Gillardite, $Cu_3NiCl_2(OH)_6$, a new mineral from the 132 North deposit, Widgiemooltha, Western Australia

David M. Colchester, Peter Leverett*, Meagan E. Clissold, Peter A. Williams*
School of Natural Sciences
University of Western Sydney
Locked Bag 1797
Penrith South DC, New South Wales, 1797, Australia

David E. Hibbs
School of Pharmacy
University of Sydney
Sydney, New South Wales, 2006, Australia

Ernest H. Nickel
CSIRO Exploration and Mining
PO Box 5
Wembley, Western Australia, 6913, Australia

*E-mail: p.leverett@uws.edu.au; p.williams@uws.edu.au.

ABSTRACT

Gillardite, $Cu_3NiCl_2(OH)_6$ (IMA 2006-041), is a new mineral from the 132 North deposit, Widgiemooltha, Western Australia, Australia. The name is in honour of Professor Robert D. Gillard, in recognition of his contributions to the field of inorganic chemistry. It occurs as aggregates of equant crystals up to 0.5 mm in size in a silicified ferruginous gossan, associated with a variety of secondary Ni and Cu minerals. Gillardite is rhombohedral, space group $R\bar{3}m$, with single-crystal unit-cell parameters a = 6.8364(1), c = 13.8459(4) Å, V = 560.41(2) Å^3, Z = 3, D_{calc} = 3.76 g cm^{-3}. The ten strongest lines in the X-ray powder diffraction pattern [d in Å(I)(hkl)] are 5.459(100)(101), 2.753(69)(113), 2.256(39)(204), 2.901(19)(201), 4.648(16)(003), 2.725(14)(202), 1.818(13)(303), 4.515(11)(102), 1.711(10)(220) and 3.424(8)(110). An average of 12 microprobe analyses (wt%) gave CuO, 55.6; NiO, 15.3; CoO, 0.2; FeO, 0.1; Cl, 17.3. One analysis (TGA) gave H_2O, 13.1, less O=Cl, -3.9; total, 97.7. The derived empirical formula (based on 2 Cl pfu) is $(Cu_{2.865}Ni_{0.840}Co_{0.011}Fe_{0.006})_{\Sigma 3.722}Cl_2(OH)_{5.960}$. Normalisation of the metal distribution to 4 metal ions pfu gives $(Cu_{3.08}Ni_{0.90}Co_{0.01}Fe_{0.01})_{\Sigma 4.00}Cl_2(OH)_{5.96}$. Spot analyses show variation of Cu:Ni ratios and metal occupancies from $(Cu_{3.135}Ni_{0.853}Co_{0.012})$ to $(Cu_{2.922}Ni_{1.058}Co_{0.020})$. The simplified formula is thus $Cu_{3.1}Ni_{0.9}Cl_2(OH)_6$ or $Cu_3NiCl_2(OH)_6$. The formula is entirely consistent with the results of a single-crystal X-ray structure analysis. Equant rhombohedral crystals showing the forms {101}, {021}, {0001} and {100} (probable) are dark green in colour and larger crystals are nearly black. No twinning was observed. Gillardite is non-fluorescent, has a green streak and is transparent with a vitreous lustre. Mohs hardness is 3, fracture is splintery and uneven, and cleavage is good on {101}. Gillardite is uniaxial (+), with ω = 1.836 (0.002, ε = 1.838 (0.002 (white light). No dispersion or pleochroism was observed. Gillardite is isomorphous with herbertsmithite, $Cu_3ZnCl_2(OH)_6$, but can be conveniently distinguished from the latter by chemical analysis and a careful examination of X-ray powder diffraction data.

INTRODUCTION

The 132 North deposit, Widgiemooltha, Western Australia, Australia, is situated 5 km north-north-west of the hamlet of Widgiemooltha (31° 30' S, 121° 34' E) and about 80 km south of the city of Kalgoorlie (Figure 1). An open cut exposed an extensive oxidized zone developed on a komatiite-hosted sulphide deposit. Main sulfide minerals present were pyrrhotite, pentlandite, pyrite and chalcopyrite (McQueen, 1981; Marston *et al.*, 1981). A remarkable array of secondary Ni and Cu minerals was found in the oxidized zone and these have been thoroughly documented by Nickel *et al.* (1994). Among these, specimens of 'nickeloan paratacamite', with compositions reaching $Cu_3NiCl_2(OH)_6$, were noted. In light of the report of the new species herbertsmithite, $Cu_3ZnCl_2(OH)_6$ (Braithwaite *et al.*, 2004), it seemed likely that this material was in fact a new species as well. This has been shown to be the case and the material is described below as gillardite.

The new mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names,

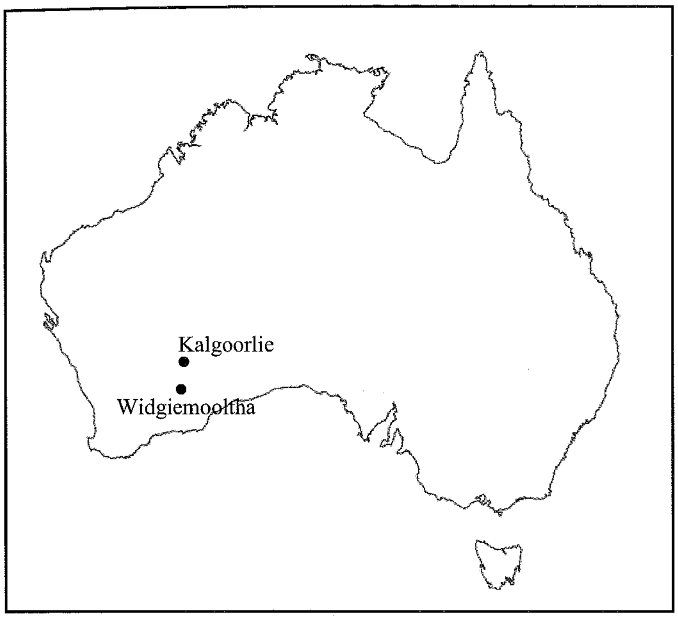

Figure 1: Locality map.

IMA (IMA 2006-041). The holotype is housed in the Gartrell Collection, specimen number 8774, of the Department of Earth and Planetary Sciences, Western Australian Museum, Perth Cultural Centre, Perth, WA, 6000, Australia. The mineral is named in honour of Professor Robert David Gillard (1936-), formerly of the Department of Chemistry, Cardiff University, Wales, UK, in recognition of his contributions to inorganic chemistry, especially in the field of coordination chemistry.

OCCURRENCE

Aggregates of equant, rhombohedral crystals up to 0.5 mm in size in a silicified ferruginous gossan were examined. The specimen was from the Gartrell Collection of the Department of Earth and Planetary Sciences, Western Australian Museum. On the holotype specimen, clusters of dark green gillardite and smaller, paler bottle-green, Ni-bearing clinoatacamite crystals are scattered across the ferruginous gossan matrix (Figure 2). Nickel *et al.* (1994) reported "nickeloan paratacamite" crystals up to several mm in size from throughout the carbonate zone of the oxidized profile. Associated secondary minerals in the deposit are gaspéite, magnesite, carrboydite, glaukosphaerite, hydrohonessite, retgersite, pyrolusite, huntite, aragonite, pecoraite, dolomite, kambaldaite, annabergite, azurite, lavendulan, nepouite, nullaginite, olivenite, otwayite, pharmacosiderite, reevesite, takovite, widgiemoolthalite and kambaldaite in a silicified ferruginous gossan (Nickel *et al.*, 1994).

Table 1: Analytical data for gillardite.

Constituent	Wt.%	Range	Probe Standard
CuO	55.6	54.2-58.6	Cu
NiO	15.3	14.3-17.4	Ni
CoO	0.2	<0.1-0.4	Co
FeO	0.1	<0.1-0.3	FeS_2
Cl	17.3	15.9-18.8	TlCl
H_2O*	13.1		
Less O=Cl	-3.9		
Total	97.7		

*From TGA.

CHEMICAL COMPOSITION

A crystal cluster of gillardite was embedded in epoxy resin, polished and carbon-coated. Twelve spot analyses were carried out using a Jeol 8600 electron microprobe (WDS mode, 30 kV, 20 nA, 3 μm beam diameter). No Zn was detected in any analysis. The sample used for microprobe analysis was somewhat unstable in the beam. A single TGA analysis (TA Instruments SDT 2960) for H_2O was performed. Analytical results are given in Table 1. No other elements than those reported were detected (Jeol JXA-840 SEM equipped with a light element detector EDS system). The empirical formula (based on 2 Cl apfu) is $(Cu_{2.865}Ni_{0.840}Co_{0.011}Fe_{0.006})_{\Sigma 3.722}Cl_2(OH)_{5.960}$. Normalisation of the metal content to four metal ions pfu gives $(Cu_{3.08}Ni_{0.90}Co_{0.01}Fe_{0.01})_{\Sigma 4.00}Cl_2(OH)_{5.96}$. Spot analyses show variation of Cu:Ni ratios and metal occupancies range from $(Cu_{3.135}Ni_{0.853}Co_{0.012})$ to $(Cu_{2.922}Ni_{1.058}Co_{0.020})$. Other analyses are given in Nickel *et al.* (1994). The simplified formula is thus $Cu_{3.1}Ni_{0.9}Cl_2(OH)_6$ or $Cu_3NiCl_2(OH)_6$.

PHYSICAL AND OPTICAL PROPERTIES

Equant, rhombohedral crystals showing the forms {101}, {021}, {0001} and {100} (probable) are dark green in colour and larger crystals are nearly black. No twinning was observed. Gillardite is non-fluorescent, has a green streak and is transparent with a vitreous lustre. Mohs hardness is 3, fracture is splintery and uneven, and the tenacity is brittle. No parting was observed, but cleavage is good on {101}. The calculated density is 3.76 g cm^{-3}, from the single-crystal structure analysis. Gillardite is uniaxial (+), with $\omega = 1.836 \pm 0.002$, $\varepsilon = 1.838 \pm 0.002$ (white light). No dispersion or pleochroism was observed. The Gladstone-Dale compatibility index (Mandarino, 1981), calculated using the empirical formula $(Cu_{3.08}Ni_{0.90}Co_{0.01}Fe_{0.01})_{\Sigma 4.00}Cl_2(OH)_{5.96}$ and unit-cell parameters from the single-crystal structure analysis is -0.032 (excellent). After dissolution of gillardite in 6M HNO_3, reaction with dimethylglyoxime and excess NH_3 gives a heavy precipitate of $Ni(DMGH_{-1})_2$. Reaction of the acidic solution with potassium mercuric thiocyanate gives pale yellow-green rosettes of copper mercuric thiocyanate crystals. Addition of $AgNO_3$ solution and adjustment of pH with ammonia gives a white precipitate of AgCl. The mineral decomposes with loss of water between 150 and 300 °C.

SINGLE-CRYSTAL X-RAY STRUCTURE

The single-crystal structure of gillardite has been reported elsewhere (Clissold *et al.*, 2007). Gillardite is rhombohedral, space group $R\bar{3}m$, with $a = 6.8364(1)$, $c = 13.8459(4)$ Å, $V = 560.41(2)$Å^3, Z = 3. The c:a ratio calculated from unit-cell parameters is 2.0253. The locations of the metal (Cu and Ni) and chlorine atoms lie in similar positions to the analogous atoms in the $R\bar{3}m$ substructure of paratacamite reported by Fleet (1975). In gillardite, the divalent copper ion fully occupies the M site in the tetragonally distorted MO_4Cl_2 'octahedron', and nickel occupies the centre of the undistorted MO_6 octahedron. This is analogous to the metal ion distribution reported for herbertsmithite (Braithwaite *et al.*, 2004), with which gillardite is isomorphous. The unit cell of gillardite is slightly smaller than that of herbertsmithite (a = 6.834(1), c = 14.075(2) Å). This is consistent with the smaller radius of the Ni^{2+} ion, 0.69 Å, as compared to the Zn^{2+} ion, 0.74 Å, for coordination number 6 (Shannon, 1976).

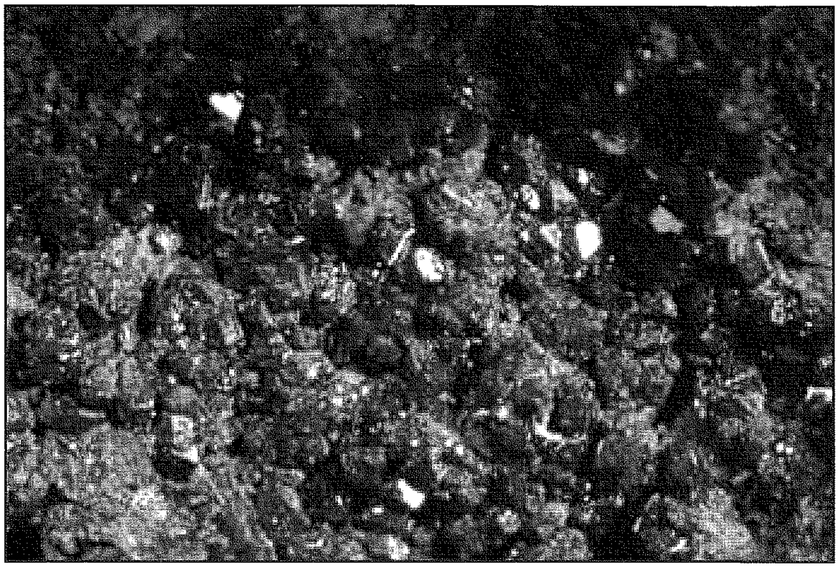

Figure 2: Section of the holotype specimen of gillardite. Individual crystals range up to 0.3 mm in length. Photo: Specimen: Western Australian Museum, M20.2006 (Gartrell collection, 8774).

X-RAY POWDER DIFFRACTION

X-ray powder diffraction data were recorded using a Philips PW1925-20 powder diffractometer (Ni-filtered Cu Kα radiation with pure Si as internal standard; λ = 1.5406 Å). Table 2 lists these data, together with those of herbertsmithite (Braithwaite *et al.*, 2004) for comparison. Refined unit-cell dimensions (Langford, 1973) from the powder diffraction data are a = 6.843(2) c = 13.902(8) Å, V = 563.8(3) $Å^3$. Unit-cell dimensions are within three esds of those derived in the single-crystal study. The ten strongest lines in the X-ray powder diffraction pattern are given in the abstract. Indexing of the powder data was effected using a simulated pattern (Kraus and Nolze, 1996a,b) based on the single-crystal structure analysis (Clissold *et al.*, 2007). Calculated intensities are included in Table 2.

RELATIONSHIP OF GILLARDITE TO HERBERTSMITHITE AND OTHER POLYMORPHS

Gillardite belongs to Strunz class 3.DA.10 (atacamite family; Strunz and Nickel, 2001) and is the Ni-analogue of herbertsmithite, $Cu_3ZnCl_2(OH)_6$ (Braithwaite *et al.*, 2004). Gillardite is the species with ideal end-member composition $Cu_3NiCl_2(OH)_6$, forming a solid-solution series with Ni-rich paratacamite, with Cu occupying the Jahn-Teller distorted octahedral site in the lattice (at 1/2,0,0) and Ni occupying more than half of the more regular site (at 0,0,1/2). Methods for distinguishing gillardite and herbertsmithite from clinoatacamite and paratacamite on the basis of the powder X-ray diffraction record are dealt with elsewhere (Jambor *et al.*, 1996; Braithwaite *et al.*, 2004). Gillardite can be distinguished from herbertsmithite also by using powder X-ray diffraction if accurate data are available for d-spacings (Table 2). However, differences between observed and calculated intensities in the powder diffraction record for gillardite indicate the influence of preferred orientation effects. Calculated intensities for herbertsmithite (Kraus and Nolze, 1996a,b), also given in Table 2, show that it too suffers from preferred orientation effects in powder diffraction. In fact, there is, as expected, a close correlation between calculated intensities for the two minerals. Gillardite can best be distinguished from nickel-bearing paratacamite and herbertsmithite by

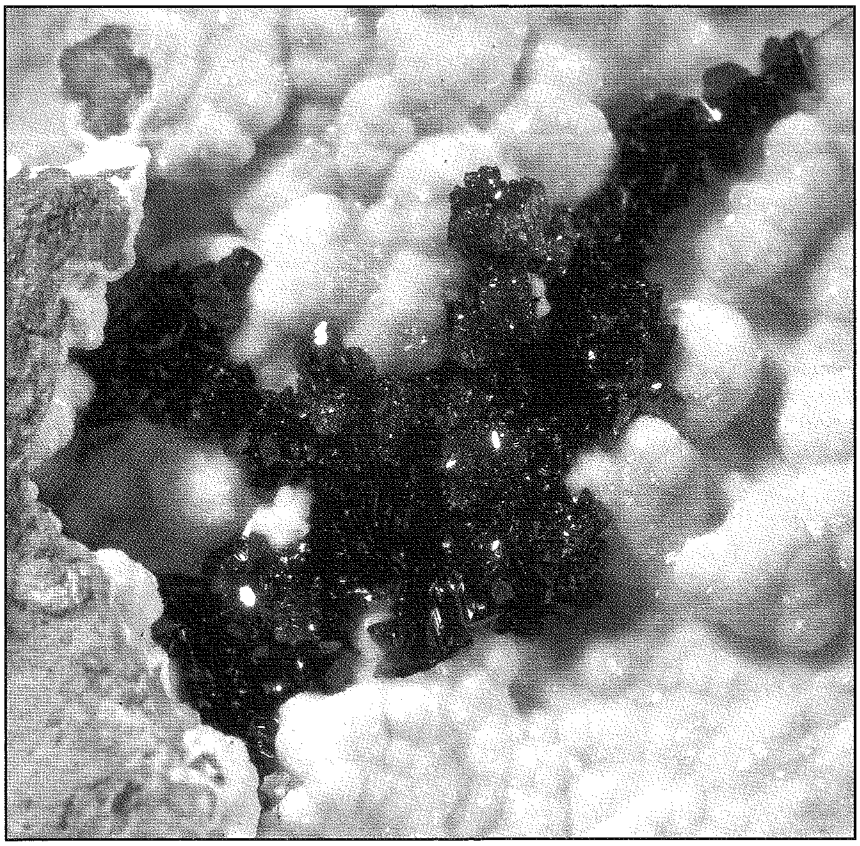

Figure 3: Gillardite crystals range up to 0.3 mm in length. Photo: R. Start. Specimen: Museum Victoria, M 43749.

Table 2: Powder X-ray diffraction data for gillardite and herbertsmithite.

gillardite					herbertsmithite[a]		
I_{meas}	I_{calc}	d_{meas}Å	d_{calc}Å	*h k l*	I_{meas}	I_{calc}	d_{meas}/Å
100	69	5.459	5.452	1 0 1	55	67	5.466
16	13	4.648	4.634	0 0 3	14	11	4.702
11	2	4.515	4.510	1 0 2	11	1	4.537
8	5	3.424	3.422	1 1 0	5	6	3.423
6	3	2.998	2.998	1 0 4	1	2	3.028
19	31	2.901	2.898	2 0 1	11	27	2.899
69	100	2.753	2.753	1 1 3	100	100	2.764
14	22	2.725	2.726	2 0 2	13	22	2.730
7	15	2.314	2.317	0 0 6	4	15	2.346
39	99	2.256	2.255	2 0 4	36	97	2.266
5	6	2.213	2.211	2 1 1	2	7	2.210
8	18	2.028	2.028	2 0 5	4	16	2.040
				1 1 6	1	3	1.934
5	17	1.882	1.883	1 0 7	5	18	1.905
13	10	1.818	1.817	3 0 3	13	11	1.820
4	3	1.745	1.744	2 1 5	2	7	1.752
10	56	1.711	1.711	2 2 0	18	55	1.709
4	9	1.650	1.650	2 0 7	1	7	1.664
4	11	1.632	1.632	3 1 1	3	12	1.631
4	6	1.600	1.605	2 2 3	1	5	1.606
				3 1 2	1	3	1.599
				208	4	16	1.513
5	24	1.486	1.486	2 1 7	3	24	1.496
3	9	1.473	1.473	4 0 1	1	8	1.472
3	11	1.449	1.449	4 0 2	1	11	1.448
7	33	1.377	1.376	2 2 6	6	33	1.381
5	19	1.364	1.363	4 0 4	4	19	1.363
					plus 10 lines to 1.020		

[a] Braithwaite *et al.* (2004).

chemical analysis in conjunction with X-ray methods (unit-cell measurements). Kapellasite (trigonal, space group $P\bar{3}m1$) is a recently described polymorph of herbertsmithite (Krause *et al.*, 2006). Its powder diffraction record is quite unlike that of herbertsmithite, and is somewhat similar to that of botallackite.

ACKNOWLEDGEMENTS

The authors are grateful to Dr Uwe Kolitsch and Professor Allan Pring for their thoughtful reviews of the manuscript.

REFERENCES

Braithwaite, R.S.W., Mereiter, K., Paar, W.H. and Clark, A.M., 2004: Herbertsmithite, $Cu_3Zn(OH)_6Cl_2$, a new species, and the definition of paratacamite. *Mineralogical Magazine*, 68, 527-539.

Clissold, M E., Leverett, P., Williams, P.A., Hibbs, D.E. and Nickel, E.H., 2007: The structure of gillardite, $Cu_3NiCl_2(OH)_6$, from Widgiemooltha, Western Australia: the Ni-analogue of herbertsmithite. *Canadian Mineralogist*, 45,317–320.

Fleet, M.E., 1975: The crystal structure of paratacamite, $Cu_2(OH)_3Cl$. *Acta Crystallographica*, B31, 183-187.

Jambor, J.L., Dutrizac, J.T., Roberts, A.C., Grice, J.D. and Szymanski, J.T., 1996: Clinoatacamite, a new polymorph of $Cu_2(OH)_3Cl$, and its relationship to paratacamite and "anarakite". *Canadian Mineralogist*, 34, 61-72.

Kraus, W. and Nolze, G., 1996a: PowderCell - a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *Journal of Applied Crystallography*, 29, 301-303.

Kraus, W. and Nolze, G., 1996b: *PowderCell 1.8 and Windows version 1.0*. Federal Institute for Materials Research and Testing (BAM), Berlin.

Krause, W., Bernhardt, H.-J., Braithwaite, R.S.W., Kolitsch, U. and Pritchard, R., 2006: Kapellasite, $Cu_3Zn(OH)_6Cl_2$, a new mineral from Lavrion, Greece, and its crystal structure. *Mineralogical Magazine*, 70, 329-340.

Langford, J.I., 1973: Least-squares refinement of cell dimensions from powder data by Cohen's method. *Journal of Applied Crystallography*, 6, 190-196.

Mandarino, J.A. 1981: The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist*, 19, 441-450.

McQueen, K.G., 1981: Volcanic-associated nickel deposits from around the Widgiemooltha dome, Western Australia. *Economic Geology*, 76, 1417-1443.

Marston, R.J., Groves, D.I., Hudson, D.R. and Ross, J.R., 1981: Nickel sulphide deposits in Western Australia: a review. *Economic Geology*, 76, 1330-1363.

Nickel, E.H., Clout, J.F.M. and Gartrell, B.J., 1994: Secondary minerals from Widgiemooltha, Western Australia. *Mineralogical Record*, 25, 283-291, 302.

Shannon, R.D., 1976: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751-767.

Strunz, H. and Nickel, E.H., 2001: *Strunz Mineralogical Tables*. Ninth Edition, E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.