

Marshite–miersite solid solution and iodargyrite from Broken Hill, New South Wales, Australia

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ABSTRACT

Microprobe analysis of marshite and miersite from Broken Hill, Australia, demonstrate extensive solid solution between the end-members CuI and AgI, indicating the possibility of a complete solid-solution series. Unit-cell parameters increase from 6.054 Å for marshite to 6.504 Å for miersite, closely following Vegard's Law. The Cu content of iodargyrite is generally below the limit of detection, but one zoned crystal contained 0.28 wt.% Cu. Crystallization of either miersite or iodargyrite at Broken Hill appears to be dependent upon the local availability and ratio of copper, silver and iodine ions.

KEYWORDS: marshite, miersite, iodargyrite, Broken Hill, solid solution, copper, silver.

Introduction

THE Broken Hill silver-lead-zinc deposit, in western New South Wales, Australia, is renowned for its rare and exotic secondary mineral assemblages. The iodine-bearing minerals marshite, miersite and iodargyrite have all been reported from various locations within the secondary zone of the orebody. Spencer (1901) originally proposed that isomorphous replacement takes place between the cubic minerals miersite and marshite. Later, Barclay and Jones (1971) also proposed that a complete solid solution series may exist between pure cubic copper iodide and pure silver iodide.

Previous analysis of silver copper halides include a wet analysis by Prior (1902) which gave a composition for miersite corresponding to Ag 0.8 Cu 0.2 I. Two miersite specimens analysed by Barclay and Jones (1971) contained 3.3 and 11.4 wt.% Cu respectively, while Birch *et al.* (1982) report a miersite specimen containing 34 mol.% Cu. Cuproiodargyrite was recorded to contain equal amounts of silver and copper; see Spencer (1898), Quercigh (1914) and Barclay and Jones (1971). Specimens of this composition have been reported from Iquique, Chile (Spencer, 1901), but not found at Broken Hill. Synthetic crystals of cuproiodargyrite have been produced by Quercigh (1914), Brightwell and Sephton

(1987) and Kazunaka and Teruaki (1990), having complete solid solution.

In order to investigate the original proposition of Spencer (1901) that a solid solution series incorporates these minerals, the author has systematically analysed a wide range of specimens from Broken Hill, by electron-microprobe and X-ray diffraction methods.

Procedure

The chemical analyses of 16 of marshite, miersite and iodargyrite specimens were performed with a Camebax microbeam electron microprobe No 544, in the Australian National University Research School of Earth Science, using combined energy- and wavelength-dispersive techniques. Cu and I were calibrated using a synthetic CuI standard. The analyses were mainly undertaken using a lithium-drifted silicon detector; the beam current averaged 1.45 nA and the accelerating voltage was 25 kV.

In order to correlate any trends in compositional values with unit-cell dimension, X-ray diffraction patterns of the specimens from the copper silver iodide series were collected. For some determinations single crystals were mounted on fibres and the powder patterns were recorded on a Gandolfi camera using filtered Cu-K α radiation: ($\lambda = 1.5418 \text{ \AA}$). For others, crystals

were crushed lightly and mounted on adhesive tape in a Guinier-Hagg camera using monochromated Cu- $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). In both cases Si was added to the specimen as an internal standard ($a = 5.43030 \text{ \AA}$ at 298 K). All X-ray diffraction analyses were performed in the Australian National University Research School of Chemistry.

X-ray diffraction patterns were measured optically using a vernier film reader. The corrected data were used to refine the unit cell dimensions of each specimen using a least-squares unit-cell refinement program. All observable lines were used in these refinements.

Multiple crystals were identified by 'single crystal' Buerger precession X-ray analysis using

Mo- $K\alpha$ radiation and by densitometer-trace X-ray analysis.

Results

The compositional data from electron microprobe analysis of 16 marshite, miersite and iodargyrite specimens are presented in Table 1 and plotted in Fig. 1. Some analyses do not total 100% due to volatilisation and loss of iodine.

A systematic microprobe analysis survey was undertaken on some individual crystals in the series to determine whether compositional zoning is present. Zoning of up to 2.19 mol.% Cu was detected within the same miersite crystals. Marshite and iodargyrite show subtle silver and

TABLE 1. Electron microprobe analysis (wt.%) of 16 specimens of marshite, miersite and iodargyrite

	R19802	R19803	PM5	R24990	M22727	M33171
Cu	33.03	32.93	32.22	32.28	27.40	29.64
Ag	—	0.48	0.07	1.51	8.68	11.86
I	67.36	66.65	67.13	66.20	64.27	58.37
Total	100.40	100.08	100.42	100.02	100.35	99.87
Formula	Cu _{1.00} I	Cu _{0.99} Ag _{0.001} I	Cu _{0.99} Ag _{0.001} I	Cu _{0.97} Ag _{0.03} I	Cu _{0.84} Ag _{0.16} I	Cu _{0.40} Ag _{0.60} I
	M30240-2	R19809	M37670-1	R19808-1	M37670-2	R19808-2
Cu	7.83	5.00	4.67	4.10	3.65	2.46
Ag	35.49	39.99	40.36	43.64	49.53	44.22
I	56.87	54.97	55.69	51.42	45.81	52.47
Total	100.19	99.96	100.72	99.16	98.99	99.15
Formula	Cu _{0.27} Ag _{0.73} I	Cu _{0.18} Ag _{0.82} I	Cu _{0.16} Ag _{0.84} I	Cu _{0.14} Ag _{0.86} I	Cu _{0.11} Ag _{0.89} I	Cu _{0.09} Ag _{0.91} I
	M39191-1	PM6	R19805	PM1		
Cu	—	0.28	—	—		
Ag	46.74	45.78	45.95	45.98		
I	53.76	53.17	52.13	52.64		
Total	100.23	99.23	98.08	98.62		
Formula	Ag _{1.00} I	Cu _{0.01} Ag _{0.99} I	Ag _{1.00} I	Ag _{1.00} I		

R - Australian Geological Survey Organisation specimens

M - National Museum of Victoria specimens

PM - Authors specimens

Marshite R19802 - R24990

Miersite M22727 - M39191-1

Iodargyrite PM6 PM1

Analyst: P. Millsted. (—) element not detected during analysis.

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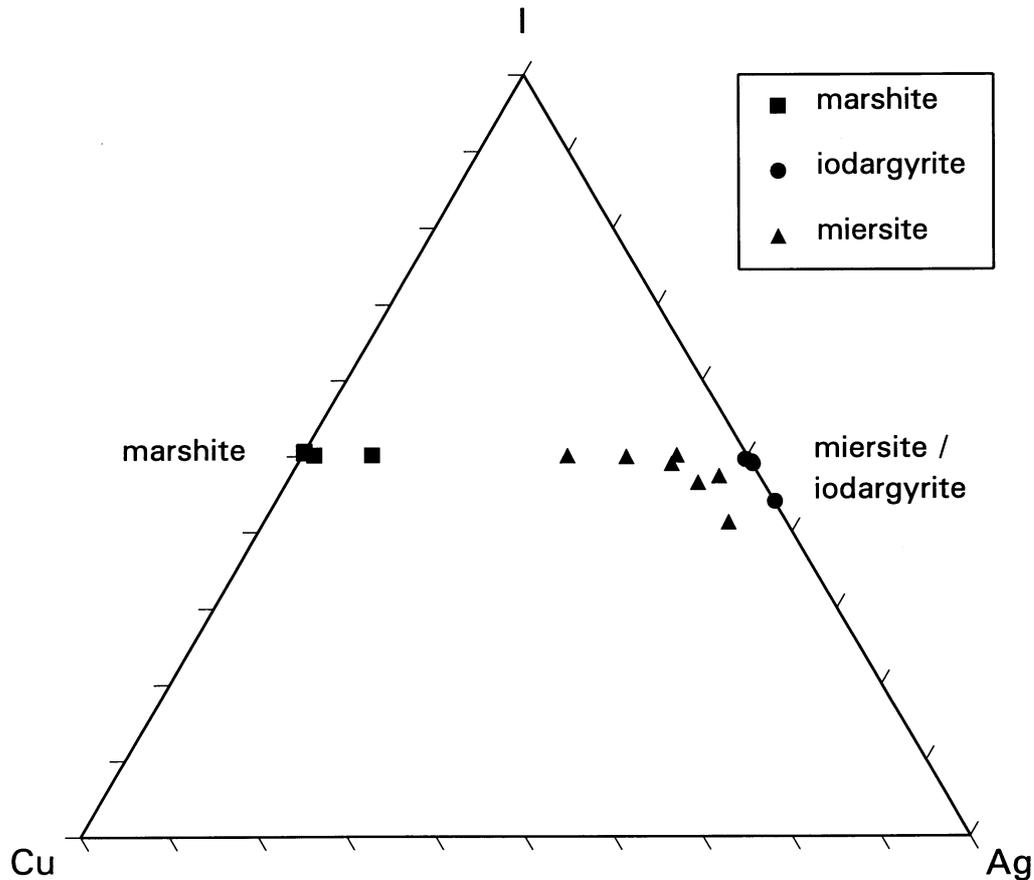


FIG. 1. Compositional data for marshite, miersite and iodargyrite.

copper enrichment respectively toward the edge of the crystal. Composition also varies between crystals of the same hand specimen. Specimen M37670 contains individual miersite crystals ranging from 11.11 mol.% to 15.90 mol.% Cu. On specimen R19808, miersite compositions vary from 8.67 mol.% to 13.75 mol.% over a distance of 6 cm.

Corrected data from X-ray diffraction analysis used to calculate refined cell dimensions of each specimen along with correlating compositional analysis are presented in Table 2. The refined cell dimensions for each specimen are plotted against compositional data in Fig. 2.

Refined cell dimensions calculated from X-ray diffraction lines show the presence of the cubic sphalerite-type miersite-marshite (ccp structure). The unit-cell parameters show an increase from 6.054 Å for marshite to 6.504 Å for miersite.

The composition of crystals with cubic structure ranged from 100 mol.% Cu for sample R19802 (marshite), through a number of intermediate compositions, to 0 mol.% Cu for sample M39191-1, (miersite), therefore a complete solid solution may be inferred. The unit-cell lattice constant parameter changes linearly with Cu: Ag in obeying Vegard's Law, indicating a complete solid-solution.

Discussion

The compositional range of the inferred solid solution series may be influenced by local ratios of Cu^{2+} and Ag^+ and availability of I^- . These ratios may be dependent upon sources of these ions within primary sulphide minerals such as chalcopyrite (CuFeS_2) and tetrahedrite $[(\text{Cu,Fe})_{12}(\text{Sb,As})_4\text{S}_{13}]$ within galena, hosted

TABLE 2. Unit cell dimensions in Ångstroms, () indicates error (fractions), vs composition in mol.% CuI

Sample no	Unit-cell dimension (Å)	Composition mol.% CuI
Marshite-miersite		
R19802	6.0541 (7)	100%
R19803	6.0669 (12)	100%
PM5	6.06	99.9%
R24990	6.0661 (8)	97.3%
M22727	6.1321 (9)	84.3%
M33171	6.332 + (5)	40.5%
M30240-2	6.3832 (8)	27.2%
R19809	6.4178 (11)	17.8%
M37670-1	6.4408 (6)	15.9%
R19808-1.	6.4418 (8)	13.8%
M37670-2	6.4884 (7)	11.1%
R19808-2	6.487 (3)	8.7%
M39191-1	6.5039	0%

Analysts: J. Thompson and P. Millstead

within lead lode No3 lens northern. The average copper and silver content of the lead lodes are 0.14% and 0.12% (Hawkins, 1968).

A variable fluid source resulting from a fluctuating water table, may result in changes in solubility and pH conditions. These changes may be an important control over distribution and precipitation of solid-solution members, especially with respect to zoned crystals.

Plimer (1984, 1994) suggests that changes in climatic conditions of Broken Hill may have changed the chemistry and temperature of groundwater. It can be assumed that the formation of the silver copper halides may be directly related to changes in solution chemistry. Williams (1990) proposes that the Broken Hill silver halides have crystallised at an average temperature of 25°C. Bloch and Moller (1931) in Wilman (1940), observed that specimens of silver iodide precipitated from KI and AgNO₃ solution always yielded mixed cubic and hexagonal forms. Excess silver forms primarily cubic silver iodide while excess iodine, primarily hexagonal silver iodide. Barclay and Jones (1971) found that 1 mol.% copper iodide in the silver iodide structure was sufficient to stabilise the miersite structure even when precipitating from a solution containing excess iodine ions.

The author has identified a rare pure cubic silver end member (miersite), (M39191-1),

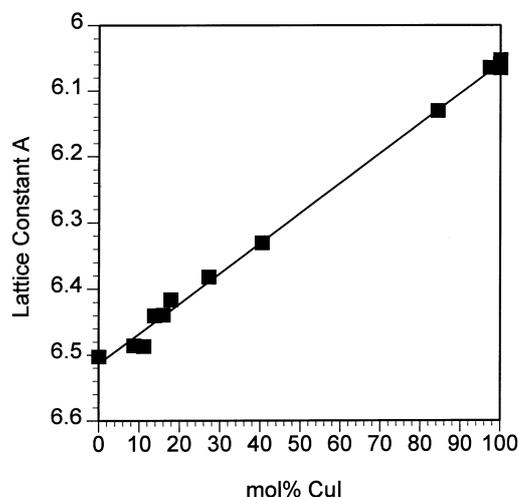


FIG. 2. Unit-cell dimension of complete solid solution $Cu_xAg_{1-x}I$ crystals vs CuI/AgI ratio, Cu mol.%. The solid line is the Vegard Law; Vegard and Scottland (1942).

occurring alongside iodargyrite crystals, both having identical iodine values. Assuming that the minerals crystallized together it would suggest that the solution contained equal amounts of I and Ag. Miersite (M37670-2) of composition 89 mol.% Ag contains a minor hexagonal component which would indicate the limit of precipitating copper rich solutions. Marshite, and copper rich miersite would be precipitated from copper and silver rich solutions, and iodargyrite from iodine rich solutions. Unfortunately the electron microprobe analyses lack the accuracy for a detailed discussion of the iodine stoichiometry, but one would expect that high accuracy determinations would reveal that miersites are depleted in iodine relative to iodargyrite.

Kazunaka and Teruaki (1990) have plotted unit cell dimension of complete solid solution of mixed synthetic crystals, $Cu_xAg_{1-x}I$, vs CuI/AgI ratios, a relationship which obeys Vegard's Law. These experimental observations are consistent with the data recorded by the author for the naturally occurring mixed crystals.

Conclusion

The minerals marshite and miersite analysed in this study indicate an inferred complete solid solution at Broken Hill. The cubic unit cell

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dimensions versus composition of mixed crystals $\text{Cu}_x\text{Ag}_{1-x}\text{I}$, obey Vegard's Law from pure CuI to pure AgI .

Precipitation is controlled by availability and ratio of copper, silver and iodine ions, in conjunction with a fluctuating water table and temperature. The cubic forms of marshite and miersite would precipitate in an environment with excess copper and silver ions. Specimens containing mixed cubic and hexagonal forms would precipitate with equivalent amounts of available silver and iodine ions. The iodargyrite however would require excess iodine ions to precipitate.

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References

- Barclay, E.C. and Jones, J.B. (1971) The Broken Hill Silver Halides, *J. Geol. Soc. Australia*, **18**, 149–57.
- Birch, W.D. Chapman, A. and Pecover, S., (1982) The

- Minerals, in Worner, H.K. and Mitchell, R. (Eds), *Minerals of Broken Hill*. Aust. Mining and Smelting.
- Brightwell, B. and Sephton, P. (1987) Red Emitting centre in $\text{Ag}_{1-x}\text{Cu}_x\text{I}$. *J. Luminescence*, **37**, 133–7.
- Hawkins, B.W. (1968) A quantitative chemical model of the Broken Hill lead-zinc deposit. *Austral. Inst. Mining Metall. – Proceedings*, **227**, 11–15.
- Kazunaka, E. and Teruaki, F. (1990) Structure analysis of metal (I) halides mixed crystal by Cu MAS NMR and X-ray diffraction methods. I. $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ crystal. *Bull. Chem. Soc. Jpn.*, **63**, 1860–4.
- Plimer, I.R. (1984) The mineralogical history of the Broken Hill lode, N.S.W. *Austral. J. Earth Sci.*, **31**, 379–402.
- Plimer, I.R. (1994) *Minerals and rocks of the Broken Hill, White Cliffs and Tibooburra District*. Published for Broken Lifeline Incorporated by Peacock Publications.
- Prior, G.T. (1902) The identity of Kilbrickenite with geochronite and analysis of miersite, marshite and copper pyrites. *Mineral. Mag.*, **13**, 186–90.
- Quercigh, E. (1914) On the true nature of miersite and cupriodargyrite Atti, *Reale Accad. Lincei, Cl. Sci, Sci. Mat. Nature. Rend.*, **23**, 825–33.
- Spencer, L.J. (1898) Miersite a cubic modification of native silver iodide. *Nature*, **57**, 574.
- Spencer, L.J. (1901) Marshite, miersite and iodyrite from Broken Hill, New South Wales. *Mineral. Mag.*, **13**, 38–53.
- Vegard, L. and Scofteland, G. (1942) Röntgenometrische Untersuchungen der aus den Substanzen CuCl , CuBr und CuI gebildeten binären Mischkristallsysteme. *Archiv. Math. Naturv.*, **45**, 163–92.
- Williams, P.A. (1990) *Oxide Zone Geochemistry*. E. Horwood, New York, 286 p.
- Wilman, H. (1940) The structure and orientation of silver halides. *Proc. Phys. Soc.*, **52**, 323–47.

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