

# Yancowinnaite, a new mineral from the Kintore open cut, Broken Hill, New South Wales

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## ABSTRACT

Yancowinnaite, ideally  $\text{PbCuAl}(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ , is a new member of the tsumcorite group of minerals from the Kintore open cut, Broken Hill, New South Wales. The new mineral occurs in seams in a goethite-garnet matrix associated with beudantite-seginitite, mimetite, agardite-Y, carminite and chlorargyrite. Yancowinnaite is triclinic, space group  $P\bar{1}$ ,  $a = 5.444(2)$ ,  $b = 5.640(2)$ ,  $c = 7.518(2)$  Å,  $\alpha = 67.89(2)$ ,  $\beta = 69.48(2)$ ,  $\gamma = 70.18(2)^\circ$ ,  $V = 194.51(7)$  Å<sup>3</sup> and  $Z = 1$ . Crystals are  $< 10$  µm in maximum dimension and occur as rosette-like aggregates forming overgrowths on gartrellite. The colour is yellowish-green to green, the streak is yellow and the lustre is vitreous. The Mohs hardness is estimated to be  $\sim 3$ . The new mineral is brittle with irregular fracture and one perfect cleavage. The calculated density is 5.31 g/cm<sup>3</sup> based on the empirical formula. The minimum and maximum values of the refractive indices are 1.906(5) and 1.963(5). Pleochroism is weak, from pale yellow, almost colourless, to yellow and pale orange. The empirical chemical formula (mean of 23 electron microprobe analyses) calculated on the basis 10 O pfu is  $\text{Pb}_{1.02}\text{Al}_{0.63}\text{Fe}^{3+}_{0.32}\text{Cu}_{1.02}\text{Zn}_{0.06}(\text{AsO}_4)_{1.98}(\text{OH})_{1.11}(\text{H}_2\text{O})_{0.97}$ . The strongest powder X-ray diffraction lines are  $[d(\text{Å})](I)(hkl)$ : 3.286 (65) (0 1 2), 2.949 (100) (1 1 -1), 2.891 (40) (1 -1 -1), 2.850 (45) (1 -1 1), 2.501 (40) (1 2 0, 1 0 -2), 2.492 (80) (0 1 -2, 1 1 3), 1.110 (50) (1 5 3, 1 -4 1).

## INTRODUCTION

Yancowinnaite belongs to the tsumcorite group, comprising more than 30 minerals and synthetic compounds (*e.g.* Tillmanns and Gebert, 1973; Krause *et al.*, 1998a; Brugger *et al.*, 2000; Mihajlovic and Effenberger, 2004). The general formula can be given as  $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{H}_2\text{O},\text{OH})_2$  and natural end members have been described with Pb, Bi, Ca and Na dominating on the Me(1) site, Zn, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Mn<sup>3+</sup>, Al, Mg and Co on the Me(2) site, and As<sup>5+</sup>, P<sup>5+</sup>, V<sup>5+</sup>, and S<sup>6+</sup> on the X-site. Charge balance is maintained by the coupled exchange of cations of different valences in the Me(1), Me(2) and X sites and by adjustment of the OH:H<sub>2</sub>O ratio. The space group of these predominantly monoclinic minerals is generally C2/m (tsumcorite type) with  $Z=2$ . The remaining members of the group, yancowinnaite, gartrellite, zincgartrellite, phosphogartrellite, lukrahnite, rappoldite and helmutwinklerite, are triclinic, space group  $P\bar{1}$  and  $Z=1$ . The reduction in symmetry from monoclinic to triclinic is due either to an ordering of cations on two Me(2) sites in the structure (gartrellite type) or to an ordering of the hydrogen bonds (helmutwinklerite type).

In 1988, several specimens of tsumcorite group minerals were collected on ore stockpiles from the Kintore open cut, Broken Hill. The new mineral, yancowinnaite, has been identified on two of these specimens. The name is for Yancowinna County, the county of New South Wales in which Broken Hill is situated. The name Yancowinna is believed to have been derived from a local Aboriginal word. The new mineral and mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2010-030). The type specimen is housed in the collection of the South Australian Museum, Adelaide, South Australia, under registration number G33029.



Figure 1: Crystal groups of yellow to greenish yellow yancowinnaite with orange beudantite-seginitite from Kintore open cut, Broken Hill. Field of view is 2.5 mm across. Photo and specimen: P. Elliott.

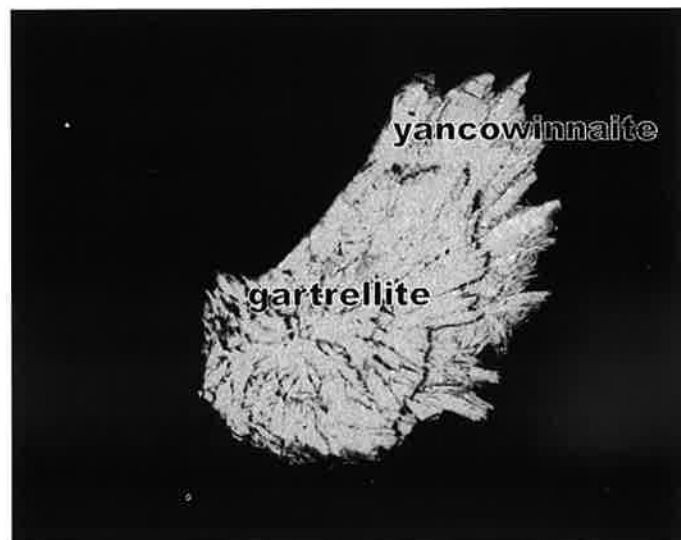
## OCCURRENCE AND PARAGENESIS

The source of the yancowinnaite specimens is most likely a zone rich in secondary arsenates in the No. 3 lens, at the base of the southern end of the Kintore open cut (Birch and van der Heyden, 1997). Platy crystals of gartrellite–zincgartrellite–yancowinnaite form rosette-like aggregates to 0.5 mm across in seams in a goethite–garnet matrix. The earliest-formed mineral on the specimens is mimetite, which occurs as white prismatic crystals. Gartrellite–zincgartrellite–yancowinnaite overgrows pale-blue needles of agardite-Y and tiny bladed carminite crystals and is sprinkled with yellow–orange crystals of beudantite–segnitite. Also present are yellowish brown crystals of chlorargyrite. Yancowinnaite has formed as a secondary mineral as part of the arsenate-rich assemblage in the Kintore open cut (Birch and van der Heyden, 1988; Birch, 1990), which is characterized by arsenates of Pb, Cu, Zn, Ca, Fe and Al. Solutions rich in these elements Pb, Fe, Cu, Zn and As have been derived from weathering of primary galena, sphalerite, chalcocopyrite and arsenopyrite–löllingite. Acid attack of host rocks would have provided Al.

## APPEARANCE AND PHYSICAL PROPERTIES

Yancowinnaite occurs as yellowish-green to green rosette-like aggregates of platy crystallites to 0.5 mm across which form overgrowths on cores of yellow to brownish-yellow gartrellite (Figures 1, 2). Individual crystallites of yancowinnaite are <10 µm in size. The mineral is translucent, has a vitreous lustre and a yellow streak.

Tenacity is brittle, the fracture is irregular and the hardness is estimated to be ~ 3. One perfect cleavage was observed, whose direction could not be determined, however, by



**Figure 2:** SEM photomicrograph showing a polished crystal aggregate of an overgrowth of green yancowinnaite (top and right hand side) over yellow gartrellite (bottom and left hand side). The boundary between the two is clearly visible. The scale bar is 50 µm in length.

**Table 1:** Compositional data for yancowinnaite.

Constituent	Wt. %	Range	Stand. Dev.	Probe Standard
PbO	36.43	35.07–37.38	0.57	galena
CuO	12.98	12.45–13.89	0.33	chalcocopyrite
ZnO	0.74	0.37–1.36	0.23	sphalerite
Fe <sub>2</sub> O <sub>3</sub>	4.08	2.81–5.96	0.79	almandine
Al <sub>2</sub> O <sub>3</sub>	5.14	3.74–6.17	0.71	almandine
As <sub>2</sub> O <sub>5</sub>	36.25	34.37–37.39	0.77	GaAs
H <sub>2</sub> O*	4.38			
Total	100.00			

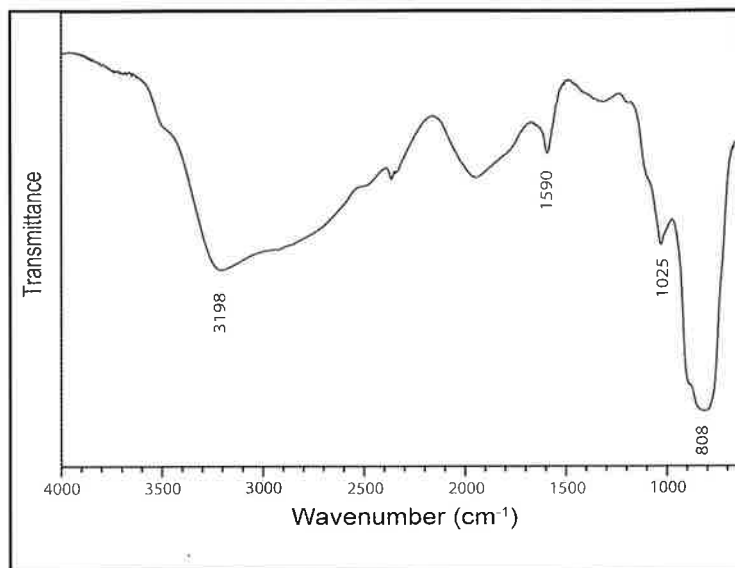
Number of analysis = 23.  
\* water content by difference.

analogy with gartrellite, the cleavage is parallel to {111}. An accurate density could not be measured, however, the mineral sinks in the heaviest liquid that was available, diluted Clerici solution ( $d \sim 3.8 \text{ g/cm}^3$ ). The calculated density is  $5.31 \text{ g/cm}^3$  from the empirical formula and  $5.17 \text{ g/cm}^3$  from the ideal formula. Due to the minute size and very thin, platy nature of the crystallites, complete optical data could not be determined. The measured minimum and maximum values of the refractive indices are 1.906(5) and 1.963(5). The average refractive index calculated using the Gladstone-Dale relationship is 1.896. By analogy with gartrellite, zincgartrellite and phosphogartrellite, the mineral is biaxial positive. Pleochroism is weak, from pale yellow, almost colourless, to yellow and pale orange.

## CHEMICAL AND SPECTROSCOPIC DATA

Chemical analyses were obtained using a crystal aggregate showing an overgrowth of green yancowinnaite on yellow gartrellite (Figure 2). Wavelength-dispersive electron-microprobe analyses were carried out with a Cameca SX51 electron probe at an accelerating voltage of 20 kV, a specimen current of 20 nA and a beam diameter of 20 µm. The data were reduced and corrected by the  $\phi(\rho Z)$  method of Pouchou and Pichoir (1985). The results of 23 microprobe analyses of the yancowinnaite region of the crystal aggregate are given in Table 1. The empirical formula, calculated on 10 O *pfu*, is  $\text{Pb}_{1.02}\text{Al}_{0.63}\text{Fe}^{3+}_{0.32}\text{Cu}_{1.02}\text{Zn}_{0.06}(\text{AsO}_4)_{1.98}(\text{OH})_{1.11}(\text{H}_2\text{O})_{0.97}$ . The end-member formula is  $\text{PbCuAl}(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ , which requires: PbO 36.56, Al<sub>2</sub>O<sub>3</sub> 8.35, CuO 13.03, As<sub>2</sub>O<sub>5</sub> 37.64, H<sub>2</sub>O 4.43.

The powder infrared-absorption spectrum of yancowinnaite (Figure 3) was recorded in the range 4000 to 650  $\text{cm}^{-1}$  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  $\sim 3570$  to  $2208 \text{ cm}^{-1}$ , centred around  $2915 \text{ cm}^{-1}$  with peaks at 3198,  $2362 \text{ cm}^{-1}$ ), H-O-H bending of H<sub>2</sub>O groups (at  $1590 \text{ cm}^{-1}$ ), and stretching vibrations of AsO<sub>4</sub> tetrahedra ( $808 \text{ cm}^{-1}$  with a shoulder at  $882 \text{ cm}^{-1}$ ). The IR spectrum shows the features distinctive of those of the gartrellite-type, tsumcorite-group minerals region (Effenberger et al., 2000), namely a region with a broad OH-



**Figure 3: FT-IR spectrum of powdered yancowinnaite**

stretching band and a relatively weak H<sub>2</sub>O-bending band, and can be distinguished from spectra of the tsumcorite-type or helmutwinklerite-type minerals, which show a sharp band near 3550 cm<sup>-1</sup>.

### X-RAY DIFFRACTION DATA

An attempt was made to obtain single-crystal X-ray data using synchrotron radiation, however, all crystals large enough for data collection proved to be composed of multiple crystallites. X-ray powder diffraction data (Table 2) were collected using a 100 mm Guinier-Hägg camera using monochromatic Cu K $\alpha$  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 using the Le Bail profile-fitting method (Le Bail *et al.*, 1988; Hunter, 1998), starting from the unit-cell parameters for gartrellite (Krause *et al.*, 1998a), gave the following parameters:  $a = 5.444(2)$ ,  $b = 5.640(2)$ ,  $c = 7.518(2)$  Å,  $\alpha = 67.89(2)$ ,  $\beta = 69.48(2)$ ,  $\gamma = 70.18(2)^\circ$ ,  $V = 194.51(7)$  Å<sup>3</sup>.

### CONCLUSIONS

Yancowinnaite is the Al analogue of gartrellite, PbCuFe<sup>3+</sup>(AsO<sub>4</sub>)<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub> which was described from Ashburton Downs, Western Australia, as fine-grained, powdery encrustations and cavity fillings associated with a variety of secondary Pb and Cu minerals, and from the Kintore open cut, Broken Hill, NSW, where it formed powdery encrustations and possible pseudomorphs after a hexagonal mineral (Nickel *et al.*, 1989). Yancowinnaite is the second tsumcorite group mineral to contain Al in the Me(2) site, after cabalzarite, Ca(Mg,Al,Fe,Mn)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O,OH)<sub>2</sub> which lies in the middle of a solid solution series, with compositions in which either Mg<sup>2+</sup> or Al<sup>3+</sup> can dominate the Me(2) site (Brugger *et al.*, 2000). Chemical analysis of gartrellite-yancowinnaite from Broken Hill shows Al contents in the range 0.03 to 0.82 *apfu*, which

suggests that complete solid solution exists between gartrellite and yancowinnaite. The crystal habit and powder X-ray pattern of the two minerals are very similar, however yancowinnaite is distinguished by its yellowish-green to green colour.

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Table 2: X-ray powder diffraction data for yancowinnaite

$I_{obs}$	$d_{obs}$	$I_{calc}$	$d_{calc}$	h	k	l	$I_{obs}$	$d_{obs}$	$I_{calc}$	$d_{calc}$	h	k	l
20	6.737	16	6.734	0	0	1			13	1.861	0	1	-3
5	5.069	4	5.074	0	1	0	5	1.789	13	1.788	2	0	-2
		4	4.952	1	0	0			8	1.760	2	3	2
25	4.771	32	4.779	0	1	1			5	1.736	1	3	3
35	4.590	53	4.588	1	0	1	10	1.731	8	1.732	1	3	0
25	4.467	43	4.462	1	1	1			5	1.725	3	2	2
10	4.064	21	4.062	1	1	0	15	1.691	26	1.691	0	3	0
5	3.578	12	3.576	1	0	-1			5	1.678	2	-1	-2
5	3.379	4	3.367	0	0	2	20	1.584	32	1.584	2	3	0
65	3.286	80	3.282	0	1	2	5	1.539	6	1.539	1	3	-1
		4	3.189	1	0	2	5	1.533	10	1.529	3	0	3
30	3.179	34	3.184	1	-1	0	5	1.500	8	1.500	1	-1	-4
100	2.949	100	2.947	1	1	-1			6	1.470	3	-1	0
40	2.891	25	2.900	1	-1	-1			4	1.469	1	-3	-2
45	2.850	84	2.858	1	-1	1			6	1.445	2	-1	-3
15	2.761	26	2.767	1	2	1	5	1.408	5	1.410	2	3	-1
5	2.640	10	2.643	0	2	1			5	1.407	1	-3	1
5	2.602	16	2.606	1	2	2			4	1.405	1	4	2
40	2.501{	29	2.515	1	2	0		1.401	6	1.399	3	2	-1
		50	2.502	1	0	-2			4	1.310	4	2	1
80	2.492{	73	2.490	0	1	-2			5	1.303	2	4	4
		10	2.486	1	1	3			10	1.272	4	0	2
5	2.384	12	2.390	0	2	2			4	1.270	3	4	2
5	2.325	17	2.319	0	1	3			8	1.263	2	-3	0
		10	2.294	2	0	2			5	1.262	2	-3	-1
5	2.272	16	2.275	1	0	3	5	1.246	8	1.246	0	3	5
		6	2.245	0	0	3			5	1.245	0	2	-4
15	2.166{	11	2.174	0	2	-1			12	1.244	3	-2	1
		26	2.163	1	1	-2			11	1.229	1	-2	4
		4	2.152	2	0	-1			4	1.216	0	1	-5
		8	2.136	2	1	3			4	1.210	4	3	1
		8	2.086	1	2	-1	10	1.191	10	1.192	3	0	-3
		5	2.068	2	1	-1			5	1.188	2	1	-4
		5	2.053	1	-2	-1			6	1.152	1	-3	3
10	2.039	13	2.041	2	-1	0			7	1.142	4	-1	2
5	2.027	21	2.031	2	2	0	5	1.138	5	1.137	2	0	6
15	2.011	20	2.015	2	2	3	10	1.122	6	1.122	0	0	6
		10	2.006	2	-1	1	50	1.110{	30	1.109	1	5	3
5	1.993	23	1.995	0	2	3			14	1.109	1	-4	1
20	1.875{	12	1.877	1	1	4							
		21	1.874	1	-2	-2							
		10	1.872	1	0	-3							

Note: Intensities estimated visually.

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