

Aldridgeite, a new mineral from the Block 14 open cut, Broken Hill, New South Wales

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ABSTRACT

Aldridgeite, $(\text{Cd,Ca})(\text{Cu,Zn})_4(\text{SO}_4)_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, is a new Cd-bearing sulphate mineral, the Cd analogue of serpierite, from the Block 14 open cut, Broken Hill, New South Wales. It occurs in cavities in a quartz-garnet-smithsonite matrix associated with niedermayrite and pyromorphite. Aldridgeite forms sprays of pale blue acicular crystals to 0.8 mm across. Individual crystals are up to 0.4 mm in length and 0.005 mm across. The crystals have a vitreous lustre and a pale blue streak. Mohs hardness is about 3 (estimated). The fracture is irregular and the tenacity is brittle. The measured density is 3.25(3) g/cm³ and the calculated density is 3.33 g/cm³ (for the empirical formula). Aldridgeite crystals are biaxial (-), with $\alpha=1.596(3)$, $\beta=1.636(3)$ and $\gamma=1.643(3)$, measured using white light, and $2V_{\text{calc}} = 44.5^\circ$. Orientation is uncertain. Pleochroism is weak with X pale yellowish blue, Y pale blue, Z pale greenish blue. Chemical analysis by electron microprobe gave (wt.%): CdO 11.70, CaO 3.25, PbO 0.08, CuO 33.87, ZnO 13.21, SO₃ 23.61 and H₂O_{calc} (calculated to obtain a total of 12 H pfu) 15.94. The empirical formula (based on 17 O atoms) is $[(\text{Cd}_{0.52}\text{Ca}_{0.39})_{1.01}(\text{Cu}_{2.59}\text{Zn}_{1.10})_{2.19}(\text{SO}_4)_2(\text{OH})_2] \cdot 3\text{H}_2\text{O}$. Aldridgeite is monoclinic, space group C2/c, $a = 22.049(2)$, $b = 6.212(2)$, $c = 21.839(2)$ Å, $\beta = 113.19(3)^\circ$, $V = 2749.8(4)$ Å³ and $Z=8$. The six strongest lines in the powder X-ray diffraction pattern are $[d(\text{\AA})]$: 10.167(100)(200), 5.076(55)(400), 3.380(35)(600,51-4), 2.645(60)(02-4), 2.439 (50)(422, 51-8, 224), 2.167(35)(424).

INTRODUCTION

In recent years, eight new mineral species have been described from specimens collected from the Kintore and Block 14 open cuts from the mid 1980s to the early 2000s; birchite (Elliott *et al.*, 2008), kolitschite (Mills, *et al.*, 2008), plimerite (Elliott *et al.*, 2009a), nyholmite (Elliott *et al.*, 2009b), liversidgeite (Elliott *et al.*, 2010a), edwardsite (Elliott *et al.*, 2010b), yancowinnaite (Elliott and Pring, 2014) and the subject of this paper, aldridgeite. Other potentially new species are currently under investigation. Aldridgeite occurs on specimens collected in 2000 from ore recovered from the Block 14 open cut and transported to the Pinnacles Mine, 15 km south west of Broken Hill, for processing. The exact section of the Block 14 open cut that was the source of the specimens is not known. The name is for Edward William Aldridge, owner of the Duke of Cornwall Hotel at Broken Hill, who during the years 1888 to 1891 formed the first major Broken Hill mineral specimen collection (Rankin, 2008). In 1892, the collection was catalogued by Charles W. Marsh so that it could then be offered for sale. Initially, Aldridge transported the collection to England in 150 boxes, put it on display and attempted to sell it. The British Museum was prepared to buy some of the

specimens but not the whole collection and Aldridge had to return to Australia with most of the collection unsold. In 1908, the collection was purchased for £7,050 by the University of Sydney, which kept the best specimens. Five hundred specimens were sent to England for exhibition, the remainder going to the Australian Museum, the Museum of Applied Arts and Sciences and the Geological and Mining Museum.

The new mineral and mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2010-030). Type material is housed in the collection of the South Australian Museum, Adelaide, South Australia, under registration number G33030.



Figure 1: Crystal spray of acicular aldridgeite crystals from the Block 14 open cut, Broken Hill. Field of view is 1.5 mm across. Photo and specimen: P. Elliott.

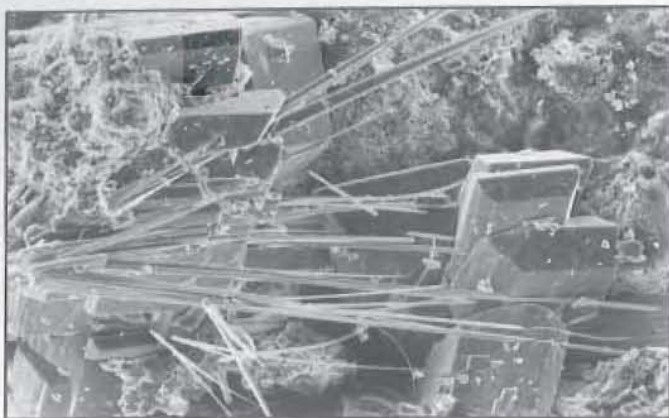


Figure 2: Scanning electron photomicrograph of pale blue acicular crystals of alldridgeite to 150 μm in length with niedermayrite from the Block 14 open cut, Broken Hill. Photo and specimen: P. Elliott.

OCCURRENCE AND PARAGENESIS

Aldridgeite is part of a suite of secondary sulphate minerals that formed under late stage supergene low-temperature conditions and were exposed in the Kintore and Block 14 open cuts (Birch and van der Heyden, 1988; Birch, 1990). The following paragenesis for the suite of secondary sulphate minerals was proposed by Birch (1990):

antlerite $\Rightarrow$ linarite $\Rightarrow$ brochantite $\Rightarrow$ serpierite $\Rightarrow$ ktenasite $\Rightarrow$ connellite

Solutions rich in Cu, Zn, Cd and S have been derived from weathering of primary galena, Cd-bearing sphalerite and chalcopryrite. Aldridgeite has formed contemporaneously with crystals of pale blue niedermayrite, $\text{Cu}_4\text{Cd}(\text{SO}_4)_2(\text{OH})_6 \cdot 4\text{H}_2\text{O}$, in small cavities in a quartz-garnet-smithsonite matrix. The only other associated mineral is pyromorphite, which forms tiny, white prismatic crystals.

APPEARANCE AND PHYSICAL PROPERTIES

Aldridgeite occurs as sprays of acicular crystals up to 0.8 mm across (Figures 1, 2). Individual crystals are up to 0.4 mm in length and 0.005 mm across and often form intergrowths of subparallel individuals. The streak is pale blue. Crystals are transparent to translucent with a vitreous lustre. The Mohs hardness is estimated to be approximately 3. The tenacity is brittle, the fracture is irregular and one perfect cleavage was observed. By analogy with serpierite, this would be parallel to {100}. Density, determined by the sink-float method using a Clerici solution-water mixture, is 3.25(3) g/cm^3 . The density calculated from the empirical formula is 3.33 g/cm^3 . Crystals are readily soluble in cold 10% HCl. The mineral is optically biaxial (-), with the following optical constants measured in white light: $\alpha = 1.596(3)$, $\beta = 1.636(3)$ and $\gamma = 1.643(3)$. The calculated $2V$ is 44.5° . Pleochroism is weak, X = pale yellowish blue, Y = pale blue, Z = pale greenish blue. The optical orientation is uncertain. The crystals show positive elongation (length-slow) and inclined extinction.

Table 1: Compositional data for alldridgeite.

Constituent	Wt.%	Range	Stand. Dev.
CdO	11.70	10.70–13.03	0.41
CaO	3.25	2.21–3.70	0.66
PbO	0.08	0.00–0.33	0.12
CuO	33.87	31.53–35.17	1.10
ZnO	13.21	11.61–15.12	1.03
SO_3	23.61	21.70–25.55	1.19
H_2O^*	15.94		
Total	101.66		

* calculated to obtain 12 H atoms and charge balance.

CHEMICAL AND SPECTROSCOPIC DATA

Aldridgeite was analysed using a Cameca SX51 electron microprobe with an accelerating voltage of 15 kV, a specimen current of 10 nA and a beam diameter of 20 μm . The standards used were cadmium metal (Cd $L\alpha$), hydroxylapatite (Ca $K\alpha$), chalcopryrite (Cu $K\alpha$ and S $K\alpha$), sphalerite (Zn $K\alpha$) and galena (Pb $M\alpha$). The data were reduced and corrected by the $\phi(\rho Z)$ method of Pouchou and Pichoir (1985). No other elements with an atomic number greater than eight were detected by energy dispersive spectroscopy. Water could not be determined directly as there is insufficient material available; thus in the analyses, water was calculated to give a total of 12 H *pfu*. The presence of H_2O groups was shown by infrared spectroscopy. A total of 12 analyses were obtained, for which the average is given in Table 1. The empirical formula, calculated on the basis of 17 oxygen atoms, is $(\text{Cd}_{0.62}\text{Ca}_{0.39})_{\Sigma 1.01}(\text{Cu}_{2.89}\text{Zn}_{1.10})_{\Sigma 3.99}(\text{SO}_4)_{2.00}(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ and the simplified formula is $(\text{Cd,Ca})(\text{Cu,Zn})_4(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$.

The infrared spectrum (Figure 3) of powdered alldridgeite, in the range 4000 to 650 cm^{-1} , was obtained using a Nicolet 5700 FTIR spectrometer equipped with a Nicolet Continuum IR microscope and a diamond-anvil cell. The spectrum shows bands due to OH stretching vibrations (a broad band ~ 3640 to ~ 2805 cm^{-1} , centred around 3358 cm^{-1}), H–O–H bending of H_2O groups (at 1652 cm^{-1}), ν_3 vibration of the SO_4 tetrahedra (1120 cm^{-1}) and ν_1 vibration of the SO_4 tetrahedra (at 985 cm^{-1}).

Table 3: Compositional data for cadmian serpierite.

Constituent	Wt.%	Range	Stand. Dev.
CdO	9.25	7.50–11.33	1.13
CaO	4.98	4.29–5.83	0.51
PbO	0.04	0.00–0.18	0.06
CuO	40.49	36.71–44.96	1.89
ZnO	8.48	5.41–9.64	0.98
SO_3	24.01	22.36–27.08	1.43
H_2O^*	16.59		
Total	103.83		

* calculated to obtain 12 H atoms and charge balance.

X-RAY DIFFRACTION DATA

An attempt was made to obtain single-crystal X-ray data using synchrotron radiation, however, all crystals proved to be either too small to obtain sufficient intensity, were composed of multiple subparallel individuals or were bent. X-ray powder-diffraction data for alldridgeite (Table 2) were recorded using a 100 mm Guinier-Hägg camera using monochromatic Cu K α radiation ($\lambda = 1.54060$ Å) and calibrated using an internal standard of silicon powder (NBS SRM 640a). The intensities were visually estimated. Unit-cell refinement from the powder data using the Le Bail profile-fitting method (Le Bail *et al.*, 1988; Hunter, 1998), starting from the unit-cell parameters for serpierite (Sabelli and Zanazzi, 1968), gave the following parameters: $a = 22.049(2)$, $b = 6.212(2)$, $c = 21.839(2)$ Å, $\beta = 113.19(3)^\circ$ and $V = 2749.8(4)$ Å³.

DISCUSSION

Aldridgeite is the Cd analogue of serpierite (Bertrand, 1881; Sabelli and Zanazzi, 1968). Serpierite is dimorphous with and structurally related to orthoserpierite (Sarp, 1985) and is structurally related to devilline (Sabelli and Zanazzi, 1972). The serpierite structure consists of a sheet of edge-sharing (Cu,Zn) octahedra parallel to (100) decorated on both sides by SO₄ tetrahedra. The sheets are linked in the a -direction via Ca²⁺ cations. A crystal aggregate of a Cd-bearing serpierite from the Block 14 open cut was also analysed by microprobe analysis (Table 3). A plot of atoms of Ca versus atoms of Cd pfu (per formula unit) (Figure 4) for all analyses of alldridgeite and cadmian serpierite shows a distinct negative linear correlation, with $R^2 = 0.782$ and a slope close to -1 indicating a simple replacement of Ca by Cd in the structure. A single crystal X-ray study using a crystal of Cd-rich serpierite from the Block 14 open cut, Broken Hill confirms that Ca²⁺ is replaced by Cd in the structure (Elliott, 2010).

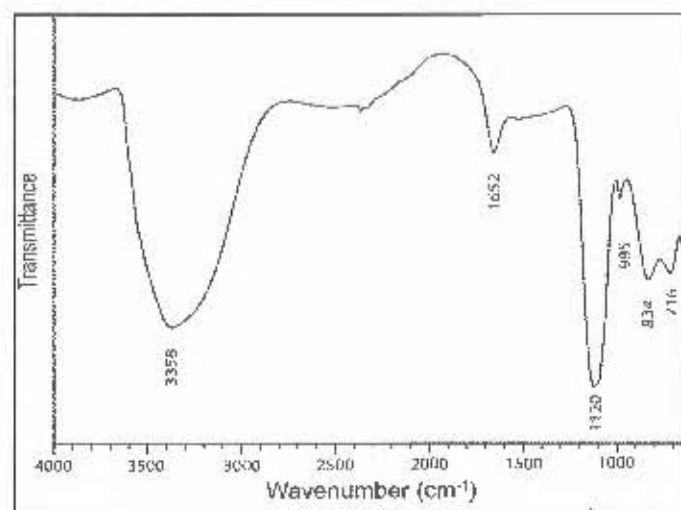


Figure 3: FT-IR spectrum of powdered alldridgeite.

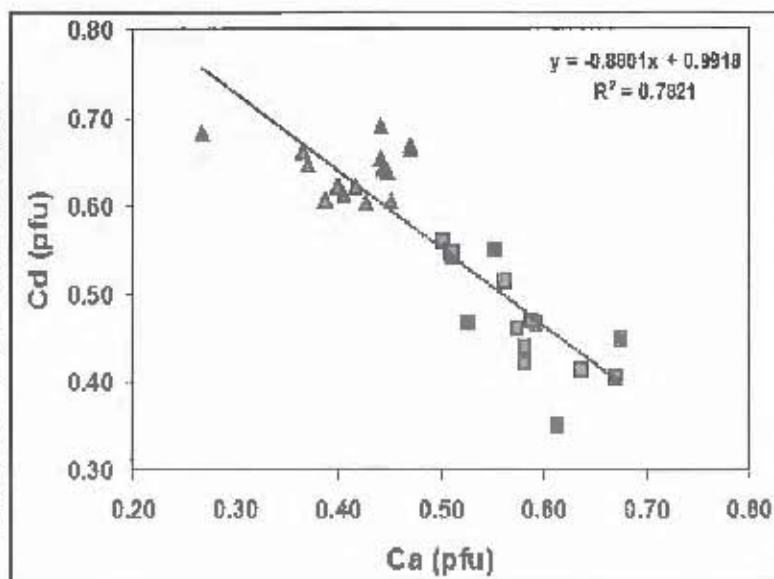


Figure 4: Bivariate plot illustrating the negative correlation between Ca and Cd in alldridgeite and cadmian serpierite.

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Table 2: X-ray powder diffraction data for aldridgeite.

I_obs	d_obs	I_calc	d_calc	h	k	l	I_obs	d_obs	I_calc	d_calc	h	k	l		
100	10.167 {	100	10.133	2	0	0	30	2.511	21	2.513	0	0	8		
		2	10.052	0	0	2	10	2.486	5	2.491	7	1	1		
		6	9.169	2	0	-2	5	2.477	15	2.476	1	1	7		
5	5.935	4	5.947	1	1	0	50	2.439 {	7	2.442	4	2	2		
		4	5.891	1	1	-1		6	2.442	5	1	-8			
5	5.531	7	5.531	1	1	1		54	2.439	2	2	4			
5	5.406	13	5.399	1	1	-2	10	2.386	9	2.394	4	0	6		
55	5.076	62	5.067	4	0	0	20	2.329	12	2.330	6	2	-4		
20	4.737 {	5	4.745	3	1	-1	5	2.292	5	2.292	8	0	-8		
		15	4.728	1	1	-3		2.263	4	2.264	7	1	-8		
		4	4.584	4	0	-4	10	2.250	8	2.248	9	1	-5		
	4.362	6	4.360	3	1	-3	15	2.187 {	4	2.188	4	0	-10		
5	3.930	6	3.928	2	0	4		4	2.184	3	1	7			
5	3.554	6	3.547	5	1	-1	35	2.167	38	2.167	4	2	4		
10	3.523	4	3.525	1	1	-5		8	2.112	6	2	2			
		8	3.523	3	1	-5	10	2.111	4	2.110	0	2	-7		
		4	3.518	6	0	-4	5	2.058 {	7	2.061	1	3	-1		
		23	3.382	3	1	3		7	2.055	8	2	-4			
35	3.380 {	6	3.378	6	0	0	5	2.025	3	2.026	8	2	-5		
		20	3.379	5	1	-4	10	1.994	8	1.995	3	3	-1		
5	3.354	13	3.351	0	0	6		3	1.964	3	3	-3			
10	3.181	2	3.181	5	1	1	5	1.950	12	1.950	1	3	3		
25	3.163 {	3	3.165	1	1	5		4	1.932	9	1	2			
		13	3.159	5	1	-5	5	1.922 {	16	1.922	3	3	-4		
20	3.131	21	3.131	3	1	-6		10	1.917	8	2	-7			
		7	3.111	0	2	0		6	1.914	4	2	-9			
10	3.057	14	3.056	6	0	-6		4	1.904	3	3	2			
5	3.027	7	3.022	4	0	4	15	1.901	7	1.900	8	2	1		
15	2.978	14	2.974	2	2	0		7	1.900	6	2	4			
15	2.944	19	2.946	2	2	-2		7	1.884	11	1	-6			
		9	2.937	5	1	2		4	1.850	10	0	2			
10	2.889	6	2.894	2	2	1	5	1.849	5	1.848	11	1	-7		
5	2.879	11	2.878	6	0	2		4	1.821	11	1	-1			
10	2.791	4	2.809	7	1	-3		4	1.784	12	0	-2			
		5	2.791	3	1	-7		7	1.780	7	1	6			
25	2.756	19	2.766	2	2	2	10	1.771	6	1.775	3	3	4		
10	2.722	6	2.724	8	0	-2		8	1.768	10	2	-6			
15	2.717	9	2.718	4	0	-8		4	1.763	2	2	-10			
		23	2.704	4	2	-2		4	1.760	5	3	2			
30	2.704 {	13	2.701	4	2	-1	5	1.759	5	1.756	5	3	-6		
		6	2.700	2	0	-8		5	1.746	8	2	3			
		11	2.700	2	2	-4		4	1.743	11	1	-9			
10	2.678	8	2.680	7	1	-5		7	1.739	9	1	-11			
20	2.669	15	2.671	5	1	-7		6	1.732	7	3	-3			
		9	2.651	4	2	0	5	1.728	2	1.729	7	3	-2		
60	2.645	46	2.645	0	2	-4		6	1.726	1	3	6			
30	2.612	14	2.608	2	2	3		6	1.713	7	3	-1			
20	2.573	14	2.574	4	2	-4	15	1.708	18	1.708	1	3	-7		
15	2.564	6	2.565	8	0	-6		4	1.686	8	2	-10			
		6	2.561	4	2	1		4	1.683	3	1	10			
20	2.535	13	2.533	8	0	0		5	1.675	4	2	-11			
		5	2.535	2	2	-5	10	1.666	12	1.667	7	3	-6		

Note: Intensities estimated visually. I_{calc} calculated with program Rietica (Hunter 1998).

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OBITUARY

Francis John (Frank) Griffiths

13th June, 1939 - 22nd May, 2014

Mineral collectors that regularly visit the West Coast of Tasmania would be familiar with keen local collector Frank Griffiths who lived at Rosebery Tasmania. Born in the mining region of Williamsford, Tasmania, Frank developed a passion for rocks and minerals from an early age. He was an avid and knowledgeable collector for over 40 years and extremely proud of his collection of West Coast minerals, many of which he had collected.

Frank commenced work in the Rosebery mine on the West Coast of Tasmania at the tender age of 13 and worked as a miner for some 59 years. Working at the Williamsford Hercules mine and the Rosebery Zinc mine both provided opportunities to add to his collection with the mines producing classy mineral specimens including barite, cerussite, jamesonite and quartz crystals, many of which found their way into Frank's collection. Frank's also acquired through buying and trading specimens with other miners and collectors.

Fortunately, living on the West Coast of Tasmania afforded many collecting opportunities, Frank often spent his weekends exploring the old mines and mineral deposits in the region. Fellow Rosebery collector, Mike Phelan, recollected “collecting with Frank was a bit of an ‘extreme sport’ we had to think of safety as well as results. The weather on the West Coast can throw everything at you in



the one day. Frank would say “that is a high altitude so we need to take warm clothes”. On that occasion it snowed of course”. Frank would pack a chainsaw to enable access into tracks blocked by trees, all in the hunt of a good specimen in areas others feared to tread. Mike noted “Frank had a great sense of humour, which even held when conditions became uncomfortable. We could always count on a positive comment and an appropriate joke”.

Ever the keen miner, Frank was involved in the annual Rosebery competitive rock drilling event at the local Rosebery Carnival and became a major sponsor of the event.

He was known as a close family man, with great integrity, generous, self-disciplined and he will be greatly missed.