) $(1\bar{2}1, 12\bar{1})$; and 2.668 (13) $(1\bar{2}\bar{1}, 210)$. Reaphookhillite is isostructural with parahopeite, with Mg replacing Zn in the 6-coordinated site in the structure. The structure contains ZnO_4 and PO_4 tetrahedra which share corners to form a sheet in the (001) plane. Sheets are linked in the c direction by corner sharing $MgO_2(H_2O)_4$ octahedra.

Keywords: reaphookhillite, new mineral species, magnesium zinc phosphate, crystal structure, Reaphook Hill, Australia

(Received 16 November 2021; accepted 4 January 2022; Associate Editor: Anthony R Kampf)

Introduction

The Reaphook Hill Zn deposit is one of several non-sulfide zinc occurrences discovered in the northern Flinders Ranges of South Australia during the 1960s. Rock chip sampling near Reaphook Hill by the South Australian Department of Mines in 1963 and subsequent stream sediment sampling undertaken by Kennecott Explorations (Australia) Pty. Ltd. revealed zinc concentrations of up to 1170 ppm (Johns, 1972). Scholzite was discovered as prismatic needles in three discrete near-surface mineralised zones associated with ferruginised and manganiferous limestone. Exploratory drilling failed to disclose sulfides or mineralisation below the base of oxidation and the prospect was considered to be incapable of sustaining a mining operation. The deposit was mined for specimens in the late 1960s and 1970s and many hundreds of specimens are now in collections worldwide (Johnson, 1978; Johnston and Hill, 1978). Investigations of collinsite, tarbuttite, parahopeite and scholzite from Reaphook Hill were undertaken by Hill and Milnes (1974) and Hill (1975) using powder X-ray diffraction and electron-probe analyses. An X-ray single-crystal study of scholzite was also completed (Hill *et al.*, 1973; Hill, 1975). Parahopeite crystals were found to be compositionally zoned with their cores enriched in Fe and Mn and outer zones enriched in Mg, with MgO contents of up to 6.3 wt.%. Parahopeite at Reaphook Hill has several morphological varieties belonging to two generations. First-generation parahopeite occurs as translucent white to yellow–brown crystals with a prismatic habit and up to 1 cm in length. On the surface of some crystals, a second generation of parahopeite and reaphookhillite has formed as parallel growths. These second-generation crystals are colourless to white in colour and are bladed and thin tabular to equant in habit. In the present study, electron-probe analyses of 24 second generation parahopeite crystals found that the content of MgO is typically in the range 2.3 to 4.6 wt.%. Two of the analysed crystals had a MgO content in the range 5.5 to 9.7 wt.% and these represent the new mineral reaphookhillite, the Mg analogue of parahopeite. The new species (IMA 2018-128) and its name were approved by the Commission on New Minerals Nomenclature and Classification of the International Mineralogical Association (IMA2018-128, Elliott 2019). The holotype specimen, registration number G34798, is deposited in the mineral collections of the South Australian Museum, Adelaide, South Australia, Australia.

---

*__Author for correspondence:__ Peter Elliott, Email: peter.elliott@adelaide.edu.au

This paper is part of a thematic set that honours the contributions of Peter Williams.

Cite this article: Elliott P. (2022) Reaphookhillite, $MgZn_2(PO_4)_2{\cdot}4H_2O$, the Mg analogue of parahopeite from Reaphook Hill, South Australia. *Mineralogical Magazine* **86**, 525–530. https://doi.org/10.1180/mgm.2022.2

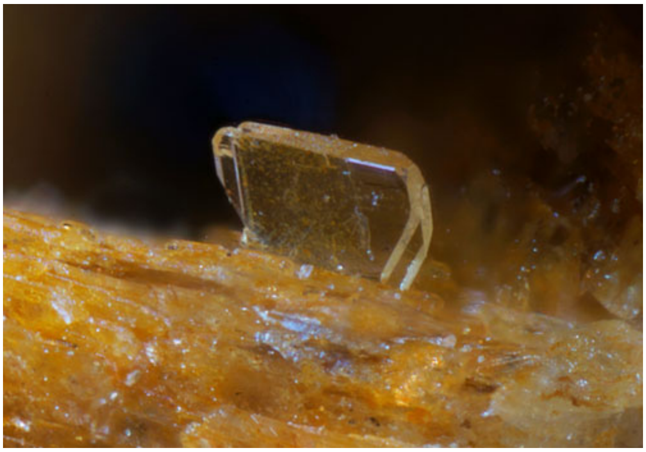

Fig. 1. Crystal of reaphookhillite, 0.3 mm in width, on parahopeite.

Table 1. Analytical data for reaphookhillite.

Constituent	Wt.%	Range	S.D.	Probe standard
ZnO	41.57	39.67–43.04	1.15	Willemite
MgO	7.96	6.85–9.49	0.84	Almandine–pyrope
MnO	0.40	0.14–0.60	0.16	Rhodonite
P_2O_5	33.72	32.11–35.39	1.13	Apatite
H_2O*	16.92			
Total	100.57			

*based on the structure refinement. S.D. – standard deviation

Occurrence

Reaphook Hill deposit comprises three discrete, near-surface mineralised zones, less than 3 m below the surface in unmetamorphosed sediments of the Lower Cambrian Parachilna Formation. These sediments comprise sandy, poorly sorted argillaceous siltstones with conglomerate lenses containing well-rounded quartz pebbles dispersed in a matrix of weakly consolidated sand and grit (Johns, 1972). The Wilkawillina Limestone conformably overlies the Parachilna Formation and contains high Mn, Zn and P concentrations. Phosphate deposit occurrences in the Parachilna Formation have resulted from the near-surface enrichment by groundwater of zinc and phosphorus derived from originally low-grade mineralisation. The mineralised zones at Reaphook Hill have ferruginous and manganiferous cappings, which grade downwards into complexly fractured phosphatic pebble conglomerates, sandstones, and siltstones. They seem to have developed in fractured and faulted zones in the Parachilna Formation as a result of the action of groundwater causing near-surface enrichment of manganese, iron, zinc and phosphorus (Hill and Milnes, 1974).

Appearance, physical and optical properties

The holotype specimen of reaphookhillite comprises crystalline parahopeite. Parahopeite crystals line small cavities and reaphookhillite crystals have formed as an overgrowth on parahopeite crystals (Fig. 1). Crystals are bladed to thin tabular in habit and are up to 0.6 mm in width. Reaphookhillite is colourless and transparent. It has a vitreous lustre and shows a perfect cleavage on {010}. The mineral is brittle and shows an irregular fracture. By analogy with parahopeite, Mohs hardness is estimated at ~ 4. The calculated density is 3.09 g/cm^3 from the empirical formula; 3.03 g/cm^3 from the ideal formula. Optically, the mineral is biaxial (+) and is nonpleochroic. The indices of refraction are $\alpha = 1.583(3)$, $\beta = 1.596(3)$, $\gamma = 1.611(3)$ and $2V_{calc} = 88.7°$.

Chemical analysis

Chemical data for reaphookhillite (Table 1) were obtained using a CAMECA SX50 electron microprobe operating in wavelength dispersive mode. Operating conditions were: accelerating voltage 15 kV, beam current 20 nA and beam diameter 5 µm. The following standards were used: willemite (Zn$K\alpha$), almandine–pyrope (Mg$K\alpha$), rhodonite (Mn$K\alpha$) and apatite (PKα). No other elements with $Z > 8$ were detected from analyses using energy dispersive spectroscopy mode. Raw X-ray intensities were corrected for matrix effects with a φ(ρz) algorithm (Pouchou and Pichoir, 1985). The empirical formula (based on 12 O atoms per formula unit) is $Mg_{0.83}Zn_{2.16}Mn^{2+}_{0.02}(PO_4)_{2.01}\cdot3.97H_2O$. The ideal formula is $MgZn_2(PO_4)_2\cdot4H_2O$ which requires MgO 9.66, ZnO 39.02, P_2O_5 34.03, H_2O 17.28, Total 100.00 wt.%.

Infrared spectroscopy

The infrared absorption spectrum of reaphookhillite (Fig. 2) was obtained using a powdered sample using a Nicolet 5700 Fourier-transform infrared (FTIR) spectrometer (range 4000 to 650 cm^{-1}, transmission mode) equipped with a Nicolet Continuum IR microscope and a diamond-anvil cell. A broad band is observed in the OH-stretching region with maxima at 3456, 3331 and 3174 cm^{-1} and a shoulder at 3068 cm^{-1}. Calculated d(O···O) hydrogen donor–acceptor distances are in the range ~2.9–2.6 Å using the correlation function given by Libowitzky (1999) which are in good agreement with the results of the single-crystal structure analysis. The band at 1690 cm^{-1} is attributable to H–O–H bending vibrations of water molecules. The bands at 1062 and 957 cm^{-1} are assigned to ν_3 antisymmetric stretching vibrations of the PO_4 tetrahedra ν_1 and bands at 802 and 704 cm^{-1} to ν_1 symmetric stretching vibrations of the PO_4 tetrahedra.

Powder X-ray diffraction

Powder X-ray diffraction data of reaphookhillite (Table 2) were collected using a Rigaku Hiflux Homelab diffractometer (Cu$K\alpha$ X-radiation, $\lambda = 1.541870$ Å). The experimental powder pattern was indexed based on the calculated values of intensities obtained from the crystal-structure refinement, using the *LAZY PULVERIX* program (Yvon *et al.*, 1977). The unit-cell parameters were derived from least-squares refinement using the program *UNITCELL* (Holland and Redfern, 1997): $a = 5.7625(4)$, $b = 7.5412(5)$, $c = 5.2881(4)$ Å, $\alpha = 93.405(7)$, $\beta = 91.135(7)$, $\gamma = 91.317(5)°$ and $V = 229.28(1)$ Å^3.

Single-crystal X-ray diffraction

Structure determination

A crystal 125 µm × 30 µm × 15 µm in size was attached to a MiTeGen polymer loop and mounted on a an Oxford Diffraction Xcalibur E diffractometer equipped with an Eos CCD detector. An ω scan rotational method was used to collect the intensity data at room temperature using Mo$K\alpha$ radiation

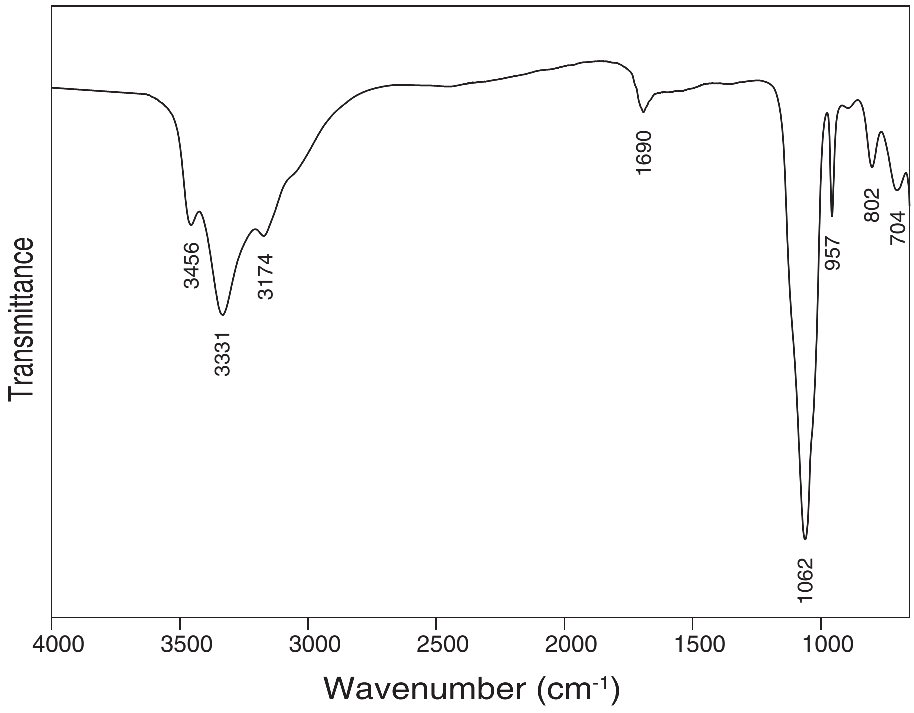

Fig. 2. The FTIR spectrum of powdered reaphookhillite.

Table 2. Calculated* and observed powder X-ray diffraction data for reaphookhillite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	*h k l*	I_{obs}	d_{obs}	I_{calc}	d_{calc}	*h k l*
100	**7.577**	100	7.518	0 1 0			3	2.086	1 $\bar{1}$ 3
8	5.785	2	5.756	1 0 0	4	2.039	4	2.043	1 1 3
10	5.296	8	5.268	0 0 1			10	2.036	1 2 2
3	4.642	1	4.624	1 $\bar{1}$ 0	2	1.961	6	1.966	2 $\bar{2}$ 0
6	4.533	2	4.518	1 1 0	1	1.920	4	1.921	2 2 0
24	**4.461**	27	4.443	0 1 $\bar{1}$	2	1.878	2	1.880	0 0 4
12	**4.213**	29	4.197	0 1 1	1	1.867	1	1.870	0 3 $\bar{1}$
4	3.856	3	3.841	1 0 1	1	1.812	2	1.817	1 $\bar{3}$ 0
14	**3.771**	4	3.759	0 2 0	3	1.797	3	1.800	0 1 $\bar{4}$
10	3.532	14	3.527	1 1 $\bar{1}$	3	1.778	4	1.782	2 1 $\bar{3}$
		7	3.507	1 $\bar{1}$ 1			3	1.781	1 $\bar{2}$ 3
2	3.446	1	3.444	1 $\bar{1}$ $\bar{1}$			2	1.781	2 $\bar{1}$ $\bar{3}$
3	3.351	3	3.340	1 1 1			2	1.774	0 1 4
5	3.188	2	3.183	1 $\bar{2}$ 0			4	1.763	2 $\bar{2}$ $\bar{2}$
13	**3.158**	24	3.152	0 2 $\bar{1}$	3	1.755	2	1.758	1 3 $\bar{1}$
32	**2.982**	38	2.976	0 2 1			2	1.756	3 0 0
27	**2.880**	38	2.878	2 0 0			5	1.754	2 2 $\bar{2}$
14	**2.775**	18	2.771	1 $\bar{2}$ 1	1	1.725	3	1.728	1 2 3
		12	2.757	1 2 $\bar{1}$	1	1.684	4	1.688	3 0 1
12	**2.721**	13	2.710	2 $\bar{1}$ 0	1	1.675	2	1.677	1 $\bar{1}$ 4
13	**2.668**	2	2.679	1 $\bar{2}$ $\bar{1}$			2	1.634	1 $\bar{3}$ $\bar{2}$
		14	2.667	2 1 0	1	1.628	2	1.632	3 $\bar{1}$ 1
9	2.637	30	2.634	0 0 2			2	1.629	3 0 $\bar{2}$
5	2.538	9	2.534	0 1 $\bar{2}$	3	1.587	5	1.591	0 2 $\bar{4}$
11	2.508	4	2.506	0 3 0	1	1.566	5	1.572	3 $\bar{1}$ $\bar{2}$
2	2.411	2	2.422	2 1 $\bar{1}$			2	1.563	3 1 $\bar{2}$
		2	2.410	2 $\bar{1}$ $\bar{1}$	2	1.552	6	1.557	0 2 4
1	2.377	4	2.374	1 0 2			2	1.555	3 0 2
5	2.313	3	2.318	1 $\bar{3}$ 0			2	1.526	2 $\bar{2}$ 3
		8	2.312	2 $\bar{2}$ 0			2	1.522	2 1 $\bar{4}$
4	2.277	4	2.278	1 3 0	2	1.514	4	1.518	2 $\bar{1}$ $\bar{4}$
		2	2.271	1 $\bar{1}$ $\bar{2}$	2	1.500	2	1.504	0 0 5
1	2.260	4	2.259	2 2 0	1	1.484	2	1.490	3 1 2
4	2.131	7	2.132	2 $\bar{2}$ 1	4	1.434	7	1.439	0 4 0
4	2.116	7	2.119	2 2 $\bar{1}$	2	1.431	2	1.432	3 1 $\bar{3}$
4	2.100	9	2.103	2 $\bar{2}$ $\bar{1}$					
		2	2.098	0 2 2					

*I_{calc} calculated with the *LAZY PULVERIX* program (Yvon *et al.*, 1977).
The strongest lines are given in bold.

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

Crystal data	
Space group	$P\bar{1}$
a, *b*, *c* (Å)	5.7588(12), 7.5341(15), 5.2786(11)
α, β, γ (°)	93.44(3), 91.27(3), 91.30(3)
V (Å^3), Z	228.49(8), 1
F(000)	211
μ (mm^{-1})	6.381
Absorption correction	multi-scan, T_{min},T_{max} = 0.84, 1.00
Crystal dimensions (μm)	125 × 30 × 15
Data collection	
Diffractometer	Oxford Diffraction Xcalibur E
Temperature (K)	293
Radiation	Mo*Kα*, λ = 0.71073 Å
θ range (°)	3.54–27.09
Rotation axes	ω
Rotation width	1.0
Total no. of frames	1076
Collection time per frame (s)	14.46
h, k, l ranges	−7 → 7, −9 → 9, −6 → 6
Total reflections measured	4856
Unique reflections	999 (R_{int} = 0.0560)
Refinement	
Refinement on	F^2
R_1 for $F_0 > 4\sigma(F_0)$	2.91%
wR_2* for all F_0^2	8.93%
Reflections used $F_0^2 > 4\sigma(F_0^2)$	889
Number of restraints/parameters refined	6/93
Extinction factor	0.002(5)
(Δ/σ)max	0.000
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e^-/Å^3)	−0.546, 0.864
GooF	0.838

*$w = 1/[\sigma^2(Fo^2) + (0.0739\ P)^2 + 0.32\ P]$; $P = (\text{Max}\ (F_0^2,0)] + 2Fc^2)/\ 3$

(λ = 0.71073 Å). The unit cell was refined from 1697 reflections using the least-squares algorithm in the *CrysalisPro* software package (Rigaku Oxford Diffraction, 2015). *CrysalisPro* was used to process the structure data, including the application of an empirical absorption correction. The structure was solved by direct methods using *SHELXT* (Sheldrick, 2015a) and refined in

Table 4. Fractional coordinates and displacement parameters (Å^2) for atoms for reaphookhillite.

	x	y	z	U^{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg*	0	0	0	0.0148(5)	0.0196(7)	0.0139(7)	0.0106(7)	−0.0027(4)	0.0004(4)	0.0006(5)
Zn	0.25068(8)	0.59800(6)	0.81627(8)	0.0129(2)	0.0196(7)	0.0139(7)	0.0106(7)	−0.0027(4)	0.0004(4)	0.0006(5)
P	0.25022(17)	0.36146(13)	0.29531(18)	0.0102(3)	0.0160(3)	0.0135(3)	0.0088(3)	−0.00210(18)	0.00091(18)	0.00085(18)
O1	0.4679(5)	0.2595(4)	0.2282(5)	0.0147(6)	0.0135(5)	0.0097(5)	0.0072(5)	−0.0018(4)	0.0000(4)	−0.0002(4)
O2	0.2330(5)	0.3904(4)	0.5842(5)	0.0156(6)	0.0125(13)	0.0136(14)	0.0179(14)	−0.0021(11)	0.0026(11)	0.0017(11)
O3	0.0310(5)	0.2507(3)	0.1967(5)	0.0131(6)	0.0252(16)	0.0121(14)	0.0092(13)	−0.0025(10)	−0.0002(11)	−0.0015(11)
O4	0.2506(5)	0.5418(4)	0.1723(5)	0.0158(6)	0.0165(14)	0.0088(13)	0.0133(14)	−0.0039(10)	−0.0019(11)	0.0007(11)
OW5	0.2223(5)	0.8919(4)	0.2613(6)	0.0179(6)	0.0280(16)	0.0108(14)	0.0087(13)	0.0003(11)	0.0006(11)	0.0015(12)
OW6	0.2669(5)	0.0578(4)	0.7526(6)	0.0177(6)	0.0299(17)	0.0128(14)	0.0104(14)	−0.0035(11)	−0.0036(12)	0.0021(12)
H5A	0.233(9)	0.942(6)	0.406(7)	0.027	0.0206(16)	0.0173(15)	0.0147(14)	−0.0006(12)	−0.0003(12)	−0.0024(12)
H5B	0.220(9)	0.780(4)	0.273(9)	0.027						
H6A	0.249(8)	0.165(4)	0.709(10)	0.027						
H6B	0.413(5)	0.051(6)	0.801(10)	0.027						

*Site occupancy: $Mg_{0.735(6)}Zn_{0.265(6)}$

Table 5. Selected interatomic distances and hydrogen bonds (d in Å, angles in °) for reaphookhillite.

Mg–OW5 ×2	2.075(3)	Zn–O2	1.927(3)
Mg–OW6 ×2	2.094(3)	Zn–O1	1.950(3)
Mg–O4 ×2	2.102(3)	Zn–O3	1.951(3)
<Mg–O>	2.090	Zn–O4	2.006(3)
		<Zn–O>	1.959
P1–O1	1.522(3)		
P1–O2	1.533(3)		
P1–O3	1.560(3)		
P1–O4	1.540(3)		
<*T*–O>	1.539		

Hydrogen bonds

D–H···*A*	*D*–H	H···*A*	*D*···*A*	∠*D*–H···*A*
OW5-H5A···OW6	0.83(3)	1.98(3)	2.814(4)	178(5)
OW5-H5B···O4	0.85(3)	1.85(3)	2.661(4)	158(5)
OW6-H6A···O2	0.86(3)	1.86(3)	2.719(4)	174(5)
OW6-H6B···O1	0.88(3)	2.45(5)	2.872(4)	110(4)
OW6-H6B···OW5	0.88(3)	2.17(4)	2.961(4)	150(5)

Table 6. Bond-valence analysis for reaphookhillite*.

	Zn	Mg	P	H5A	H5B	H6A	H6B	Sum
O1	0.50		1.29				0.15	1.94
O2	0.53		1.26			0.20		1.99
O3	0.49		1.25		0.22			1.96
O4	0.43	$0.33^{\times 2\downarrow}$	1.18					1.94
OW5		$0.35^{\times 2\downarrow}$		0.83	0.78		0.11	2.07
OW6		$0.34^{\times 2\downarrow}$		0.17		0.80	0.74	2.05
Sum	1.95	2.04	4.98	1.00	1.00	1.00	1.00	

*Bond valence parameters are from Gagné and Hawthorne (2015). Hydrogen-bond strengths are based on O–O bond lengths from Ferraris and Ivaldi (1988).

space group $P\bar{1}$ using the *SHELXL-2018* program (Sheldrick, 2015b) implemented in the *WinGX* suite (Farrugia, 1999). Following the solution of the structure, the atom coordinates were transformed to correspond to those in the structure of parahopeite (Chao, 1969). The final R_1 is 2.91% for 889 observed reflections [$F_0 > 4\sigma(F_0)$]. Difference-Fourier syntheses located all H atom positions. The H sites were refined with soft restraints on the O–H distances of 0.90(3) Å, H–H restraints of 1.40 Å and temperature factors $U_{iso}(H) = 1.5U_{eq}(O)$. Details of data collection and structure refinement are provided in Table 3. Fractional coordinates and atom displacement parameters are provided in Table 4, selected interatomic distances and hydrogen bonds in Table 5 and bond valences in Table 6. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Description of the crystal structure

Reaphookhillite is isostructural to its Zn-analogue parahopeite, $Zn_3(PO_4)_2{\cdot}4H_2O$, (Table 7) whose structural details were described by Chao (1969). In the crystal structure of parahopeite, there are two Zn sites with different coordination numbers: 6-fold coordination and 4-fold coordination. In reaphookhillite, the [6]-coordinated site is occupied by Mg. The refined site-scattering value at the site is 16.77 epfu (electrons per formula unit), which is slightly greater than the result from the electron-microprobe analysis of 15.26 epfu, but still consistent with strong dominance of Mg at the site. The average <*M*–O> distance is similar in both structures; 2.090 Å for reaphookhillite and 2.108 Å for parahopeite. Calculation of bond-length distortion (BLD) coefficients (Robinson *et al.*, 1971) indicates that the site in reaphookhillite is more strongly distorted (BLD 5.10) than in parahopeite (BLD 2.00). The tetrahedrally coordinated Zn site in reaphookhillite has a <Zn–O> distance of 1.960 Å, similar to the same distance in parahopeite of 1.952 Å. Bond-length distortion coefficients are 1.19 and 1.13 respectively.

Tetrahedra of ZnO_4 and PO_4 share common corners to form a sheet of 4-membered rings parallel to (001) (Fig. 3). Sheets are linked in the c direction by $MgO_2(H_2O)_4$ octahedra which share O4 anions with P tetrahedra (Fig. 4). A system of hydrogen bonds (O···O range: 2.66–2.96 Å) further stabilises the structure (Table 5, Fig. 5). The structure contains two independent H_2O molecules each belonging to the $MgO_2(H_2O)_4$ octahedron. OW5 donates one hydrogen bond and OW6 donates two hydrogen bonds to neighbouring O atoms of the tetrahedral sheet. Both OW5 and OW6 donate hydrogen bonds to the other H_2O group in the structure on an adjacent Mg octahedron.

Structural relations

Reaphookhillite is a rare example of a non-silicate oxysalt mineral in which Mg and Zn are ordered in separate sites. Other structures that contain [6]-coordinated Mg sites and [4]-coordinated Zn sites are falsterite (Kampf *et al.*, 2012), ferraioloite (Mills *et al.*, 2016), rinmanite (Holtstam *et al.*, 2001) and zemannite (Cametti *et al.*, 2017; Missen *et al.*, 2019).

Table 7. Comparison of reaphookhillite and parahopeite.

Mineral name	Reaphookhillite	Parahopeite*
Locality	Reaphook Hill, Martins Well, Flinders Ranges, South Australia, Australia	Kabwe Mine (Broken Hill Mine), Kabwe, Central Province, Zambia
Reference	This work	Chao (1969)
Formula	$MgZn_2(PO_4)_2{\cdot}4H_2O$	$Zn_3(PO_4)_2{\cdot}4H_2O$
Crystal system	triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	5.7588(12)	5.768(5)
b (Å)	7.5341(15)	7.550(5)
c (Å)	5.2786(11)	5.276(5)
α (°)	93.44(3)	93.42
β (°)	91.27(3)	91.18
γ (°)	91.30(3)	91.37
V (Å^3)	228.49(8)	228.34
Z	1	1
Strongest lines in the X-ray powder pattern d, Å, (I, %)	7.577 (100), 4.461 (24), 4.213 (12), 3.771 (14),3.158 (13), 2.982 (32), 2.880 (27), 2.775 (14), 2.721 (12), 2.668 (13)	7.53 (100), 2.981 (80), 4.44 (70), 5.27 (40), 2.887 (40), 5.78 (30), 3.77 (30)

*X-ray powder pattern from Anthony *et al.* (2000).

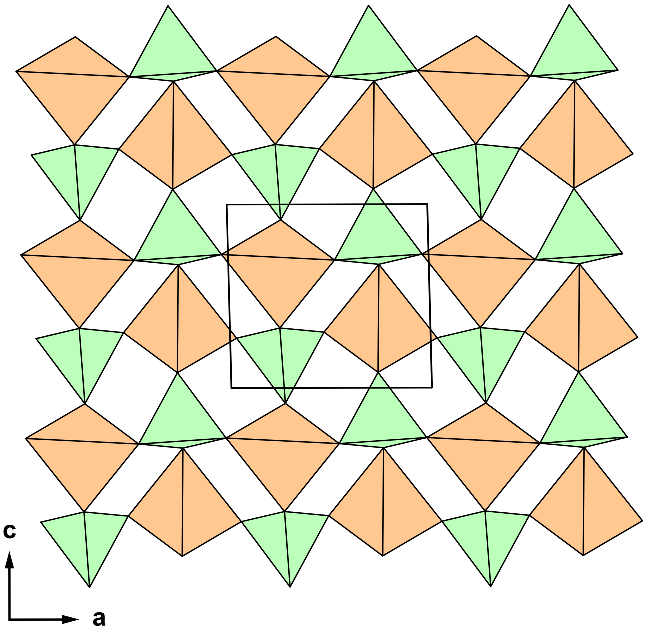

Fig. 3. The sheet of corner-sharing ZnO_4 and PO_4 tetrahedra in the structure of reaphookhillite viewed along [010]. ZnO_4 tetrahedra are orange; PO_4 tetrahedra are green. The unit cell is outlined.

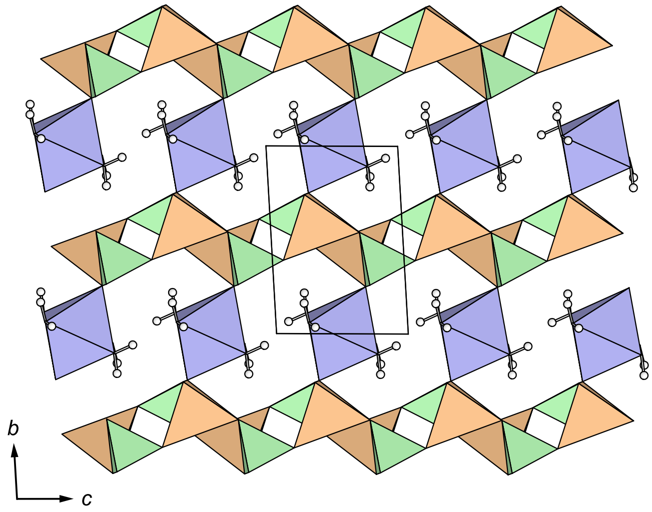

Fig. 4. The crystal structure of reaphookhillite viewed along [100]. $MgO_2(H_2O)_4$ octahedra are blue; ZnO_4 tetrahedra are orange; PO_4 tetrahedra are green; hydrogen atoms are small white spheres. The unit cell is outlined.

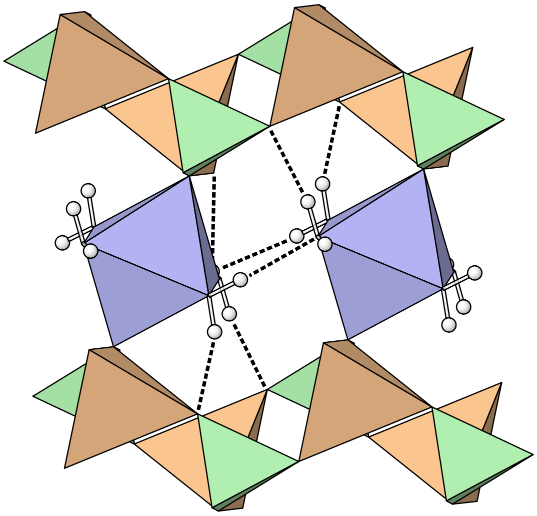

Fig. 5. The hydrogen bonding in reaphookhillite.

Reaphookhillite and parahopeite are structurally related to davidlloydite, $(Zn,Cu)Zn_2(AsO_4)_2{\cdot}4H_2O$ (Hawthorne *et al.*, 2012), which is also triclinic and contains topologically identical sheets of ZnO_4 and XO_4 tetrahedra that form 4-membered rings. However, the structures have different linkages between sheets. The structural relationship between parahopeite and davidlloydite as stacking variants was discussed by Hawthorne *et al.* (2012). Sheets of ZnO_4 and XO_4 tetrahedra, with $X = P$ or As, of the form $[ZnXO_4]$ are found in the structures of phosphophyllite, $FeZn_2(PO_4)_2{\cdot}4H_2O$ (Hill, 1977; Thomas and Weller, 1992), stergiouite, $CaZn_2(AsO_4)_2{\cdot}4H_2O$ (Rieck *et al.*, 2020) and in the orthorhombic members of the hopeite group; hopeite, $Zn_3(PO_4)_2{\cdot}4H_2O$ (Hill and Jones, 1976), arsenohopeite, $Zn_3(AsO_4)_2{\cdot}4H_2O$ (Neuhold *et al.*, 2012) and nizamoffite, $MnZn_2(PO_4)_2{\cdot}4H_2O$ (Kampf *et al.*, 2013). In contrast to reaphookhillite, parahopeite and davidlloydite, the $ZnXO_4$ sheets in phosphophyllite and related minerals are composed of tetrahedra that link to form 3- and 4-membered rings. Sheets link via $MO_2(H_2O)_4$ octahedra, $M = \text{Mn, Fe, Zn}$.

Acknowledgements. Ben Wade of Adelaide Microscopy, The University of Adelaide is thanked for assistance with the microprobe analysis. The infrared spectrum was acquired with the assistance of the Forensic Science Centre, Adelaide. The single-crystal X-ray data set was collected at the Bragg Crystallography Facility, The University of Adelaide. Structures Editor Peter Leverett, Fernando Colombo and anonymous reviewer are thanked for constructive comments that improved the quality of the manuscript.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2022.2

References

Anthony J.W., Bideaux R.A., Bladh K.W. and Nichols M.C. (2000) *Handbook of Mineralogy. Vol. IV: Arsenates, Phosphates, Vanadates*. Mineral Data Publishing, Tucson, Arizona, USA, 680 pp.

Cametti G., Churakov S. and Armbruster T. (2017) Reinvestigation of the zemannite structure and its dehydration behavior: a single-crystal X-ray and atomistic simulation study. *European Journal of Mineralogy*, **29**, 53–61.

Chao G.Y. (1969) Refinement of the crystal structure of parahopeite, *Zeitschrift für Kristallographie*, **130**, 261–266.

Elliott, P. (2019) Reaphookhillite, IMA 2018-128. CNMNC Newsletter No. 47, February 2019, page 146. *Mineralogical Magazine*, **83**, 143–147.

Farrugia L.J. (1999) WinGX Suite for Single Crystal Small Molecule Crystallography. *Journal of Applied Crystalography*, **32**, 837–838.

Ferraris G. and Ivaldi G. (1988) Bond valence vs. bond length in O···O hydrogen bonds. *Acta Crystallographica*, **B44**, 341–344.

Gagné O.C. and Hawthorne F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica*, **B71**, 562–578.

Hawthorne F.C., Cooper M.A., Abdu Y.A., Ball N.A., Back M.E. and Tait K.T. (2012) Davidlloydite, ideally $Zn_3(AsO_4)_2(H2O)_4$, a new arsenate mineral from the Tsumeb mine, Otjikoto (Oshikoto) region, Namibia: description and crystal structure. *Mineralogical Magazine*, **7**, 45–57.

Hill R.J. (1975) *The Crystals Structure of the Mineral Scholzite and a Study of the Crystal Chemistry of Zinc in Some Related Phosphate and Arsenate Minerals*. PhD Thesis, The University of Adelaide, Australia.

Hill R.J. (1977) The crystal structure of phosphophyllite. *American Mineralogist*, **62**, 812–817.

Hill R.J. and Jones J.B. (1976) The crystal structure of hopeite. *American Mineralogist*, **61**, 987–995.

Hill R.J. and Milnes A.R. (1974) Phosphate minerals from Reaphook Hill, Flinders Ranges, South Australia. *Mineralogical Magazine*, **39**, 684–695.

Hill R.J., Johnson J.E. and Jones J.B. (1973) Scholzite and other phosphate minerals from Reaphook Hill, South Australia. *Neues Jahrbuch für Mineralogie – Monatshefte*, 1–8.

Holland T.J.B. and Redfern S.A.T. (1997) Unit cell refinement from powder diffraction data; the use of regression diagnostics. *Mineralogical Magazine*, **61**, 65–77.

Holtstam D., Gatedal K. Söderberg K. and Norrestam R. (2001) Rinmanite, $Zn_2Sb_2Mg_2Fe_4O_{14}(OH)_2$, a new mineral species with a nolanite-type structure from the Garpenberg Norra mine, Dalarna, Sweden. *The Canadian Mineralogist*, **39**, 1675–1685.

Johns R.K. (1972) *Base Metal Occurrences with Lower Cambrian Sediments of the Northern Flinders Ranges*. South Australian Geological Survey, Report of Investigations, 37.

Johnson J.E. (1978) Zinc phosphate minerals from Reaphook Hill, South Australia. *Australian Mineralogist*, **1**, 65–68.

Johnston C.W. and Hill R.J. (1978) Zinc phosphates at Reaphook Hill South Australia. *Mineralogical Record*, **9**, 20–24.

Kampf A.R., Mills S.J., Simmons W.B., Nizamoff J.W. and Whitmore R.W. (2012) Falsterite, $Ca_2MgMn_2^{2+}(Fe_{0.5}^{2+}Fe_{0.5}^{3+})_4Zn_4(PO_4)_8(OH)_4(H_2O)_{14}$, a new secondary phosphate mineral from the Palermo No. 1 pegmatite, North Groton, New Hampshire. *American Mineralogist*, **97**, 496–502.

Kampf A.R., Falster A.U., Simmons W.B. and Whitmore R.W. (2013) Nizamoffite, Mn^{2+} $Zn_2(PO_4)_2(H_2O)_4$, the Mn analogue of hopeite from the Palermo No. 1 pegmatite, North Groton, New Hampshire. *American Mineralogist*, **98**, 1893–1898.

Libowitzky E. (1999) Correlation of O-H stretching frequencies and O-H···O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, **130**, 1047–1059.

Mills S.J., Grey I.E., Kampf A.R., Macrae C.M., Smith J.B., Davidson C.J. and Glenn A.M. (2016) Ferraioloite, a new secondary phosphate mineral from the Foote mine, USA. *European Journal of Mineralogy*, **28**, 655-661.

Missen O.P., Mills S.J., Spratt J., Birch W.D. and Brugger J. (2019) Crystal chemistry of zemannite-type structures: I. A re-examination of zemannite from Moctezuma, Mexico. *European Journal of Mineralogy*, **31**, 519–527.

Neuhold F., Kolitsch U., Bernhardt H.-J. and Lengauer C.L. (2012) Arsenohopeite, a new zinc arsenate mineral from the Tsumeb mine, Namibia. *Mineralogical Magazine*, **76**, 603–612.

Pouchou J.L. and Pichoir F. (1985) “PAP” φ(ρZ) procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, California, USA.

Rieck B., Giester G., Lengauer L.C., Chanmuang C. and Topa D. (2020) Stergiouite, $CaZn_2(AsO_4)_2{\cdot}4H_2O$ – a new mineral from the Lavrion Mining District, Greece. *Mineralogy and Petrology*, **14**, 319–327.

Rigaku Oxford Diffraction (2015) *CrysAlisPro Software system, version 1.171.38.43*. Rigaku Corporation.

Robinson K., Gibbs G.V. and Ribbe P.H. (1971) Quadratic elongation; a quantitative measure of distortion in coordination polyhedra. *Science*, **172**, 567–570.

Sheldrick G.M. (2015a) SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallographica*, **A71**, 3–8.

Sheldrick G.M. (2015b) Crystal structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.

Thomas I.M. and Weller M.T. (1992) Synthesis, structure and thermal properties of phosphophyllite, $Zn_2Fe(PO_4)_2{\cdot}4H_2O$. *Journal of Materials Chemistry*, **2**, 1123–1126.

Yvon K., Jeitschko W., and Parthé E. (1977) LAZY PULVERIX, a computer program, for calculating X-ray and neutron diffraction powder patterns. *Journal of Applied Crystallography*, **10**, 73–74.