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Refinement of the crystal structure of sieleckiite and revision of its symmetry

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ABSTRACT

The crystal structure of the copper aluminium phosphate mineral sieleckiite, $Cu_3Al_4(PO_4)_2\,(OH)_{12}{\cdot}2H_2O$, from the Mt Oxide copper mine, Queensland, Australia was solved from single-crystal X-ray diffraction data utilizing synchrotron radiation. Sieleckiite has monoclinic rather than triclinic symmetry as previously reported and is space group $C2/m$ with unit-cell parameters $a = 11.711(2)$, $b = 6.9233(14)$, $c = 9.828(2)$ Å, $\beta = 92.88(3)°$, $V = 795.8(3)$ Å^3 and $Z = 2$. The crystal structure, which has been refined to $R1 = 0.0456$ on the basis of 1186 unique reflections with $Fo > 4\sigma F$, is a framework of corner-, edge- and face- sharing Cu and Al octahedra and PO_4 tetrahedra.

KEYWORDS: sieleckiite, copper aluminium phosphate, crystal structure, synchrotron radiation.

Introduction

SIELECKIITE was described as a new copper aluminium phosphate mineral from the Mt Oxide copper mine, 150 km north of Mt Isa, Queensland, Australia, (Birch and Pring, 1988), where it formed blue spherulitic aggregates up to 0.5 mm in diameter consisting of fibrous radiating crystals up to 100 µm long and 2 µm wide. The aggregates are grown on quartzite and shale and associated minerals are variscite, turquoise, libethenite and pseudomalachite. Specimens of sieleckiite came from the zone of oxidation of the Mt Oxide deposit, a small but rich copper orebody. The primary ore comprises massive pyrite containing minor chalcopyrite and chalcocite. Birch and Pring (1988) suggested that, in the sequence of crystallization of the Cu-bearing phosphate minerals, sieleckiite was the earliest formed, with acid conditions prevailing for most of the period of crystallization but with more alkaline solutions prevailing during the final stages. The mineral occurs in similar assemblages at Wheal Gorland, Cornwall, England (Rumsey and Cressey, 2010) and at the Girilambone Mine, Girilambone, New South Wales, Australia (Chapman *et al.*, 2005).

Unit-cell parameters for sieleckiite were determined by Birch and Pring (1988) from electron diffraction patterns and the mineral was described as triclinic with $a = 9.41(8)$, $b = 7.56(5)$, $c = 5.95(6)$ A, $\alpha = 90.25(12)$, $\beta = 91.27(12)$, $\gamma = 104.02(7)°$, $V = 410.8(5)$ Å^3 and $Z = 1$. The very small size of crystals prevented a single-crystal X-ray study. Single-crystal X-ray diffraction data from synchrotron radiation has permitted the determination of the crystal structure and shows that sieleckiite crystallizes in space group $C2/m$ rather than $P1$ or $P\bar{1}$ as reported previously.

Experimental

An aggregate of sieleckiite crystals was removed from a specimen from the Mt Oxide mine in the collection of the South Australian Museum, Adelaide, South Australia (Registration number G15169). Examination by qualitative energy-dispersive spectroscopy showed the presence of only Cu, Al and P. A crystal 0.028 mm × 0.007 mm × 0.006 mm in size was selected for

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X-ray data collection at the micro-focus macromolecular beam line MX2 of the Australian Synchrotron. Data were measured with an ADSC Quantum 210r detector using monochromatic Mo$K\alpha$ X-radiation ($\lambda = 0.710800$ Å), a crystal-to-detector distance of 89.832mm and by scanning in ϕ with frame widths of 1° and 1s spent counting per frame. The intensity data sets were processed using *XDS* (Kabsch, 2010) with absorption correction and

TABLE 1. Crystal data, data collection and refinement details.

Crystal data	
Formula	$Cu_3Al_4(PO_4)_2(OH)_{12}\cdot 2H_2O$
Space group	$C2/m$
a,b,c (Å)	11.711(2), 6.9233(14), 9.828(2)
β (°)	92.88(3)
V (Å^3), Z	795.8(3), 2
D (calc.) (g/cm^3)	3.041
F(000)	692
μ (mm^{-1})	4.253
Crystal dimensions (mm)	0.028 × 0.007 × 0.006
Data collection	
Temperature (K)	293
Wavelength	0.7108 Å
θ range (°)	3.96–30.02
Detector distance (mm)	89.83
Rotation axes	ϕ
Rotation width (°)	1.0
Total no. of frames	360
Collection time per frame (s)	1
h,k,l ranges	$-16 \rightarrow 16$, $-9 \rightarrow 9$, $-13 \rightarrow 13$
Total reflections measured	6967
Data completeness (%)	95.6
Unique reflections	1201 ($R_{\text{int}} = 0.0656$)
Refinement	
Refinement on	F^2
$R1$* for $Fo > 4\sigma(Fo)$	4.56%
w$R2$† for all Fo^2	12.56%
Reflections observed $Fo > 4\sigma(Fo)$	1186
Number of parameters refined	96
Extinction coefficient	0.055(6)
$(\Delta/\sigma)_{\max}$	0.000
$\Delta\rho$min, $\Delta\rho$max (e/Å^3)	1.959, –1.151
GooF	1.204

*$R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$.
†$wR2 = \{\Sigma w(|Fo|^2-|Fc|^2)^2/\Sigma w|Fo^2|^2\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (0.0524\,P)^2 + 7.5066\,P]$; $P = ([\max \text{ of } (0 \text{ or } Fo^2)] + 2Fc^2)/3$.

TABLE 2. Fractional atomic coordinates and displacement parameters (in Å^2) for sieleckiite.

Atom	x	y	z	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.25	0.25	0.5	0.0092(3)	0.0083(5)	0.0086(5)	0.0114(5)	0	0.0028(3)	0
Cu2	0.5	0.5	0.5	0.0094(3)	0.0079(4)	0.0096(4)	0.0100(4)	–0.00018(19)	–0.0014(2)	–0.00043(18)
Al1	0.75	0.25	0	0.0095(6)	0.0070(7)	0.0099(7)	0.0095(7)	0	0.0001(4)	0
Al2	0.62861(12)	0.5	0.26008(14)	0.0088(5)	0.0099(8)	0.0087(8)	0.0097(8)	–0.0009(4)	–0.0002(5)	–0.0006(4)
P	0.88469(10)	0.5	0.21606(12)	0.0081(4)	0.0061(6)	0.0085(6)	0.0098(6)	0	–0.0002(4)	0
O1	0.9984(3)	0.5	0.2956(4)	0.0138(8)	0.0084(15)	0.0152(17)	0.0174(17)	0	–0.0043(12)	0
O2	0.7840(3)	0.5	0.3121(4)	0.0121(8)	0.0106(16)	0.0140(16)	0.0117(15)	0	0.0017(11)	0
O3	0.8735(2)	0.3187(4)	0.1232(2)	0.0113(6)	0.0098(11)	0.0111(12)	0.0131(11)	–0.0001(9)	0.0003(8)	0.0021(8)
OH4	0.5994(2)	0.3175(4)	0.4082(2)	0.0109(6)	0.0094(11)	0.0109(11)	0.0125(11)	–0.0009(9)	0.0014(8)	–0.0005(8)
OH5	0.2552(3)	0.5	0.4057(4)	0.0145(11)	0.0143(19)	0.0089(17)	0.020(2)	0	0.0006(13)	0
OH6	0.6439(2)	0.3012(4)	0.1339(2)	0.0132(8)	0.0127(12)	0.0139(13)	0.0130(12)	–0.0016(9)	0.0007(8)	0.0002(9)
OH7	0.7610(3)	0	0.0630(3)	0.0124(9)	0.0138(16)	0.0076(14)	0.0156(16)	0	0.0004(11)	0
OW8	0.4654(3)	0.5	0.2284(4)	0.0160(12)	0.0115(18)	0.0165(19)	0.020(2)	0	–0.0001(13)	0

Note: Site symmetries with Wyckoff positions in parentheses are –1 (*f*) for Cu1; 2/*m* (*c*) for Cu2; –1 (*e*) for Al1; *m* (*i*) for P, Al2, O1, O2, OH5, OH7 and OW8; 1 (8*j*) for O3, OH4 and OH6.

scaling completed using *SADABS* (Bruker, 2001). The following unit-cell dimensions were obtained by least-squares refinement of the positions of 9631 reflections: $a = 11.711(2)$, $b = 6.9233(14)$, $c = 9.828(2)$ Å, $\beta = 92.88(3)°$, $V = 795.8(3)$ Å^3 and $Z = 2$.

E-statistics ($|E^2–1| = 0.932$) indicated a centrosymmetric space group and systematic absences were compatible with space groups *C*2/m, *C*2 or *C*m. The structure was solved by direct methods and refined in *C*2/m. The heavy Cu, Al and P atoms were found using *SHELXS-97* (Sheldrick, 2008) within the *WinGX* program suite (Farrugia, 2012). All O atoms were then located via subsequent difference-Fourier syntheses during the refinement, performed using *SHELXL-97* (Sheldrick, 2008). An unambiguous location of H atoms in difference-Fourier maps could not be obtained. The refinement with anisotropic temperature factors converged at $R1 = 0.0456$ for 1186 independent reflections with $F_o > 4\sigma(F_o)$. Details concerning data collection and structure refinement are provided in Table 1. Fractional coordinates and atom displacement parameters are provided in Table 2, selected interatomic distances in Table 3 and bond valences (Brese and O'Keeffe, 1991) are given in Table 4.

Crystal structure

The structure contains two Cu sites, two Al sites, one P site and eight O sites. Refinement of the Cu, Al and P sites showed that all are fully occupied. The Cu1 and Cu2 sites are each coordinated by six oxygen atoms in strongly distorted Jahn-Teller [4 + 2] octahedral arrangements (Jahn and Teller, 1937; Eby and Hawthorne, 1993; Burns and Hawthorne, 1996). Maximum distortion is shown by the Cu2-centred octahedron. Four short bonds yield a square-planar array with O–Cu–O angles of 87.69 and 92.32° for Cu1 and 79.89 and 100.11° for Cu2. Apical distances are 2.576(4) Å to O2 × 2 for Cu1 and 2.680(4) Å to OW8 × 2 for Cu2. Intra-octahedral angles deviate up to 18.45 and 23.11° from ideal angles for Cu1 and Cu2, respectively. Two more oxygen ligands (OH5 × 2) are present within the coordination sphere around Cu2 at a distance of 2.969 Å. The calculated Cu1–OH5 bond-valence is very low (0.03 valence units, vu), hence the Cu2 site is considered to be 6- rather than 8- coordinated.

The Al1 and Al2 sites are each coordinated by six oxygen atoms in an octahedral arrangement. The octahedra show a narrow range of bond lengths and very little distortion from ideal octahedral geometry. The Al2ϕ_6 octahedron is especially regular with *cis* ϕ–Al2–ϕ angles in the range 88.83 to 91.17° and *trans* ϕ–Al–ϕ angles of 180°. The PO_4 tetrahedron has one short apical P–O1 bond of 1.510(4) Å and three longer P–O bonds of 1.547(4) and 1.553(3) × 2 giving a <P–O> of 1.541 Å.

The Cu1ϕ_6 octahedra link by edge-sharing into chains along [010] (Fig. 1). The chains are linked in the *a* direction by corner-sharing Cu2ϕ_6 octahedra.

TABLE 3. Selected interatomic distances (Å) and possible hydrogen bonds for sieleckiite.

Cu1	–OH5	1.9657(19) × 2	Al1	–OH7	1.8407(12) × 2
	–OH4	1.996(2) × 2		–OH7	1.888(3) × 2
	–O2	2.576(4) × 2		–O3	1.900(3) × 2
<Cu–O>		2.179	<Al–O>		1.876
Cu2	–OH4	1.968(2) × 4	Al2	–O2	1.865(4)
	–OW8	2.680(4) × 2		–OH6	1.867(3) × 2
<Cu–O>		2.205		–OW8	1.922(4)
				–OH4	1.970(3) × 2
P	–O1	1.510(4)	<Al–O>		1.910
	–O2	1.547(4)			
	–O3	1.553(3) × 2			
<P–O>		1.541			
Possible hydrogen bonds (Å)					
OH4–H1···O1		2.706	OH6–H3···O1		3.170
OH4–H1···O1		2.706	OH7–H4···OW8		2.824
OH5–H2···O1		3.142	OW8–H5···O3		2.642

TABLE 4. Bond-valence analysis for sieleckiite.

	Cu1	Cu2	Al1	Al2	P	H1	H2	H3	H4	H5	H6	Sum (excluding H)	Sum (including H)
O1					1.29	$0.25^{\times 2}\rightarrow$	0.10	0.05				1.29	1.94
O2	$0.09^{\times 2}\downarrow\rightarrow$			0.56	1.17							1.91	1.91
O3			$0.51^{\times 2}\downarrow$		$1.15^{\times 2}\downarrow$			0.05		0.30	0.30	1.66	2.01
OH4	$0.46^{\times 2}\downarrow$	$0.46^{\times 4}\downarrow$		$0.42^{\times 2}\downarrow$		0.75						1.30	2.05
OH5	$0.46^{\times 2}\downarrow\rightarrow$						0.90					0.92	1.92
OH6			$0.53^{\times 2}\downarrow$	$0.56^{\times 2}\downarrow$				0.90				1.09	1.99
OH7			$0.60^{\times 2}\downarrow\rightarrow$						1.00			1.20	2.20
OW8		$0.07\downarrow$		0.48						0.70	0.70	0.55	1.95
Sum	1.94	1.98	3.28	3.00	4.76	1.00	1.00	1.00	1.00	1.00	1.00		

Al1ϕ_6 octahedra share corners via hydroxyl anions, to form a chain that extends along [010] (Fig. 2). Al2ϕ_6 octahedra link to either side of the chain by sharing corners and PO_4 tetrahedra share vertices with two Al1ϕ_6 octahedra and one Al2ϕ_6 octahedra. Al2ϕ_6 octahedra share faces with one Cu2ϕ_6 octahedron and share edges with two Cu2ϕ_6 octahedra to form a framework structure (Fig. 3). Bond-valence calculations (Table 4) indicate that the structure contains four OH groups and one H_2O molecule. Possible hydrogen bonds are summarized in Table 3. The anion at O1 is significantly underbonded and probably receives strong hydrogen bonds from two OH4 anions and one weak hydrogen bond from each of OH5 and OH6. Hydrogen bonds donated by OH6 and OW8 are probably accepted by O3 and OW8 probably receives a hydrogen bond from OH7.

Discussion

Sieleckiite is one of four copper aluminium phosphate minerals, the others being nevadaite, turquoise and zapatalite. Nevadaite and zapatalite are rare minerals occurring in the oxidized zones of Cu deposits, whereas turquoise is a common mineral in volcanic rocks and as a weathering product of Cu sulfides. Each of these minerals has a distinct crystal structure. The crystal structure of turquoise is based on an $[Al_2CuAl_2(O,OH,H_2O)_{18}]$ polyhedral cluster formed by a central CuO_6 octahedron sharing four edges with two edge-sharing Al_2O_{10} dimers (Cid-Dresdner, 1965; Kolitsch and Giester, 2000). The clusters link by sharing corners with $Al(O_4,OH_2)$ octahedra and PO_4 tetrahedra to form an open three-dimensional framework which is strengthened by extensive hydrogen-bonding. The structure of nevadaite consists of ordered layers of corner-sharing Alϕ6 (ϕ: F, O^{2-}, H_2O) octahedra and PO_4 tetrahedra of the form $[Al_8(PO_4)_8F_8(H_2O)_8]$ alternating with layers of disordered layers of corner-sharing and face-sharing $(Cu^{2+},\square,V^{3+},Al)\phi6$ (ϕ: F, O^{2-}, H_2O) octahedra (Cooper *et al*., 2004). The ordered and disordered layers link in the **b** direction by sharing vertices between octahedra and tetrahedra. The crystal structure of zapatalite is not known.

Sieleckiite has no structural relationship to any other mineral species or synthetic compound. On the basis of the structural characterization presented here, the formula of sieleckiite is $Cu_3Al_4(PO_4)_2(OH)_{12}{\cdot}2H_2O$ as reported previously by Birch and Pring, (1988). Using C-H-N analysis,

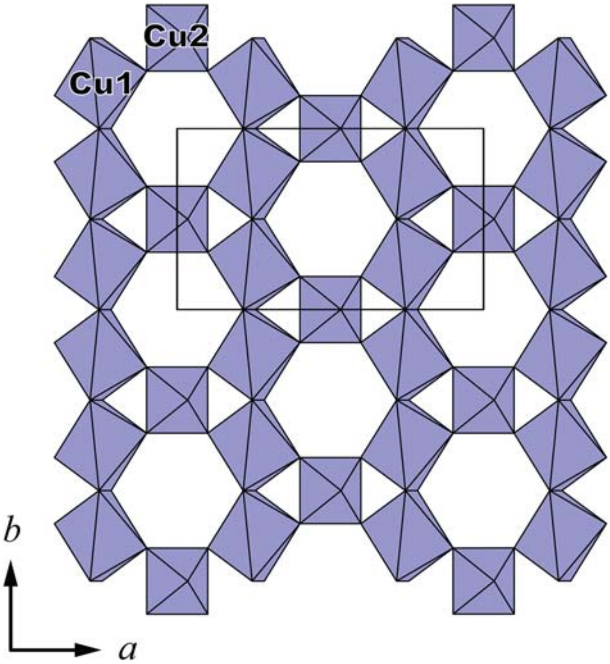

FIG. 1. The Cu sites in the crystal structure of sieleckiite viewed along [001]. The unit cell is outlined. All structure drawings were completed using *ATOMS* (Shape Software, 1997).

Birch and Pring (1988) detected a small amount of carbon (1.6 wt.%) in sieleckiite. This was considered probable due to an unknown carbonate impurity or was possibility structural as carbonate substituting for phosphate or hydroxyl. The structure refinement of sieleckiite provides no indication of the presence of carbonate.

Rumsey and Cressey (2010) completed a powder X-ray diffraction study of sieleckiite using samples from the Mt Oxide mine and Wheal Gorland. The strongest line in their pattern at ~8.9°2θ did not match the corresponding line in the JCPDS reference pattern (ICCD 46-1291) at ~9.7°2θ which suggested that these unit-cell parameters of Birch and Pring (1988) were incorrect and that sieleckiite required re-investigating. A powder pattern calculated from the crystal structure data for sieleckiite using the program *Lazy Pulverix* (Yvon *et al*. 1977) is in good agreement with those given by of Birch and Pring (1988) and Rumsey and Cressey (2010) and shows a strong line at 9.10°2θ.

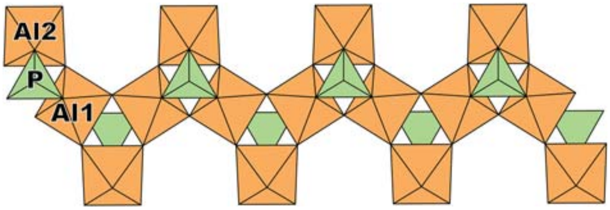

FIG. 2. The [$Al_2\phi_6(PO_4)$] chains in the crystal structure of sieleckiite viewed down an axis rotated 20° from [101].

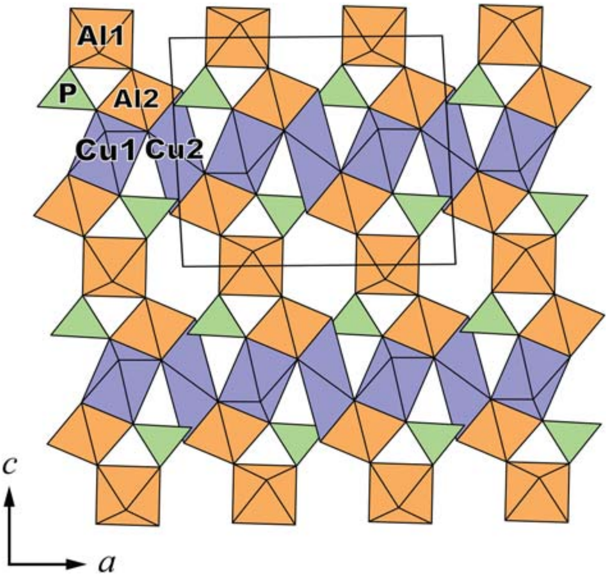

FIG. 3. The crystal structure of sieleckiite viewed along [010]. The unit cell is outlined.

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References

Birch, W.D. and Pring, A. (1988) Sieleckiite, a new copper aluminium phosphate from Mt Oxide, Queensland, Australia. *Mineralogical Magazine*, **52**, 515–518.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.

Bruker (2001) *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burns, P.C. and Hawthorne, F.C. (1996) Static and dynamic Jahn-Teller effects in Cu^{2+} oxysalts. *The Canadian Mineralogist*, **34**, 1089–1105.

Chapman, J.R., Sharpe, J.L. and Williams, P.A. (2005) The copper deposits at Girilambone, New South Wales. *Australian Journal of Mineralogy*, **11**, 91–99.

Cid-Dressner, H. (1965) Determination and refinement of the crystal structure of turquois, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$. *Zeitschrift für Kristallographie*, 87–113.

Cooper, M.A., Hawthorne, F.C., Roberts, A.C., Foord, E.E., Erd, R.C., Evans, H.T., Jr. and Jensen, M.C. (2004) Nevadaite, $(Cu^{2+},\square,Al,V^{3+})_6[Al_8(PO_4)_8F_8](OH)_2(H_2O)_{22}$, a new phosphate mineral species from the Gold Quarry mine, Carlin, Eureka County, Nevada: Description and crystal structure. *The Canadian Mineralogist*, **42**, 741–752.

Eby, R.K. and Hawthorne, F.C. (1993) Structural relationships in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallographica*, **B49**, 28–56.

Farrugia, L.J. (2012) WinGX and ORTEP for Windows: an update. *Journal of Applied Crystallography*, **45**, 849–854.

Jahn, H.A. and Teller, E. (1937) Stability of polyatomic molecules in degenerate electronic states. *Proceedings of the Royal Society, Series A*, **161**, 220–236.

Kabsch, W. (2010) XDS. *Acta Crystallographica*, **D66**, 125–132.

Kolitsch, U. and Giester, G. (2000) The crystal structure of faustite and its copper analogue turquoise. *Mineralogical Magazine*, **64**, 905–913.

Rumsey, M.S. and Cressey, G.M. (2010) The first confirmed British occurrence of sieleckiite, $Cu_3Al_4(PO_4)_2\ (OH)_{12} \cdot 2H_2O$, from spoil at Wheal Gorland, St. Day, Cornwall. *Journal of the Russell Society*, **13**, 57–61.

Shape Software (1997) *ATOMS for Windows and Macintosh V 4.0*. Kingsport, Tennessee, USA.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.

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.