

Crystal structure and cation distribution in freibergite and tetrahedrite

R. C. PETERSON AND I. MILLER

Department of Geological Sciences, Queen's University, Kingston, Ontario, Canada K7L 3N6

ABSTRACT. The crystal structure of a freibergite (Ag-tetrahedrite) from Keno Hill, Yukon, Canada, and a tetrahedrite from Turquetil Lake, NWT, Canada, have been refined. The freibergite, $\text{Cu}_{5.84}\text{Ag}_{4.22}\text{Fe}_{1.59}\text{Zn}_{0.43}\text{Sb}_{4.10}\text{As}_{0.13}\text{S}_{13}$, $a = 10.610(2)$ Å, and the tetrahedrite, $\text{Cu}_{10.24}\text{Fe}_{1.03}\text{Zn}_{0.97}\text{Ag}_{0.05}\text{Sb}_{3.66}\text{As}_{0.28}\text{S}_{13}$, $a = 10.364(2)$ Å, were both refined in space group $I43m$. The refinements confirm that Ag does occupy the threefold coordinated metal site as first described by Kalbskopf (1972) and that Fe also occupies this site. The structural changes accompanying Ag substitution are described and a model to explain the upper limit of substitution at four atoms of silver for thirteen atoms of sulphur is proposed.

WHILE investigating the extent of solid solution in natural tetrahedrites using microprobe analysis, a freibergite was found to contain 24.25 wt. % Ag which is unusually high for natural material. The specimen is from the Keno Hill-Galena Hill area in the central Yukon, Canada. The deposit is 60 km northwest of Mayo and about 360 km due north of Whitehorse. Since its discovery in 1913 a considerable portion of Canada's Pb-Ag-Cd has been mined from this area. A complete geological description is given by Boyle (1965).

The crystal structure of a tetrahedrite from Turquetil Lake, Northwest Territories, Canada ($61^{\circ} 59' \text{ N.}, 95^{\circ} 59' \text{ W.}$) has also been studied for comparison.

Freibergite has the tetrahedrite structure which was first described by Machatschki (1928) and reappraised by Pauling and Neuman (1934). More recently, several workers have refined various natural and synthetic tetrahedrites (Wuensch, 1964; Wuensch *et al.*, 1966; and Makovicky and Skinner, 1979). For a complete description of the tetrahedrite structure the reader is referred to these papers.

The crystal structure of freibergite had been refined by Kalbskopf (1972) using material containing 13 wt. % Ag. The silver was found to occupy the 12(e) site which is threefold coordinated by sulphur. More recently it has been suggested that Ag may substitute for Cu at the 12(d) site which is tetra-

hedrally coordinated by sulphur (Patrick and Hall, 1983) but Johnson and Burnham (1985) find that the 12(e) site is the most probable location for the Ag based on a series of structure refinements with fixed site occupancies. Riley (1974) noticed unusual behaviour in high-silver freibergites in that, as the Ag content increases, the unit cell edge increases up to a point where four Ag atoms per thirteen S atoms are present. Additional Ag substitution of more than four atoms causes a decrease in the unit cell edge.

The purpose of the present study is to determine where the Ag atoms reside in the structure and to explore possible explanations for the observed change in slope of the cell edge *vs.* Ag content at approximately four atoms of Ag per thirteen atoms of S.

Chemical composition. Wavelength dispersive electron microprobe analyses were obtained on an ARL-SEMQ microprobe using an accelerating voltage of 15 kV and specimen current of 0.10 μA . Synthetic tetrahedrite standards were used for Cu, Fe, Zn, Sb, As, S and synthetic AgBiS_2 for Ag; the X-ray lines Fe- $K\alpha$, Cu- $K\alpha$, Zn- $K\alpha$, Ag- $L\alpha$, Sb- $L\alpha$, As- $L\alpha$, and S- $K\alpha$ were examined. Although Cd has been reported in tetrahedrites from this area (Boyle, 1965) none was detected in this study.

The analyses are listed in Table I. The values represent the average of 60 second counts, on 8 or more points, all within an area about 100 μm across. The data were corrected by a ZAF software package supplied through Tracor Northern Inc.

There has been some doubt concerning the reliability of microprobe analyses of tetrahedrite due to copper ion movement under the electron beam (Lind and Makovicky, 1982). Also, work on the Cu-Sb-S system at low temperatures has revealed an asymmetric solvus with a composition-dependent crest between 373 and 400 K, which exsolves Cu-poor and Cu-rich tetrahedrites that are difficult to distinguish under the microscope (Makovicky and Skinner, 1979). These effects are not expected in natural samples which contain

Table I. Electron microprobe analyses

Atom	Keno Hill, Yukon		Turquetil Lk., N.W.T.	
	wt%	#atoms per formula unit	wt%	#atoms per formula unit
Cu	19.8(1)	5.84	38.8(5)	10.24
Fe	4.73(3)	1.59	3.43(7)	1.03
Zn	1.50(5)	0.43	3.8(2)	0.97
Ag	24.3(3)	4.22	0.3(2)	0.05
Cd	n.d.	--	n.d.	--
		$\Sigma=12.08$		$\Sigma=12.29$
Sb	26.6(5)	4.10	26.6(2)	3.66
As	0.52(8)	.13	1.26(3)	0.28
Te	n.d.	--	n.d.	--
		$\Sigma=4.23$		$\Sigma=3.94$
S	22.2(2)	13.0	24.9(2)	13.00
	99.6		100.0	

#atoms per formula unit is based on 13 sulfur atoms.
n.d., not detected.
Values in parentheses represent the standard deviation of at least 8 measurements on a single grain.

significant Fe and Zn, and were not observed, as can be seen by the low standard deviation of the copper analysis.

X-ray diffraction. The diffracted intensities observed by precession techniques were found to be consistent with space group $I\bar{4}3m$ for both materials. The data were collected using an Enraf-Nonius CAD4 diffractometer. The rate of the $\theta/2\theta$ scans was varied in order to obtain a σ_I/I of 0.02 if possible within a 60 second period. Three standard reflections were measured every two hours and did not vary more than 1% in intensity during the data collection. Corrections for Lorentz, polarization and spherical absorption factors were made to the data which were then averaged. Details of the data collection and least-squares refinement are listed in Table II.

Freibergite structure refinement. Neutral atomic

Table II. Details of the X-ray intensity data collection and least-squares refinement

	Keno Hill, Yukon	Turquetil Lk.
a	10.610(2) Å	10.364(2) Å
sphere radius	0.77 mm ⁻¹	0.83 mm ⁻¹
u	158.32 cm ⁻¹	166.17 cm ⁻¹
radiation	Mo K α	Mo K α
2 θ limit	90°	90°
independent measurements	1419	1334
unique reflections	520	490
averaging agreement (F)	3.3%	2.7%
absorption correction		
max trans.	25.8%	19.7%
min trans.	21.3%	14.5%
Least Squares (Unit Weights)		
reflections with $I > 2\sigma_I$	438	382
# of parameters	20	20
$S = [\sum w(F_o - F_c)^2 / N - p]^{1/2}$	1.41	1.30
$wR = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.027	0.026
$r = [\sum (F_o - F_c)^2 / \sum F_o^2]^{1/2}$	0.053	0.032

scattering curves from table 2.2B International Tables for X-ray Crystallography vol. IV (Cromer and Waber, 1974) and the atomic parameters of Kalbskopf (1972) were used in least-squares refinement program RFINE4 (Finger and Prince, 1975). Initial refinement of atomic positions and isotropic temperature factors, with Cu and Ag assumed to be equally distributed between the tetrahedrally coordinated site Cu(1) and the threefold coordinated site Cu(2), resulted in $R_w = 11.4\%$. Further refinement with anisotropic temperature factors, isotropic extinction and varying the occupancies of Cu(1) and Cu(2), assuming full occupancies and only Cu and Ag in these sites gave $R_w = 2.7\%$. Cu(1) occupancy was 103(3)% Cu while Cu(2) was 37(1)% Cu and 63% Ag. It was not possible to refine three different atomic populations on one crystallographic site, so, to evaluate the possible distribution of iron, Cu(1) was assumed to be occupied by either Cu or Ag, and Cu(2) occupied by either Fe or Ag and each site is fully occupied. The refined occupancies were found to be; Cu(1) 100(3)% Cu, 0% Ag; Cu(2) 72(1)% Ag, 28% Fe. This is in excellent agreement with the chemical analysis (Table I) which predicts 73% silver in the Cu(2) site if Cu(1) contains only Cu. There is no significant difference in agreement for the above two models, but the second is preferred as it more closely agrees with the chemical analysis. Zn was not considered in the site occupancy investigation as X-ray scattering does not allow discrimination of Cu and Zn by least-squares calculation. The atomic coordinates and temperature factors for the model constrained to be consistent with the chemical analysis are given in Table III. The tables containing the observed and calculated structure factors are deposited in the library of the Department of Mineralogy, British Museum (Natural History).

Another possible model for the distribution of Cu, Fe, and Ag in the freibergite structure is to assume that Cu and Fe occupy the Cu(1) site and that Ag and Cu occupy the Cu(2) site. Least-squares refinement using this model resulted in $R_w = 3.3\%$ which is a significantly poorer fit than the above models where iron is assumed to reside at the threefold coordinated Cu(2) site.

Tetrahedrite structure refinement. Starting parameters for the least-squares refinement were taken from Wuensch (1964). Full matrix least-squares refinement of atomic positions, temperature factors and isotropic extinction resulted in an R_w of 2.6%. The atomic coordinates and temperature factors are given in Table III. The observed and calculated structure factors are deposited in the library of the Department of Mineralogy, British Museum (Natural History).

Site occupancies of the metal sites were refined to

Table III. Atomic positions and temperature factors

1			2			3			1			2			3		
S1	X	.1213(2)	.1159(1)	.1152(3)	Cu1	X	1/4	1/4	1/4								
	Y	.1213	.1159	.1152		Y	1/2	1/2	1/2								
	Z	.3683(2)	.3615(2)	.3609(5)		Z	0	0	0								
B11		.0031(1)	.0025(1)	.0030(3)	B11		.0045(2)	.0034(2)	.0028(3)								
B22		.0031	.0025	.0030	B22		.0032(1)	.0027(1)	.0027(2)								
B33		.0026(2)	.0016(1)	.0026(4)	B33		.0032	.0027	.0027(2)								
B12		-.0003(1)	-.0005(1)	-.0008(4)	B12		0	0	0								
B13		.0002(1)	-.0001(7)	-.0001(3)	B13		0	0	0								
B23		.0002	-.0001	-.0001	B23		0	0	0								
S2	X	0	0		Cu2	X	.2167(3)	.2165(2)	.2150(5)								
	Y	0	0			Y	0	0	0								
	Z	0	0			Z	0	0	0								
B		11.5(7)	1.26(9)	1.14	B11		.0087(2)	.0024(1)	.0032(5)								
Sb	X	.2685(1)	.2679(1)	.2682(1)	B22		.0147(2)	.0129(2)	.0130(6)								
	Y	.2685	.2697	.2682	B33		.0147	.0129	.0130								
	Z	.2685	.6679	.2682	B12		0	0	0								
B11		.0032(1)	.0028(1)	.0026(1)	B13		0	0	0								
B22		.0032	.0028	.0026	B23		-.0093(2)	-.0096(2)	-.0094(14)								
B33		.0032	.0028	.0026													
B12		-.0004(1)	-.0004(3)	-.0003(1)													
B13		-.0004	-.0004	-.0003													
B23		-.0004	-.0004	-.0003													

1. Keno Hill, Yukon Territory, Canada.
2. Turquetil Lake, Northwest Territories, Canada.
3. Wuensch (1964).

determine if a significantly better fit could be obtained by distributing the iron on one particular metal site. No significant difference in the model fit was obtained.

Discussion. Several aspects of the freibergite refinement require additional comment. Kalbskopf (1972) suggested that the threefold coordinated Cu(2) site may be positionally disordered between two sites on either side of the coordination plane. This was based on an observed high rms displacement for the Cu atom normal to the plane. The present refinement also found large atomic displacements normal to the plane (Table IV). However, no evidence was found for two discrete cation sites either in the difference Fourier or by a significantly better fit with a split atom position. The rms displacements presented in Table IV indicate that although the apparent thermal motions of the atoms at the Cu(2) site are increasing

with increased Ag content, the degree of anisotropy is decreasing, with the most anisotropy occurring in the tetrahedrite structure which contains no Ag.

Table V compares the bond lengths and angles of the present freibergite data, the refinements of Kalbskopf (1972) and Wuensch (1964), and the Turquetil Lake material. The most obvious difference occurs in the Cu(2)-S(1) distance which increases by 0.155(2) Å on Ag substitution. The Cu(2)-S(2) bond also increases by 0.070(3) Å. This is consistent with the least-squares site refinement which found Ag to occupy the Cu(2) site. The Cu(1)-S(1) bonds on the other hand remain constant with Ag substitution.

Inspection of the change in bond angles with silver substitution (Table V) reveals that the angles within the threefold coordinated Cu site remain nearly constant and the tetrahedral site becomes slightly more regular. The greatest change in angles occurs with respect to the bonds which are formed with S(1). The response to increased Ag substitution in freibergite is, therefore, an increase in metal-sulphur bond lengths at the threefold site combined with polyhedral rotation about S(1) which forms part of the coordination spheres of both metal sites and the Sb site.

Another structural aspect of the substitution of Ag into freibergite is the relationship between the temperature factor of the sulphur at site S(2) and the number of Ag atoms present in the structure. Fig. 1 shows the temperature factor to increase dramatically as a function of the number of silver atoms. The

Table IV. Root-mean-square amplitudes of thermal vibration (Å)

		1	2	3			1	2	3
S1	min	.121	.111	.093	Sb	min	.126	.118	.114
	int	.131	.113	.111		int	.139	.127	.128
	max	.136	.127	.122		max	.139	.127	.128
Cu1	min	.135	.127	.121	Cu2	min	.223	.170	.114
	int	.135	.127	.121		int	.239	.212	.210
	max	.160	.155	.136		max	.332	.299	.310

1. Keno Hill, Yukon Territory, Canada.
2. Kalbskopf (1972).
3. Turquetil Lake, Northwest Territories, Canada.

Table V. Bond lengths and angles

		1	2	3	4
Bond lengths (angstroms)					
S1-Sb	1	2.448(1)	2.435(5)	2.446(7)	2.432(1)
Cu(1)	2	2.340(2)	2.336(4)	2.342(4)	2.332(2)
Cu(2)	1	2.429(2)	2.360(8)	2.27(1)	2.274(2)
S2-Cu(2)	6	2.299(3)	2.278(8)	2.234(5)	2.229(2)
Sb-S1	3	2.448(2)	2.435(5)	2.446(7)	2.432(1)
Cu(1)-S1	4	2.340(2)	2.336(4)	2.342(4)	2.332(2)
Cu(2)-S1	2	2.429(2)	2.360(8)	2.27(1)	2.274(2)
-S2	1	2.299(3)	2.278(8)	2.234(5)	2.229(2)
Inter-atomic angles (degrees)					
S1-Cu2-S1	1	97.1(1)	97.5	96.3(2)	96.4(1)
S1-Cu2-S2	2	131.4(1)	131.3	131.9(2)	131.8(1)
S1-Cu1-S1	2	108.6(1)	108.1	106.5(2)	106.7(1)
	4	109.9(1)	110.2	111.(2)	110.9(1)
S1-Sb-S1	3	98.3(1)	97.2	95.1(1)	95.49(1)
Cu1-S1-Sb		103.7(1)	102.7	100.7(1)	101.0(1)
Cu1-S1-Cu1		106.6(1)	105.3	103.3(1)	103.6(1)
Cu2-S1-Sb		113.0(1)	114.0	115.0(2)	114.7(1)
Cu1-S1-Cu2		114.4(1)	115.2	117.2(1)	117.0(1)

1. Keno Hill, Yukon Territory, Canada

2. Kalbskopf (1972)

3. Wuensch (1964)

4. Turquetil Lake, Northwest Territories, Canada

octahedral coordination sphere of S(2) is formed exclusively by Cu(2) which is the site Ag occupies in the structure. The increased temperature factor may be explained as the result of positional disorder of the S atom. In any one S(2) coordination sphere there will be an average of four Ag atoms. The remaining two coordinating metal sites will be either Cu, Fe or Zn. The longer Ag-S bond will tend to position the S atom off site 2(a) and towards the coordinating copper or iron atoms which form shorter bonds on average. The increases in Cu(2)-S(1) bond lengths (Table V) support this hypothesis. The Cu(2)-S(2) bond length does not increase to the same extent as the Cu(2)-S(1) with Ag substitution, but this apparent difference is not significant if the rms displacement of S(2) is considered to be the result of positional disorder and only appears as thermal motion because the X-ray experiment gives only the average S(2) position in many unit cells. The increased rms displacement of the Cu(2) site may be due to a slight positional disorder at this site as well.

The high apparent thermal motion of S(2) could also be attributed to only partial occupancy of the site. Although some degree of vacancy may exist, the large deficiency required to explain the high thermal parameter is more than that allowed by the chemical analysis.

This structural control of Ag substitution may explain the behaviour described by Riley (1974) where the *a* cell edge of the freibergite increases gradually as more silver is substituted into the

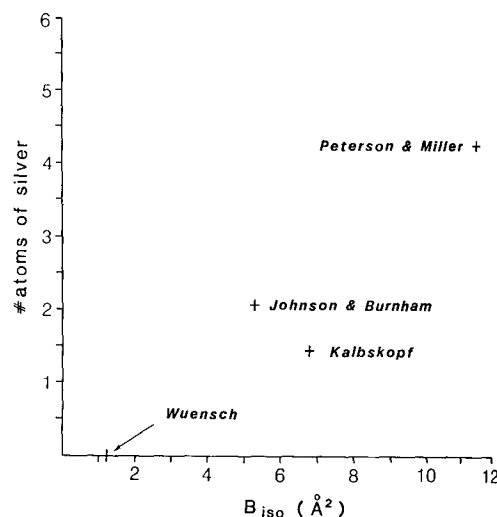


FIG. 1. The number of silver atoms in the formula based on thirteen sulphur atoms vs. the isotropic temperature factor of S(2).

structure until at about four atoms of Ag (for thirteen sulphur), the unit cell edge decreases with additional Ag substitution. This limit may be the result of the requirement that at least two Fe or Cu atoms must be present in the S(2) coordination sphere and any additional Ag substitution must occur elsewhere in the structure. This is also supported by reflectivity measurements presented by Imai and Lee (1980) which show an abrupt change in slope at about four atoms of Ag.

Patrick and Hall (1983) do not find the change in slope of the *a* cell edge vs. the number of Ag atoms present. This may be due to the synthetic crystals having a disordered arrangement of Ag atoms with both metal sites containing Ag. If this is the case, it is not surprising that the cell edge continues to increase over the full range of silver substitution. However, the upper limit of Ag substitution at about seven atoms of Ag for thirteen S may be controlled by the crystal chemical effects described above.

Conclusions. The present structure refinements have supported the conclusion of Kalbskopf (1972) that Ag occupies the threefold coordinated metal site in freibergite. No evidence was found to suggest a split position although the high thermal motion was verified. The least-squares refinement supports the substitution of Fe at this threefold coordinated site as well.

The high correlation of the temperature factor of the octahedrally coordinated S atom with the amount of Ag present in the structure is explained

as positional disorder, which is the result of the longer Ag-S bonds displacing the S atom towards the coordinating Fe and Cu atoms. When averaged over many unit cells this displacement appears as increased thermal motion.

The present structure refinement of freibergite allows evaluation of the details of Ag substitution up to about four atoms of Ag. Whether the apparent decrease of cell edge with increased Ag substitution occurs in natural freibergite, and where the additional Ag is substituted in the structure require detailed crystallographic study of well crystallized natural material with much more than four atoms of Ag.

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