

The Tetrahedrite-Freibergite Series, with Reference to the Mount Isa Pb-Zn-Ag Orebody

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Twenty eight electron microprobe analyses of freibergite from the Mount Isa (Queensland) Pb–Zn–Ag stratiform orebody, range in silver content from 18.4 to 42.5 wt. % Ag. These values significantly extend the tetrahedrite-freibergite series. The compositional range based on twenty-one complete analyses is indicated by the formula $(\text{Ag,Cu})_{9.21-11.44}(\text{Fe,Zn})_{1.59-2.31}(\text{Sb,As})_{3.87-4.43}\text{S}_{13.0}$. As far as could be determined, Mount Isa freibergite is homogeneous and no marked compositional changes were detected either across individual grains, or in different grains of the same electron microprobe sample. The linear, atom for atom, replacement of copper by silver reported for lower silver bearing tetrahedrites continues in Mount Isa freibergite. A maximum silver content of about 51 wt. % Ag is predicted. X-ray investigations indicate however that in contrast to the structural expansion with increasing silver content reported for argentian tetrahedrite, Mount Isa freibergite contracts with increase in silver. The extrapolated lattice parameter for the theoretical freibergite $(\text{Ag}_{10}(\text{Fe,Zn})_2\text{Sb}_4\text{S}_{13})$ end member is of the same order as tetrahedrite.

Introduction

As part of a research programme on silver occurrence in the Mount Isa lead-zinc-silver ore and various milling circuits, the composition of the freibergite was investigated by electron microprobe and X-ray diffraction techniques.

The Mount Isa lead-zinc-silver ores of North-Western Queensland, form one of the world's largest stratiform deposits and are well documented in GRONDIJS and SCHOUTEN (1937); BLANCHARD and HALL (1942); BENNETT (1965); and MATHIAS and CLARK (1974). They contain abundant framboidal and euhedral pyrite, pyrrhotite, galena and sphalerite; minor amounts of chalcopyrite, freibergite, marcasite, arsenopyrite; and trace amounts of boulangerite. The host sediments are carbonaceous, quartz, dolomite, K-feldspar, siltstones of Proterozoic age, which dip steeply at about 60–65° west. The deposit has been metamorphosed to Lower

Greenschist facies with accompanying intricate folding and recrystallization of the sulphides. In undeformed parts of the ores, well preserved primary sedimentary structures are still evident. The average silver content of the ores is about 200 ppm, but 2000 ppm Ag is common in the deformed areas where galena has been concentrated, and where freibergite occurs most commonly.

Nomenclature

Few analyses for tetrahedrite correspond to the ideal formula $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. Both iron and zinc are almost invariably present and the formula is better written as $(\text{Cu,Fe,Zn})_{12}\text{Sb}_4\text{S}_{13}$ or $\text{Cu}_{10}(\text{Fe,Zn})_2\text{Sb}_4\text{S}_{13}$. An extensive compositional range is also present.

The structure is extremely elastic in its ability to accept multiple substitutions, and recorded cation substitutions include, notably silver

Table 1. *Electron microprobe analyses and unit cell edges for Mount Isa freibergite*

		Cu	Ag	Fe	Zn	Sb	As
Wt. %	1	23.9	18.4	5.7	0.9	26.7	0.5
At. %		23.4	10.6	6.3	0.9	13.6	0.4
	2	21.3	20.3	5.5	1.0	27.3	0.5
		20.9	11.7	6.1	1.0	13.9	0.4
	3	19.9	22.6	5.5	1.5	26.0	0.3
		19.6	13.1	6.1	1.4	13.5	0.3
	4	19.6	22.7	5.0	0.7	26.8	0.5
		19.6	13.4	5.7	0.7	13.9	0.4
	5	20.4	23.2	5.5	0.8	28.0	n. d.
		20.6	13.9	6.3	0.8	14.9	—
	6	19.8	24.3	5.1	0.8	26.6	0.5
		19.8	14.3	5.8	0.8	13.9	0.4
	7	22.5	24.4	5.3	0.7	26.2	n. d.
		21.8	14.0	5.9	0.7	13.3	—
	8	22.6	24.4	5.1	0.6	26.1	n. d.
		22.8	14.5	5.9	0.6	13.8	—
	9	21.0	24.7	4.7	0.5	25.5	n. d.
		21.5	14.9	5.5	0.5	13.6	—
	10	18.2	25.0	5.6	1.2	26.4	0.7
		18.6	15.0	6.5	1.2	14.1	0.6
	11	17.4	25.6	5.3	2.0	26.4	0.5
		17.5	15.2	6.1	2.0	13.9	0.4
	12	17.7	26.2	5.4	0.9	26.4	0.4
		17.9	15.7	6.2	0.9	14.0	0.3
	13	16.9	29.5	5.3	0.5	24.8	0.6
		17.3	17.8	6.2	0.5	13.2	0.5
	14	15.2	29.5	4.8	1.0	27.1	0.3
		15.5	17.7	5.6	0.9	14.4	0.3
	15	13.5	31.0	4.2	1.1	25.9	1.2
		14.2	19.1	5.1	1.1	14.1	1.1
	16	14.0	32.3	4.5	0.7	26.4	0.3
		14.6	19.7	5.3	0.7	14.3	0.3
	17	13.0	33.0	3.8	1.1	26.5	0.3
		13.7	20.5	4.5	1.1	14.6	0.3
	18	13.3	33.2	5.4	1.0	25.4	0.4
		14.1	20.9	6.5	1.0	14.1	0.4
	19	16.4	33.8	5.7	0.5	24.8	n. d.
		16.7	20.2	6.6	0.5	13.2	—
	20	12.6	33.5	5.3	0.1	26.2	0.6
		13.2	20.6	6.3	0.1	14.3	0.5
	21	12.4	36.0	4.1	0.6	25.1	0.5
		12.9	22.2	4.9	0.6	13.7	0.5

S	Total	ao Å	Formula
23.2	99.3	10.547	(Cu _{6.76} Ag _{3.06}) _{9.82} (Fe _{1.82} Zn _{0.25}) _{2.07} (Sb _{3.94} As _{0.12}) _{4.06} S _{13.00}
44.8	100.0		
23.7	99.6	10.560	(Cu _{5.90} Ag _{3.31}) _{9.21} (Fe _{1.72} Zn _{0.27}) _{1.99} (Sb _{3.94} As _{0.12}) _{4.06} S _{13.00}
46.0	100.0		
23.5	99.3	10.547	(Cu _{5.54} Ag _{3.70}) _{9.24} (Fe _{1.73} Zn _{0.40}) _{2.13} (Sb _{3.80} As _{0.07}) _{3.87} S _{13.00}
46.0	100.0		
23.4	98.7	10.514	(Cu _{5.50} Ag _{3.76}) _{9.26} (Fe _{1.60} Zn _{0.20}) _{1.80} (Sb _{3.90} As _{0.11}) _{4.01} S _{13.00}
46.3	100.0		
21.8	99.7	—	(Cu _{6.14} Ag _{4.13}) _{10.27} (Fe _{1.88} Zn _{0.23}) _{2.11} Sb _{4.43} S _{13.00}
43.5	100.0		
22.8	99.9	10.560	(Cu _{5.70} Ag _{4.12}) _{9.82} (Fe _{1.67} Zn _{0.22}) _{1.89} (Sb _{4.01} As _{0.12}) _{4.13} S _{13.00}
45.0	100.0		
23.1	102.2	—	(Cu _{6.39} Ag _{4.09}) _{10.48} (Fe _{1.72} Zn _{0.20}) _{1.92} Sb _{3.88} S _{13.00}
44.3	100.0		
21.2	100.0	10.560	(Cu _{6.99} Ag _{4.45}) _{11.44} (Fe _{1.80} Zn _{0.18}) _{1.98} Sb _{4.21} S _{13.00}
42.4	100.0		
21.8	98.2	—	(Cu _{6.33} Ag _{4.39}) _{10.72} (Fe _{1.62} Zn _{0.14}) _{1.76} Sb _{4.00} S _{13.00}
44.0	100.0		
21.8	98.9	10.548	(Cu _{5.50} Ag _{4.43}) _{9.93} (Fe _{1.92} Zn _{0.35}) _{2.27} (Sb _{4.17} As _{0.18}) _{4.35} S _{13.00}
44.0	100.0		
22.5	99.7	10.554	(Cu _{5.05} Ag _{4.40}) _{9.45} (Fe _{1.75} Zn _{0.56}) _{2.31} (Sb _{4.01} As _{0.12}) _{4.13} S _{13.00}
44.9	100.0		
22.3	99.3	10.540	(Cu _{5.17} Ag _{4.54}) _{9.71} (Fe _{1.79} Zn _{0.26}) _{2.05} (Sb _{4.04} As _{0.09}) _{4.13} S _{13.00}
45.0	100.0		
21.9	99.5	10.514	(Cu _{5.07} Ag _{5.22}) _{10.29} (Fe _{1.80} Zn _{0.15}) _{1.95} (Sb _{3.87} As _{0.15}) _{4.02} S _{13.00}
44.5	100.0		
22.6	100.5	10.474	(Cu _{4.42} Ag _{5.05}) _{9.47} (Fe _{1.60} Zn _{0.26}) _{1.86} (Sb _{4.11} As _{0.09}) _{4.20} S _{13.00}
45.6	100.0		
21.9	98.8	10.514	(Cu _{4.05} Ag _{5.45}) _{9.50} (Fe _{1.45} Zn _{0.31}) _{1.76} (Sb _{4.04} As _{0.30}) _{4.34} S _{13.00}
45.3	100.0		
21.9	100.1	10.487	(Cu _{4.21} Ag _{5.68}) _{9.89} (Fe _{1.53} Zn _{0.20}) _{1.73} (Sb _{4.12} As _{0.09}) _{4.21} S _{13.00}
45.1	100.0		
21.7	99.4	10.500	(Cu _{3.94} Ag _{5.89}) _{9.83} (Fe _{1.30} Zn _{0.32}) _{1.62} (Sb _{4.19} As _{0.08}) _{4.27} S _{13.00}
45.3	100.0		
20.4	99.1	10.489	(Cu _{4.26} Ag _{6.32}) _{10.58} (Fe _{1.97} Zn _{0.3}) _{2.27} (Sb _{4.26} As _{0.12}) _{4.38} S _{13.00}
43.0	100.0		
21.3	102.5	—	(Cu _{5.05} Ag _{6.11}) _{11.16} (Fe _{2.01} Zn _{0.15}) _{2.16} Sb _{3.99} S _{13.00}
42.8	100.0		
21.7	100.0	10.500	(Cu _{3.81} Ag _{5.95}) _{9.76} (Fe _{1.82} Zn _{0.03}) _{1.85} (Sb _{4.13} As _{0.14}) _{4.27} S _{13.00}
45.0	100.0		
21.8	100.5	10.474	(Cu _{3.72} Ag _{6.37}) _{10.09} (Fe _{1.41} Zn _{0.18}) _{1.59} (Sb _{3.95} As _{0.13}) _{4.08} S _{13.00}
54.2	100.0		

(freibergite) as well as mercury, lead, nickel and cobalt. In addition arsenic, bismuth and tellurium are known substituents for antimony.

Despite the importance of argentian tetrahedrite-freibergite as a major ore mineral of silver, copper and antimony, it has never been defined, nor has the synthetic system $(\text{Cu}-\text{Ag})_{12}\text{Sb}_4\text{S}_{13}$ been investigated. The term freibergite has been loosely applied to tetrahedrites with varying silver contents.

This study shows that at about 20 wt. % Ag the tetrahedrite-freibergite series undergoes a structural change, or a convergence of two separate series. In either case the value of about 20 wt. % Ag provides a useful division, and here the terms argentian tetrahedrite, and freibergite are restricted to tetrahedrite like phases containing less than, and greater than 20 wt. % Ag.

Occurrence

Freibergite at Mount Isa generally occurs as small, shapeless grains ranging in size from less than $10\mu\text{m}$ to about $200\mu\text{m}$, but averaging about $20-30\mu\text{m}$. It is invariably included within galena and often located near grain contacts with sphalerite, pyrrhotite, pyrite, chalcopyrite or gangue. In the ores, it rarely exceeds about 0.5 vol. %. In reflected light its colour varies from a green/grey to bronze/grey and no anomalous anisotropy or internal reflection was observed.

Techniques

Electron Microprobe Data

Numerous high grade lead ore samples and laboratory flotation test products were selected for electron microprobe analysis to determine the elemental composition and range of the freibergite, as well as the variation within individual grains. From a preliminary examination of the silver content of the freibergite in a number of samples, twenty one were selected for complete analysis (Table 1). These were carried out on two different parts of the same grain in each sample for all the elements detected. Owing to severe sample damage by a fully focussed beam a defocussed beam, $20\mu\text{m}$ in diameter, was used. The beam was generated by an accelerating voltage of 20 kv, which

gave a specimen current of 0.1 micro-amperes. The electron beam was reduced for the analysis of small grains, and for the determination of compositional variations within individual grains.

The standards used in the quantitative analyses were pure metals for all the elements, except sulphur and antimony, where pyrite and stibnite were used respectively. All the probe data obtained, were corrected for mass absorption, atomic number and secondary fluorescence.

Analyses for silver and copper only, were also carried out on a variety of other miscellaneous ore and mill preparations and six of the higher silver values are listed in Table 2.

Table 2. *Miscellaneous electron microprobe analyses for Mount Isa freibergite*

	1	2	3	4	5	6
Wt. % Cu	9.0	7.4	9.2	10.0	8.6	5.9
Ag	37.2	37.6	38.9	40.0	41.4	42.5

Since point analyses were not possible using a focussed beam, compositional variations within individual grains were more difficult to establish. Scanning with a focussed beam on different parts of a single grain, however, detected no marked compositional variations, nor did analyses for silver and copper on different grains within the same ore sample.

One rare occurrence of tetrahedrite, which does not contribute significantly to the total silver content of the ores, is the coarse, secondary tetrahedrite found in transgressive veins with massive quartz and/or chalcopyrite. Three analyses of this type (Table 3) are significant because of their very low silver content which contrasts to the stratiform type.

Together with published data, the relationship between copper and silver is illustrated in Fig. 1. The published data was obtained from PRIOR and SPENCER (1899); KRETSCHMER (1911); PALACHE *et al.* (1944). SPRINGER (1969) and those authors mentioned separately under X-ray diffraction data.

X-ray Diffraction Data

The X-ray diffraction investigation of the Mount Isa freibergite proved difficult because of small grain size. Since its occurrence with galena is ubiquitous it was decided to use the galena as an internal standard. This assumed no significant variation from the normal cell size for galena,

Table 3. *Electron microprobe analyses and unit cell edges for Mount Isa tetrahedrite*

		Cu	Ag	Fe	Zn	Sb	As	S	Total	ao Å
Wt. %	1	37.8	0.4	3.7	3.9	26.7	1.7	25.5	99.7	10.3611
At. %		33.8	0.2	3.8	3.4	12.5	1.3	45.0	100.0	
	2	37.2	0.5	3.7	3.5	28.8	0.4	25.5	99.6	10.3810
		33.6	0.3	3.8	3.1	13.5	0.3	45.4	100.0	
	3	37.6	2.9	3.4	3.2	29.3	n. d.	25.5	101.9	10.3940
		33.5	1.5	3.4	2.7	13.7	—	45.2	100.0	
	1	(Cu _{9.71} Ag _{0.06}) _{9.77} (Fe _{1.08} Zn _{0.97}) _{2.05} (Sb _{3.58} As _{0.37}) _{3.95} S _{13.00}								
	2	(Cu _{9.58} Ag _{0.07}) _{9.65} (Fe _{1.08} Zn _{0.87}) _{1.95} (Sb _{3.86} As _{0.09}) _{3.95} S _{13.00}								
	3	(Cu _{9.63} Ag _{0.43}) _{10.06} (Fe _{0.98} Zn _{0.78}) _{1.76} Sb _{3.94} S _{13.00}								

which proved to be the case, after an accurate cell size determination.

Freibergite grains in polished section were encircled with a diamond scribe, carefully prised out together with a particle of associated galena, and a ball mount prepared using gum solution. The preparation was mounted on a brush hair and aligned in a 114.6 mm diameter Gandolfi camera. An exposure of 1 hour using CoK α , iron filtered radiation rated at 30 kv and 40 ma was satisfactory. It was not always possible to X-ray the same grain which was analysed by the electron microprobe, and another grain in the same sample was often used. This was considered a valid technique as only small variations of silver content of different freibergite grains within the same ore sample were observed. Except for the low silver bearing vein tetrahedrite and two of the stratiform freibergites, where adequate material was available, the back reflection region was poorly resolved. The position of the d(226) spacing was therefore chosen to determine the relationship between lattice and composition with the subsequent limitations of using only one d spacing for cell size calculation.

The variation of cell size with silver content is illustrated in Fig. 2, together with published values from MACHATSCHKI (1928), STAPLES and WARREN (1946), BERNARD (1962), TIMOFEYEVSKIY (1967), TRDLIČKA (1967), PETRUK (1971), SHIMADA and HIROWATARI (1972), and KALBSKOPF (1972). Published analyses with greater than about 3 wt. % As were rejected as substitution of As for Sb (grading towards tennantite) causes a significant decrease in cell size.

Discussion

The complete structure analysis of tetrahedrite was carried out by WUENSCH (1963, 1964). It belongs to the $I\bar{4}3m$ space group with a cell parameter of 10.3908(6)Å. Copper occurs in

both mono and divalent states. The first type is tetrahedrally co-ordinated with four sulphur atoms. The second is triangularly co-ordinated with three sulphur atoms in unusual planar groups such that the copper atoms show a highly anisotropic thermal motion. This is not unexpected for an atom in planar co-ordination, but the triangular co-ordination of the divalent copper is rare for B sub-group metals and appears to be unique to copper sulphides (BERRY 1954; BUERGER and WUENSCH 1963) and CuAgS (FRUEH 1955).

STAPLES and WARREN (1946), state that silver may substitute for copper in the tetrahedrite structure up to 25% or more. This is despite the difficulties in energetic properties imposed by the significant difference in the tetrahedral covalent radii, and the atomic radii of silver and copper.

The atom for atom substitution of silver for copper (Fig. 1), is continuous, and does not reflect a break in the series as that illustrated in Fig. 2.

The systematic increase in cell size with increase in silver content, apparent from earlier work, does not continue for the freibergites from Mount Isa (Fig. 2). In fact, beginning at about 12 At. % Ag (20 wt. % Ag), the lattice contracts in a regular manner with further increase in silver content. This maximum occurs when approximately one-third of the copper sites have been replaced by silver in (Cu,Ag)₁₀(Fe,Zn)₂Sb₄S₁₃.

This second trend is tentatively recognised in the previously published data for the very highest silver values, and both trends are only roughly linear, as would be expected of a

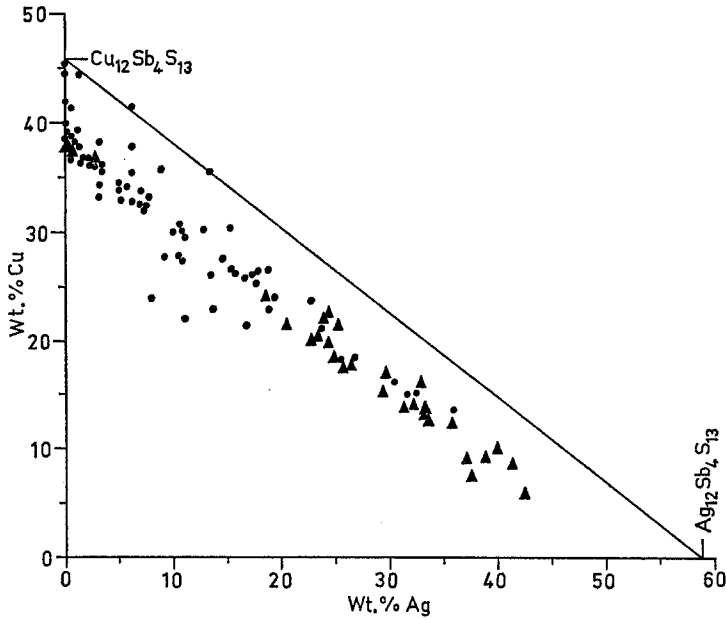


Fig. 1. Variation of silver with copper content.
 Legend: ▲ Mount Isa freibergite and tetrahedrite;
 ● Published data

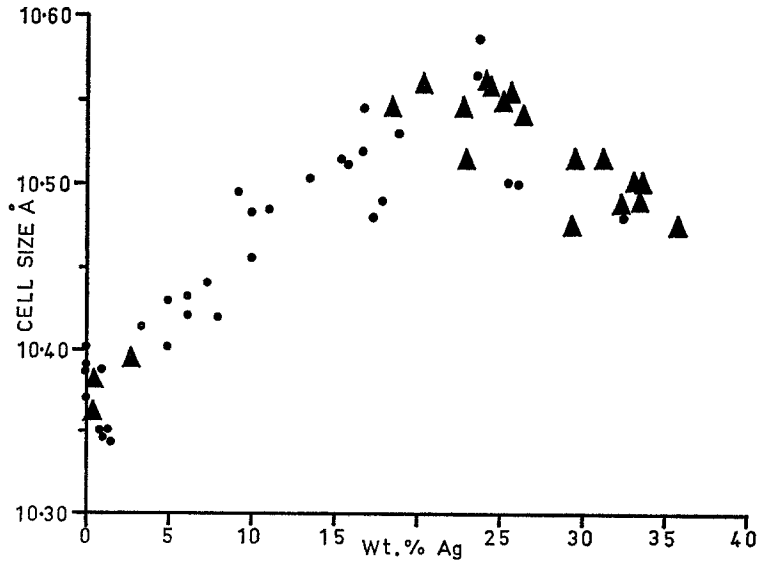


Fig. 2. Variation of cell size with silver content.
 Legend: ▲ Mount Isa freibergite and tetrahedrite;
 ● Published data

structure accepting multiple substitutions, and showing an extensive compositional field.

These two trends may represent the substitution of the two different valency states of copper by silver, but bearing in mind that a charge balance on the structure must still be maintained.

KALBSKOPF (1972) has shown that silver, in freibergite substitutes preferentially for the triangularly co-ordinated copper and not the tetrahedrally co-ordinated form.

Since however the silver ion is larger than the copper atom the second trend, showing a progressive decrease in cell size, is unusual, but by no means unique. The substitution of iron for zinc in the sphalerite lattice results in a marked increase in cell size despite atoms and ions of iron being smaller than atoms and ions of zinc. KULLERUD (1953) explains this in terms of the overall, more ionic character, of the Fe—S bonds than the Zn—S ones, resulting in a net increase in interatomic distance. A comparable situation may exist with the Cu—S and Ag—S bonds shown by the Mount Isa freibergite.

TAKÉUCHI and SADANAGA (1969), in their classification of the sulphosalts based on the use of the principal quantum numbers for the valence shells, distinguish four areas which group together species having a common structural scheme. It is worth noting that those sulphosalts containing copper in large amounts and characterized by linked CuS_4 tetrahedra or by a linkage of CuS_4 and SbS_3 , fall in a different area to those species containing a high silver content and characterised by the bonds peculiar to silver atoms.

It is proposed that the two structural series of argentine tetrahedrite and freibergite either represent different forms produced by varying conditions of formation, or is an inversion due to a different packing required by the energetic properties of the structure, on substitution of silver in amounts greater than about 20 wt. %. In the former context, however, the absence of argentine tetrahedrite or freibergite with a cell size greater than about 10.59 Å and continuing either of the two trends, should be noted.

The extrapolated lattice constant for the theoretical freibergite end member i.e. $\text{Ag}_{10}(\text{Fe}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$ is of the same order as tetrahedrite,

so that some confusion is possible on optical and X-ray data only.

Metallurgical Implications

The high silver content of the Mount Isa stratiform freibergite assumes considerable metallurgical significance when one realizes that only about 0.5 wt. % freibergite is needed to account for the 1000 ppm Ag content of the Mount Isa final lead concentrate. Work done by the author to date indicates that most of the silver present in the ores occurs in freibergite and not as a substituent in galena, with which it occurs most frequently. Silver recovery therefore, depends on the recovery of the freibergite, and this is particularly important since the flotation characteristics of the two minerals are significantly different. The results of this investigation will be published at a later stage.

Conclusions

- The silver content of the Mount Isa freibergite ranges from 18.5 to 42.5 wt. % (Tables 1 and 2). This extends the argentine tetrahedrite series, beyond the previous limit of 32.5 and 36 wt. % Ag reported with, and without, X-ray data respectively (PETRUK 1971).
- The calculated formula, based on the arithmetic average of twenty one complete analyses is $(\text{Ag}_{4.78}\text{Cu}_{5.25})_{10.03}(\text{Fe}_{1.72}\text{Zn}_{0.26})_{1.98}(\text{Sb}_{4.05}\text{As}_{0.09})_{4.14}\text{S}_{13.00}$. Individual analyses show a wide compositional field as indicated by the formula $(\text{Ag}, \text{Cu})_{9.21-11.44}(\text{Fe}, \text{Zn})_{1.59-2.31}(\text{Sb}, \text{As})_{3.87-4.43}\text{S}_{13.00}$. This compares with the range $(\text{Cu}, \text{Ag}, \text{Fe}, \text{Zn})_{9.4-14.2}(\text{Sb}, \text{As})_{2.77-4.8}\text{S}_{13.0}$ for 104 published freibergites, of which the majority (89) are in the range $\text{A}_{11.0-13.6}\text{B}_{3.5-4.6}\text{S}_{13.0}$.
- The silver distribution in single grains is relatively constant as well as the composition of different grains within one ore sample.
- The linear atom for atom substitution of silver for copper continues throughout the series (Fig. 1). The end members, tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and freibergite $\text{Ag}_{12}\text{Sb}_4\text{S}_{13}$, are also plotted, and the consistent discrepancy of the data with this join (averaging 8 wt. %) and accounted for by iron and zinc, should be noted. The predicted maximum silver content of freibergite will be about 51 wt. %.

e) This continuous linear relationship in substitution is not reflected in the variation in cell parameter (Fig. 2). In contrast to the predicted linear expansion with increasing silver content, reported for the lower silver values, the Mount Isa freibergite shows a regular contraction of cell size with increase in silver, above about 20 wt. %. This maximum occurs when about one-third of the total copper sites have been replaced by silver. The cell size of the predicted freibergite end-member will be similar to that of tetrahedrite.

f) This change, at about 20 wt. % Ag, provides a useful dividing line for the terms argentian tetrahedrite and freibergite.

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