The Canadian Mineralogist
Vol. 45, pp. 317-320 (2007)

THE STRUCTURE OF GILLARDITE, THE Ni-ANALOGUE OF HERBERTSMITHITE, FROM WIDGIEMOOLTHA, WESTERN AUSTRALIA

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Abstract

The structure of gillardite, the Ni-analogue [ideally $Cu_3NiCl_2(OH)_6$] of herbertsmithite [ideally $Cu_3ZnCl_2(OH)_6$] has been determined at 273(2) K. The crystal used was removed from a sample from the 132N nickel deposit at Widgiemooltha, Western Australia, Australia. Seventeen electron-microprobe analyses gave compositions, based on a total of four cations per formula unit, that ranged from $(Cu_{3.189}Ni_{0.803}Co_{0.002}Fe_{0.006})Cl_2(OH)_6$ to $(Cu_{2.922}Ni_{1.058}Co_{0.020})Cl_2(OH)_6$, with an average result of all analyses of $(Cu_{3.081}Ni_{0.903}Co_{0.012}Fe_{0.004})Cl_2(OH)_6$. The structure was refined using site occupancies indicated by the average composition, although refinement using the ideal composition gave identical results within standard errors. The new species gillardite is trigonal (rhombohedral), space group $R\bar{3}m$, with *a* 6.8364(1), *c* 13.8459(4) Å, *Z* = 3. The oxysalt is isostructural with herbertsmithite, with the two different sites in the paratacamite-type structure being occupied by different cations [paratacamite is $Cu_4Cl_2(OH)_6$, space group $R\bar{3}$ with a pronounced $R\bar{3}m$ substructure]. In gillardite, the Cu site is strongly Jahn–Teller-distorted, and the Ni site is regular with respect to Ni–O bond lengths, but with a slight angular distortion from regular octahedral geometry.

Keywords: gillardite, herbertsmithite, nickel analogue, new mineral species, paratacamite, crystal structure, Widgiemooltha, Western Australia.

Sommaire

Nous avons déterminé la structure cristalline de la gillardite, de formule idéale $Cu_3NiCl_2(OH)_6$, analogue nickelifère de la herbertsmithite [formule idéale: $Cu_3ZnCl_2(OH)_6$] découvert récemment, à 273(2) K. Le monocristal a été prélevé d'un échantillon provenant du gisement de nickel 132N à Widgiemooltha, en Australie occidentale. Les résultats de dix-sept analyses avec une microsonde électronique, fondés sur quatre cations par unité formulaire, vont de $(Cu_{3.189}Ni_{0.803}Co_{0.002}Fe_{0.006})Cl_2(OH)_6$ à $(Cu_{2.922}Ni_{1.058}Co_{0.020})Cl_2(OH)_6$, et la composition moyenne est $(Cu_{3.081}Ni_{0.903}Co_{0.012}Fe_{0.004})Cl_2(OH)_6$. La structure a été affinée en utilisant les occupations des sites conformes à la composition moyenne, quoique la composition idéale a donné des résultats identiques compte tenu des écarts standards. La gillardite est trigonale (rhomboédrique), groupe d'espace $R\bar{3}m$, avec *a* 6.8364(1), *c* 13.8459(4) Å, *Z* = 3. L'oxysel est isostructural de la herbertsmithite, et les deux sites dans la structure de type paratacamite sont occupés par des cations distincts [la paratacamite a la composition $Cu_4Cl_2(OH)_6$, groupe d'espace $R\bar{3}$, avec une sous-structure $R\bar{3}m$ prononcée]. Dans la gillardite, le site du Cu est fortement difforme à cause de l'effet de Jahn–Teller, et le site Ni est régulier par rapport aux longueurs des liaisons Ni–O, mais avec une légère distorsion angulaire par rapport à la géométrie d'un octaèdre régulier.

(Traduit par la Rédaction)

Mots-clés: gillardite, herbertsmithite, analogue nickelifère, nouvelle espèce minérale, paratacamite, structure cristalline, Widgiemooltha, Australie occidentale.

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INTRODUCTION

It has been pointed out that materials corresponding to $Cu_3(Cu,Ni)Cl_2(OH)_6$, $Cu_3(Ni,Cu)Cl_2(OH)_6$, and $Cu_3NiCl_2(OH)_6$ occur naturally in several oxidized Ni deposits in Western Australia (Nickel *et al.* 1994, Jambor *et al.* 1996). We have undertaken a single-crystal X-ray structural study of material from the 132N deposit at Widgiemooltha, Western Australia, the results of which are reported below. The material studied has an average composition $(Cu_{3.081}Ni_{0.903}Co_{0.012}Fe_{0.004})Cl_2(OH)_6$ and is rhombohedral, space group $R\overline{3}m$, with *a* 6.8364(1), *c* 13.8459(4) Å, $Z = 3$. The structure analysis makes it clear that the material represents a new mineral species. The new species and the name *gillardite* have been approved by the Commission on New Minerals and Mineral Names, IMA (IMA 2006–041). The formal description of the mineral will be published elsewhere (Colchester *et al.* 2007).

BACKGROUND INFORMATION

Paratacamite, nominally $Cu_2Cl(OH)_3$, was reported by Frondel (1950) to be rhombohedral with unit-cell parameters (hexagonal system) *a* 13.68, *c* 13.98 Å, with a pronounced subcell corresponding to $a' = a/2$. The latter, in space group $R\overline{3}m$, was considered to be correct by de Wolff (1953), but a single-crystal determination of the structure in space group $R\overline{3}$ using the larger unit-cell by Fleet (1975) confirmed the findings of Frondel (1950). A notable feature of the structure is the environment of the four non-equivalent copper ions. Three exhibit the usual tetragonally elongate (4 + 2) octahedral coordination geometry of Cu^{2+}, but the fourth has six symmetry-enforced equivalent bonds with an angular distortion from regular octahedral geometry. The careful work of Jambor *et al.* (1996), Grice *et al.* (1996) and Braithwaite *et al.* (2004) has clarified ambiguities concerning the nature of polymorphs of nominal composition $Cu_2Cl(OH)_3$. It is now recognized that substitution at the site that is not tetragonally elongate is responsible for considerable structural variation. Paratacamite is rhombohedral, space group $R\overline{3}$, composition $Cu_3(Cu,M)Cl_2(OH)_6$, with *M* = Zn, Co, and Ni, and with *M* occupying $^1/_3$ to ½ of the above site (Braithwaite *et al.* 2004). The structure changes to that of clinoatacamite, monoclinic, space group $P2_1/n$, where less than $^1/_3$ of the Cu ions at that site are replaced by Zn ions (Jambor *et al.* 1996, Grice *et al.* 1996). Herbertsmithite, $Cu_3(Zn,Cu)Cl_2(OH)_6$, can adopt either of the rhombohedral space-groups $R\overline{3}$ or $R\overline{3}m$ for compositions near the transition stoichiometry. Where the site is filled or nearly filled with Zn, it adopts the latter, corresponding to the subcell of Fleet (1975).

EXPERIMENTAL

Analysis

A sample from the 132N deposit, Widgiemooltha, Western Australia, was loaned for study by the Museum of Western Australia (Gartrell specimen no. 8774). Analyses of a polished specimen were carried out using a JEOL 8600 electron microprobe in wavelength-dispersion mode (30 kV, 20 nA, beam diameter 3 μm), with pure Cu, Co, Ni metals, TlCl and FeS_2 as standards. Some 17 spot analyses gave (%) CuO, 51.4–58.6 (ave. 55.2); NiO, 13.7–17.5 (ave. 15.3); CoO, 0.1–0.4 (ave. 0.2); Fe, <0.1–0.3 (ave. 0.1); Cl, 16.2–18.8 (ave. 17.46); CaO, trace. Individual analyses gave compositions that range from $(Cu_{3.189}Ni_{0.803}Co_{0.002}Fe_{0.006})Cl_2(OH)_6$ to $(Cu_{2.922}Ni_{1.058}Co_{0.020})Cl_2(OH)_6$, with an average for all points analyzed of $(Cu_{3.081}Ni_{0.903}Co_{0.012}Fe_{0.004})Cl_2(OH)_6$, all based upon four metal cations. The crystal structure (below) was refined using site occupancies indicated by the average composition. The following composition is expected for $Cu_3NiCl_2(OH)_6$ (%): CuO 56.51, NiO 17.69, Cl 16.79, H_2O 12.80, less O = Cl, –3.79, total 100.00.

Crystallography

Data collection was performed on a Bruker SMART CCD diffractometer at 273(2) K with graphite-monochromated Mo*K*α radiation (λ = 0.71073 Å). Data were corrected for Lorentz, polarization and absorption effects, the latter using SADABS (Sheldrick 1996). Maximum and minimum apparent transmission-factors were 1.225 and 0.850, respectively. The structure was solved by direct methods using SHELXS97 (Sheldrick 1997a) and refined by least-squares procedures using SHELXL97 (Sheldrick 1997b). The locations of the metal (Cu and Ni) and chlorine atoms were found to be in similar positions to the analogous atoms in the $R\overline{3}m$ substructure of paratacamite reported by Fleet (1975). In line with the results of the electron-microprobe analyses, which indicate a Cu:Ni ratio of close to 3:1, we assumed that divalent copper would fully occupy the MO_4Cl_2 site, whereas nickel would fully occupy the non-tetragonally distorted MO_6 site. This is also consistent with the metal–atom distribution reported for herbertsmithite (Braithwaite *et al.* 2004). A difference map then revealed the position of the hydroxyl oxygen atom, and in a similar position to that found for one of the two disordered oxygen atoms in the paratacamite substructure (Fleet 1975). An isotropic refinement gave $R1 = 0.025$, and a subsequent difference-map clearly revealed the hydrogen atom position of the hydroxyl group, *ca.* 0.83 Å from the oxygen atom.

The hydroxyl group is probably oriented in a similar fashion in herbertsmithite, but as no atom coordinates were listed (Braithwaite *et al.* 2004), this can only be assumed. The complete structure then refined smoothly with anisotropic displacement parameters for the non-hydrogen atoms to an $R1$ of 0.011. A final refinement was performed using a mixed occupancy for the nickel atom position, in line with the analytical results, ($Ni_{0.901}$ $Cu_{0.081}Co_{0.012}Fe_{0.004}$). This resulted in no significant change to the structure. Final $R1$ and $wR2$ values were 0.011 and 0.027, respectively, for 448 unique reflections with $I > 2\sigma(I)$. The weighting scheme used was $w = 1/(\sigma^2F_o^2 + 0.081P^2 + 1.700P)$, where $P = (F_o^2 + 2F_c^2)/3$, as defined by SHELXL97 (Sheldrick 1997b). Crystal data and structure refinement details are given in Table 1. Final coordinates of the atoms are listed in Table 2, anisotropic displacement parameters in Table 3, and selected bond-lengths and angles in Table 4.

DISCUSSION

The structure of gillardite is essentially that described by Fleet (1975) for the "substructure" of paratacamite, $Cu_4(OH)_6Cl_2$, and more recently that reported for herbertsmithite, $Cu_3Zn(OH)_6Cl_2$, by Braithwaite *et al.* (2004). Although impossible to distinguish between Cu and Ni during the structure determination on considerations of electron density, the two cation sites in the present structure are sufficiently different to allow the correct placement of the Ni atom in the non-Jahn–Teller-distorted MO_6 octahedral site and the Cu atom in the tetragonally elongate MO_4Cl_2 octahedral site. No reflections corresponding to the paratacamite superlattice are present in the diffraction pattern of the current structure. The OH–Cl system of hydrogen bonds supplements the Ni–O and Cu–O bonds in linking layers of metal–oxygen polyhedra, with an O–Cl distance of 3.049 Å. A selection of bond lengths and angles is given in Table 4, together with analogous values (where given) reported for herbertsmithite and the substructure of paratacamite, for comparison.

The unit cell of gillardite, $Cu_3NiCl_2(OH)_6$, with *a* 6.8364(1), *c* 13.8459(4) Å, is slightly smaller than that of herbertsmithite, $Cu_3ZnCl_2(OH)_6$ [*a* 6.834(1), *c* 14.075(2) Å]. This is in accord with the smaller radius of the Ni^{2+} ion, 69 pm, as compared to the Zn^{2+} ion, 74 pm, for a coordination number of six (Shannon 1976).

TABLE 1. CRYSTAL DATA AND STRUCTURE-REFINEMENT DETAILS FOR GILLARDITE

Chemical formula	$Cu_{3.081}Ni_{0.903}Co_{0.012}Fe_{0.004}Cl_2O_6H_6$
Mr	422.66
Crystal system	Rhombohedral
Space group	$R\bar{3}m$
Unit-cell dimensions (Å)	*a* 6.8364(1), *c* 13.8459(4)
V (Å^3)	560.41(2)
Z	3
Density (calc.) (Mg m^{-3})	3.76
μ (Mo$K\alpha$) (mm^{-1})	11.6
$F(000)$	609.2
Crystal size (mm)	0.22 × 0.21 × 0.23
θ range for data collection (°)	3.74 – 40.33
Index ranges	$-11 \le h \le 12$, $-11 \le k \le 12$, $-24 \le l \le 22$
Reflections measured	8443
Independent, observed reflections	454, 448 (R_{int} = 0.022)
Data, parameters	454, 20
Goodness-of-fit on F^2	1.062
Final R indices [$I > 2.0\sigma(I)$]	$R1 = 0.0112$ ($wR2 = 0.0274$)
Final R indices (all data)	$R1 = 0.0114$ ($wR2 = 0.0274$)
Largest diff. peak, hole (e Å^{-3})	0.63, -0.53

TABLE 2. FINAL COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) OF THE ATOMS IN GILLARDITE

	x/a	y/b	z/c	U_{eq}
Ni(1)	0	0	½	0.0043(1)
Cu(2)	½	0	0	0.0054(1)
Cl	0	0	0.1933(1)	0.0073(1)
O	0.2070(1)	$-x$	0.0624(1)	0.0073(12)
H	0.1440(11)	$-x$	0.0858(14)	0.022(6)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR THE NON-HYDROGEN ATOMS OF GILLARDITE

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	0.0049(1)	U_{11}	0.0031(1)	0	0	$0.5U_{11}$
Cu(2)	0.0053(1)	0.0049(1)	0.0058(1)	0.0011(1)	$0.5U_{23}$	$0.5U_{22}$
Cl	0.0080(1)	U_{11}	0.0059(1)	0	0	$0.5U_{11}$
O	0.0067(2)	U_{11}	0.0087(3)	-0.0011(1)	$-U_{23}$	0.0034(2)

The exponent of the anisotropic displacement factor takes the form $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

TABLE 4. SELECTED BOND-LENGTHS (Å) AND ANGLES (°) FOR GILLARDITE, COMPARED WITH THOSE IN HERBERTSMITHITE[*] AND THE SUBCELL OF PARATACAMITE[¶]

	herbertsmithite	gillardite	Fleet (1975)
	$M(1)$ = Zn M(2) = Cu	$M(1)$ = Ni $M(2)$ = Cu	$M(1)$ = Cu $M(2)$ = Cu
$M(1) - O$	2.119(1)	2.0791(8)	2.11 [b]
$M(2) - O$	1.985(1)	1.9812(4)	1.98 [b]
$M(2) - Cl$	2.779(1)	2.7665(3)	2.78 [b]
$O - M(1) - O$	[a]	102.93(3), 77.07(3), 180	
$O - M(2) - O$	[a]	98.34(5), 81.66(5), 180	
$O - M(2) - Cl$	[a]	97.81(2), 82.19(2), 180	
O – H	[a]	0.82(1)	1.14 [b]
H – Cl	[a]	2.26(1)	1.95 [b]
O – Cl	3.071	3.049(8)	3.07 [b]
O – H – Cl	~166	162(2)	165.7 [b]

[a] not given; [b] average distances in paratacamite with respect to split sites in space group $R3m$. * Braithwaite *et al.* (2004), ¶ Fleet (1975).

Supplementary Material

File CSD–415857 (NiParaCIF.txt) contains crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223–336033; email: deposit@ccdc.cam.ac.uk. A table of results of point electron-microprobe analyses is available from the authors upon request. A table of structure factors is available from the Depository of Unpublished Data on the MAC web site [document gillardite CM45_317].

Acknowledgements

MEC thanks the ARC for the award of a postgraduate studentship. We also thank the Museum of Western Australia for the loan of the specimen. We acknowledge the helpful comments of Drs. Herta Efferberger, Olga Yakubovich and Uwe Kolitsch.

References

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

Colchester, D.M., Leverett, P., Clissold, M.E., Williams, P.A. & Hibbs, D.E. (2007): Gillardite, $Cu_3NiCl_2(OH)_6$, a new mineral from the 132 North deposit, Widgiemooltha, Western Australia. *Aust. J. Mineral.* (in press).

de Wolff, P.M. (1953): Crystal structure of $Co_2(OH)_3Cl$. *Acta Crystallogr.* **6**, 359-360.

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

Frondel, C. (1950): On paratacamite and some related copper chlorides. *Mineral. Mag.* **29**, 34-45.

Grice, J.D., Szymański, J.T. & Jambor, J.L. (1996): The crystal structure of clinoatacamite, a new polymorph of $Cu_2(OH)_3Cl$. *Can. Mineral.* **34**, 73-78.

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

Nickel, E.H., Clout, J.F.M. & Gartrell, B.J. (1994): Secondary nickel minerals from Widgiemooltha, Western Australia. *Mineral. Rec.* **25**, 283-291, 302.

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

Sheldrick, G.M. (1996): Sadabs. Empirical Absorption Correction Program for Area Detector Data. University of Göttingen, Göttingen, Germany.

Sheldrick, G.M. (1997a): Shelxs97, A Program for the Solution of Crystal Structures. University of Göttingen, Göttingen, Germany.

Sheldrick, G.M. (1997b): Shelxl97, A Program for the Refinement of Crystal Structures. University of Göttingen, Göttingen, Germany.

Received October 26, 2005, revised manuscript accepted June 1, 2006.