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THE PROPERTIES AND MODULATED STRUCTURE OF POTOSIITE FROM THE CASSIAR DISTRICT, BRITISH COLUMBIA

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ABSTRACT

Potosiite, in its second reported occurrence, was found at the Herb Claim, Turnagain River area, Cassiar District, British Columbia, in galena- and-sphalerite-bearing veins cutting kaolinized granite. It is weakly pleochroic in reflected light (oil immersion) from bluish to yellowish grey and moderately anisotropic, without internal reflections. Cleavage is developed parallel to (001) and (010); $VHN_{50} = 71.7$. The composition, determined by electron-microprobe analysis, is very similar to that of the type material; Ag and In, however, are both present in small amounts. They are thought to be accommodated by the coupled substitution $Ag^+ + In^{3+} = 2Pb^{2+}$. The mean composition yields the structural formula: $[Pb_{48.2}Ag_{0.5}In_{0.7}]_{\Sigma 49.4}Sn_{16.3}Fe_{7.8}Sb_{15.7}S_{114.8}$, based on 204 atoms. The formula based on 25 atoms, with metal:sulfur = 11.14, is: $[Pb_{5.91}Ag_{0.07}In_{0.09}]_{\Sigma 6.07}Sn_{1.99}Fe_{0.95}Sb_{1.93}S_{14.07}$. Cell parameters of two incommensurate subcells are *a* 5.915(10), *b* 5.938(13), *c* 17.239(17) Å, α 91.63(28), β 91.02(25), γ 90.84(21)° for the pseudotetragonal (T-cell) and *a* 6.253(7), *b* 3.734(8), *c* 17.229(19) Å, α 90.80(19), β 91.71(16), γ 90.18(14)° for the pseudohexagonal (H-cell). High-resolution transmission electron-microscopy shows the subcells to be comprised of layers *ca.* 6 and 11 Å thick in the *c* direction. These are thought to correspond to layers of SnS_2-like structure and a double layer of distorted PbS-like structure. Superstructures in the incommensurate *a* and *b* directions are modulated.

Keywords: potosiite, British Columbia, sulfosalt, tin, sulfide, electron diffraction, modulated structure, incommensurate structure, HRTEM.

SOMMAIRE

On vient de trouver de la potosite à Herb Claim, dans la région du fleuve Turnagain, district de Cassiar, en Colombie-Britannique. C'est la deuxième localité connue pour cette espèce minérale, qui s'y présente dans des filons de galène et sphalérite (= blende) recoupant un granite kaolinisé. Elle est faiblement pléochroïque de bleuâtre à gris jaunâtre et modérément anisotrope en lumière réfléchie (avec immersion dans l'huile), sans aucune réflexion interne. Sa composition chimique, déterminée à la microsonde électronique, est très proche de celle de l'échantillon type, malgré la présence d'Ag et In, tous deux en petite quantité, qui peut s'expliquer par la double substitution $Ag^+ + In^{3+} = 2Pb^{2+}$. La composition moyenne correspond à la formule structurale $[Pb_{48.2}Ag_{0.5}In_{0.7}]_{\Sigma 49.4}Sn_{16.3}Fe_{7.8}Sb_{15.7}S_{114.8}$, fondée sur 204 atomes. Pour 25 atomes et un rapport (atomique) métal: soufre = 11.14, on a $[Pb_{5.91}Ag_{0.07}In_{0.09}]_{\Sigma 6.07}Sn_{1.99}Fe_{0.95}Sb_{1.93}S_{14.07}$. Deux mailles incommensurables sont: l'une, pseudotétragonale (T), *a* 5.915(10), *b* 5.938(13), *c* 17.239(17) Å, α 91.63(28), β 91.02(25), γ 90.84(21)°; l'autre, pseudoorthohexagonale (H), *a* 6.253(7), *b* 3.734(8), *c* 17.229(19) Å, α 90.80(19), β 91.71(16), γ 90.18(14)°. Ce sont des mailles sous-multiples, et l'on montre, par microscopie électronique en transmission à haute résolution, qu'elles contiennent des couches d'environ 6 ou 11 Å d'épaisseur dans la direction de *c*. Ces couches correspondraient aux couches de structure analogue à SnS_2 et une couche double d'une structure du type PbS après distorsion. Les surstructures dans les directions incommensurables *a* et *b* sont modulées.

(Traduit par la Rédaction)

Mots-clés: potosite, Colombie-Britannique, sulfosel, étain, sulfure, diffraction électronique, structure modulée, structure incommensurable, microscopie électronique en transmission à haute résolution.

INTRODUCTION

Potosiite, a tin-bearing sulfosalt, was discovered by Wolf *et al.* (1981) in the Andacaba deposit, Potosí district of the Eastern Cordillera of Bolivia. The mineral occurs in felty masses of fine, acicular crystals, associated with quartz and cassiterite, as crusts on layered sulfide ore consisting of sphalerite, semseyite and galena. Potosiite is generally closely associated with galena and is believed to have formed as a result of reactions between galena and Sn–Sb-bearing solutions. The deposits of the area are classical, xenothermal-type veins associated with subvolcanic granitic intrusive bodies (Turneaure 1960); however, the economic geology of the area is complex. The most recent descriptions are those of Wolf (1975a, b), who originally identified potosiite as franckeite; references to many early studies are provided by Turneaure and Wolf.

We found potosiite in ore samples weighing a few hundred grams. The samples (Geological Survey of Canada no. MF-V84-1) were collected by Dr. R. Mulligan from the Herb claim, Turnagain River area, Cassiar District (Liard Mining Division), British Columbia. The claim is located at 58°41′N, 128°10′W, about 8 km northwest of the confluence of the Turnagain and Cassiar rivers. The claim is described as containing galena- and sphalerite-bearing veins in highly kaolinized granite (B.C. Dep. Mines & Petroleum Res. 1970). The veins occur in association with rhyolite and rhyolite porphyry sills and dykes that intrude a granitic stock, an offshoot of the Cassiar intrusive complex (R.G. MacArthur, pers. comm. 1983).

Potosiite in the Herb claim occurs as polycrystalline aggregates up to a few millimetres in diameter in massive galena. Within the same hand specimen, in order of decreasing abundance, are quartz, a new mineral species of stannite-like composition, pyrite, sphalerite and arsenopyrite. None of these, however, is in contact with potosiite.

PHYSICAL AND OPTICAL PROPERTIES

In polished section, potosiite was seen to have a columnar habit with traces of a perfect cleavage parallel to (001). A cleavage parallel to (010) is less perfectly developed. Microhardness, as measured on a Leitz Durimet Hardness Tester, is VHN_{50} 71.7 (mean of three rotated indentations).

In reflected light under oil immersion, potosiite is faintly pleochroic from bluish grey to yellowish grey, without internal reflection. The mineral is moderately anisotropic, with interference colors of bluish grey to greyish pale yellow. Reflectivity data for potosiite were given by Wolf *et al.* (1981).

CHEMICAL DATA

Results of microprobe analyses of potosiite are given in Table 1. Analytical conditions are given in Appendix 1. Our results are very similar to those of Wolf *et al.* (1981); however, atomic proportions of the major components in our analyses show very little variation, and totals are much closer to 100%. Potosiite from the Herb claim also shows significant but minor amounts of In, not reported in the type material. Summation of In and Ag and addition to atomic proportions of Pb yield the most constant atomic proportions of metals. As this procedure also maintains charge balance in the structure, the coupled substitution $Ag^+ + In^{3+} = 2Pb^{2+}$ seems to be important.

Based on the size of the unit cell they determined, Wolf *et al.* (1981) proposed the structural formula $Pb_{48}Sn_{18}Fe_7Sb_{16}S_{115}$, assuming divalent Pb and Fe, trivalent Sb and tetravalent Sn. In order to better fit their analytical data, they suggested the alternate formula $Pb_{48}Sn^{2+}{}_4Sn^{4+}{}_{14}Fe_7Sb_{16}S_{111}$, implying that Sn occurs in two types of co-ordination. In a study that is in progress on the structural relationships among the minerals cylindrite, incaite, franckeite and potosiite, we suggest that some metals occur in more than one type of co-ordination; however, our discussion will be based on considerations of structure and bonding rather than valence.

In a later portion of this paper we further demonstrate that the supercells of potosiite are of variable size, *i.e.,* the structure is modulated. Therefore, whereas the large cell of Wolf *et al.* (1981) is probably correct for the particular area of the grain that they subjected to electron diffraction, the formula they derived is not a general one for the mineral. If we derive a formula based on 204 atoms from our mean composition as in the first one of Wolf *et al.*, we obtain: $[Pb_{48.2}Ag_{0.5}In_{0.7}]_{\Sigma 49.4}Sn_{16.3}Fe_{7.8}Sb_{15.7}S_{114.8}$, very similar to theirs. However, we will propose in a future article (Kissin & Owens, in prep.) that a more general structural formula is based on 25 atoms with a metal:sulfur ratio of 11:14. Recasting our formula on 25 atoms we obtain: $[Pb_{5.91}Ag_{0.07}In_{0.09}]_{\Sigma 6.07}Sn_{1.99}Fe_{0.95}Sb_{1.93}S_{14.07}$ as compared to: $[Pb_{6.00}Ag_{0.04}]_{\Sigma 6.04}Sn_{2.20}Fe_{0.94}Sb_{1.96}S_{13.91}$ for the mean based on the data of Wolf *et al.* (1981). Both formulae closely approach stoichiometric proportions based on 25 atoms and yield metal:sulfur ratios of 11:14. We believe the slight discrepancy to be due to analytical differences.

TABLE 1. CHEMICAL DATA FOR POTOSIITE

Wt.% Element	1	2	3	4	5	6	7	Mean
Pb	55.5	55.3	55.7	54.9	55.3	54.8	55.4	55.3
Ag	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3
Fe	2.7	2.7	2.6	2.2	2.1	2.2	2.3	2.4
Sn	10.4	10.4	10.2	11.1	11.2	11.7	9.8	10.7
Sb*	10.6	10.5	10.5	10.5	10.5	10.5	11.0	10.6
In	0.1	**	**	0.7	0.7	0.7	0.5	0.5
S	20.6	20.1	20.6	20.0	20.1	20.7	21.0	20.4
	100.3	99.4	100.0	99.7	100.2	100.9	100.3	100.2

*Sb$L\alpha$ corrected for slight overlap of Sn$L\beta$. **Indium not determined in early analyses.

CRYSTALLOGRAPHY

Wolf *et al.* (1981) demonstrated that the structure of potosiite is comprised of two incommensurate subcells, one pseudotetragonal (T cell) and one pseudohexagonal (H cell), but both metrically triclinic. The subcells coincide only in the *c* direction, hence must be indexed separately. Makovicky & Hyde (1979) defined incommensurate structures as consisting of two atomic subarrays with differing periodicities. Potosiite is a *layered misfit structure,* in which each alternating layer has its own lattice and in which corresponding intralayer periodicities do not coincide.

In Table 2, X-ray diffraction data from the present study are compared with those of Wolf *et al.* (1981). Our data were obtained on a 57.3-mm Debye–Scherrer camera using Co$K\alpha$ (λ = 1.79021 Å) radiation. Intensities were estimated visually, and cell parameters were refined using a least-squares program written by E.J. Gabe (pers. comm. 1983). Wolf *et al.* (1981) did not specify the conditions under which they obtained their data; however, the two patterns are very similar. Wolf *et al.* did not give calculated *d*-values, and we have supplied them in Table 2. Some of their indices (*e.g.*, 0.0.13) do not seem to be correct. Reflections from the supercell are very weak and can be seen only in electron-diffraction photographs.

Cell parameters of the subcells were determined by Wolf *et al.* (1981) by measurements on electron-diffraction films. Our refinements (Table 2) yielded similar parameters, although α, β and γ of both the T and H cells are different in that α and $\gamma \neq 90°$ and β is smaller. The values determined by our method are, in any event, average values of a large number of discrete cells.

ELECTRON MICROSCOPY

Potosiite was studied in high-resolution transmission-electron microscopy (HRTEM) using a JEOL 200CS electron microscope operated at 200 kV. Specimens were crushed, dispersed in acetone and deposited on a holey carbon grid. The cleavage of potosiite was an advantage in that grains oriented parallel to (001) and (010) were readily obtained.

The interpretation of the images is based on principles established by Cowley & Iijima (1972, 1976). In simplest terms, rows of atoms aligned parallel to the electron beam appear as dark areas, whereas spaces appear light. Although quantitative calculations of images are possible, they are difficult to carry out for complex structures. Using knowledge of related structures, however, it is possible to relate the features of the image to features of the related structures.

In a partial refinement of the structure of cylindrite, Makovicky (1974a, b) showed that the similar incommensurate H- and T-cells in this mineral were constructed of SnS_2-like structures and distorted PbS-like structures, respectively. In cylindrite, however, the thickness of these two layers is 11.7 Å. Makovicky was unable to determine by X-ray crys-

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR POTOSIITE

This study 57.3 mm Gandolfi CoKα						Wolf *et al.* (1981)					
		T-Cell		H-Cell				T-Cell		H-Cell	
d(obs)	I	hkl	d(calc)	hkl	d(calc)	d(obs)	I/I_{100}	hkl	d(calc)	hkl	d(calc)
5.84	VW	003	5.74	003	5.74	5.76	7	003	5.76	003	5.76
4.30	W	004	4.31	004	4.31	4.32	30	004	4.32	004	4.32
3.43	S	005	3.45	005	3.44	3.45	88	005	3.46	005	3.45
3.11	VVW	-	-	111	3.13	-	-	-	-	-	-
2.95	M	200	2.96	-	-	2.936	10	200	2.938	-	-
2.86	VS	006	2.87	006	2.87	2.876	100	006	2.878	006	2.878
2.43	VW	007	2.46	007	2.46	-	-	-	-	-	-
2.23	VVW	205	2.22	-	-	2.226	2	-	-	$\bar{2}13$	2.229
-	-	-	-	-	-	2.188	2	205	2.196	213	2.184
2.09	M	-	-	300	2.08	-	-	-	-	-	-
2.07	W	220	2.08	214	2.06	2.067	10	220 $22\bar{1}$	2.071 2.063	214	2.078
-	-	-	-	-	-	2.051	?	221	2.050	$\bar{3}02$	2.045
1.916	VW	009	1.914	009	1.913	1.920	8	009	1.919	009	1.919
-	-	-	-	-	-	1.835	5	311	1.839	020	1.850
-	-	-	-	-	-	1.818	6	$\bar{1}32$	1.811	310 216	1.817 1.812
1.783	W	-	-	120	1.787	-	-	-	-	-	-
1.709	VW	0.0.10	1.723	0.0.10	1.722	1.731	5	0.0.10	1.727	0.0.10 122	1.717 1.734
1.569	VVW	0.0.11	1.566	0.0.11	1.565	1.568	5	0.0.11	1.570	0.0.11 $\bar{2}22$	1.565 1.561
1.485	VW	$\bar{2}35$	1.485	224	1.487	-	-	-	-	-	-
1.442	VVW	0.0.12	1.436	0.0.12	1.435	1.440	8	0.0.12	1.439	0.0.12	1.439
1.361	VW	-	-	322	1.364	1.360	4	0.0.13	1.328	0.0.13	1.328
1.324	VW	0.0.13	1.325	0.0.13	1.325	.	.	.	.	.	.
1.213	VW	$\bar{2}\bar{4}6$	1.214	$\bar{1}\bar{3}2$	1.211	.	.	.	.	.	.
1.139	VW	$\bar{5}\bar{1}3$	1.139	$\bar{3}\bar{2}9$	1.140	.	.	.	.	.	.
1.047	VW	$\bar{4}\bar{3}8$	1.046	$\bar{2}37$	1.046	.	.	.	.	.	.
1.003	VW	531,444,$\bar{2}57$	1.003	$\bar{5}\bar{2}5$	1.002	.	.	.	.	.	.
0.988	VW	439	0.988	605,1.3.10	0.989	.	.	.	.	.	.
0.937	VW	$\bar{6}06$	0.938	616	0.937	.	.	.	.	.	.

Cell parameters (this study) T-Cell: *a* 5.915(10), *b* 5.938(13), *c* 17.239(17)Å α 91.63(28), β 91.02(25), γ 90.84(21)°. H-Cell: *a* 6.253(7), *b* 3.734(5), *c* 17.229(19)Å α 90.80(19), β 91.71(16), γ 90.18(14)°. (Wolf *et al.* 1981) *a* 5.88, *b* 5.84, *c* 17.28Å, α 90.0(2), β 92.2(2), γ 90.0(2)°. H-Cell: *a* 6.26, *b* 3.70, *c* 17.28Å, α 90.0(2), β 92.2(1) γ 90.0(2)°.

tallography the nature of the 17.3 Å layer seen in incaite, which has subcell dimensions identical to those of potosiite.

Our HRTEM image of (010) in potosiite (Fig. 1) shows that the 17.3 Å layer is composed of a unit approximately 6 Å thick and one approximately 11 Å thick. We propose in greater detail elsewhere (Kissin & Owens, in prep.) that the 11 Å unit is composed of two distorted PbS-like cells.

Makovicky (1976) showed that cylindrite possesses a modulated structure. Supercells formed in incommensurate *a* and *b* subcell directions yield true cells of variable sizes. Figure 2 demonstrates that similar modulations also occur in potosiite. Potosiite thus possesses an incommensurate, modulated structure.

CONCLUSIONS

Our studies on potosiite from the second known occurrence have produced the following results: 1) the proportions of major components in potosiite are essentially constant; however, minor amounts of Ag and In are apparently accommodated by the coupled substitution $Ag^{+} + In^{3+} = 2Pb^{2+}$. 2) The incommensurate subcells of potosiite are a pseudohexagonal H-cell and a pseudotetragonal T-cell. The former is an SnS_2-like structure, whereas the latter is a doubled, distorted PbS-like structure that yields a 17.3 Å *c* dimension. 3) The size of supercells is variable in potosiite, and it possesses a modulated structure. The composition of the mineral determined at a large scale is therefore a function of the statistical distribution of the subcell structures.

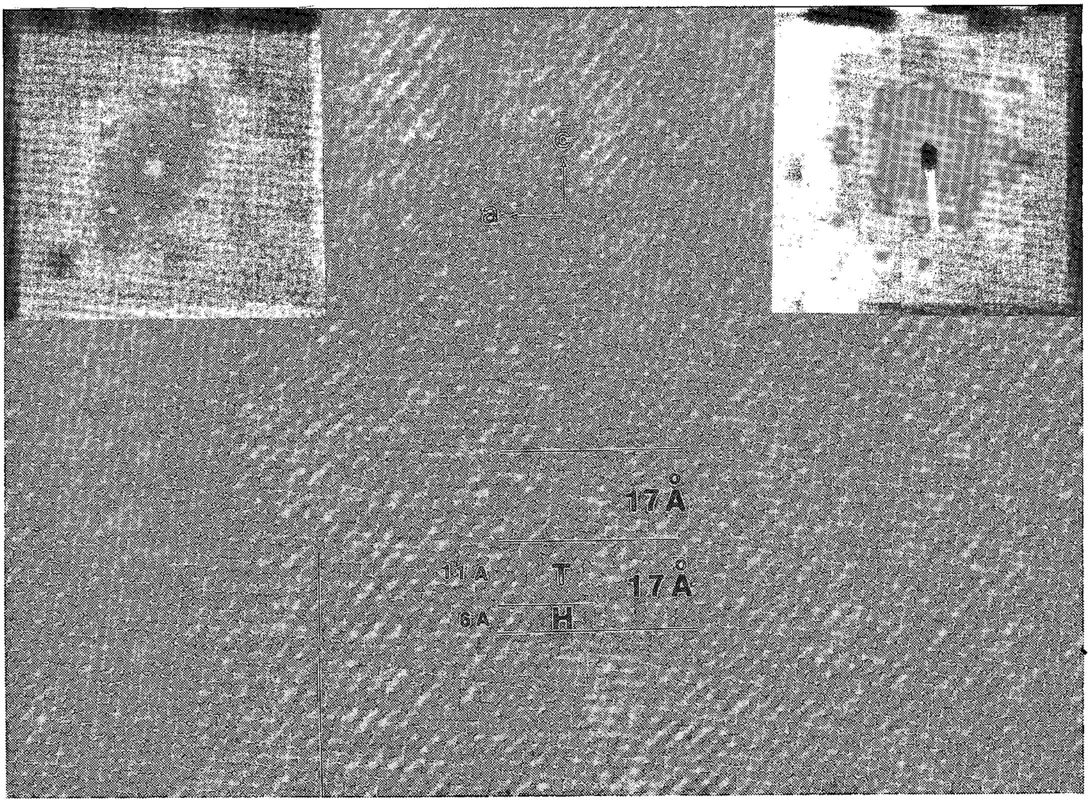

FIG. 1. HRTEM image of (010) of potosiite, illustrating the structure of 17-Å repeats perpendicular to *c*. The 17-Å unit is composed of a 6-Å-thick layer interpreted as the H-cell of SnS_2-like structure and an 11-Å-thick layer interpreted as the thickness of two PbS-like structural units. The vertical line left of centre marks a discontinuity in the *a* direction and is therefore a boundary between two supercells. In the upper right is the electron-diffraction pattern of the area, showing considerable streaking indicative of disorder. Upper left is a laser optical-diffraction pattern from an area of the image *ca.* 360 Å in diameter, revealing a much higher degree of order.

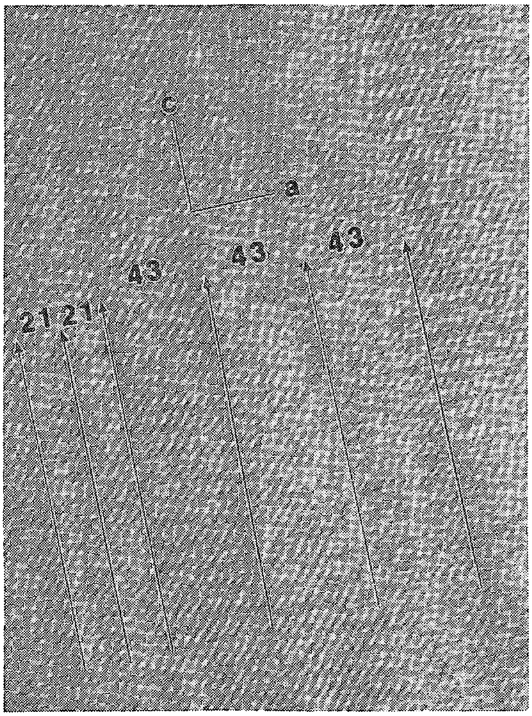

FIG. 2. HRTEM image as in Figure 1, but of lower magnification. Discontinuities perpendicular to *a* reveal that superstructures are of variable sizes, *e.g.*, 43 Å and 21 Å, and that potosiite has a modulated structure.

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APPENDIX 1. ELECTRON-MICROPROBE ANALYSES

Electron-microprobe analyses were carried out on a MAC Model 400 Electronprobe Microanalyzer using wavelength dispersion. The instrument was operated at an accelerating voltage of 20 kV with specimen currents of 0.028–0.030 μA. Counting periods were 10 s, and 10 counts were taken in each analysis. Data were reduced by ERPMAG, the CANMET modification of EMPADR VII (Rucklidge & Gasparrini 1969). A large number of standards were used for the analyses (Table A1) in order to insure that calculated concentrations were not influenced by the particular standard employed. Apart from a sympathetic variation of Pb and Sn, the results show good consistency.

TABLE A1. MICROPROBE STANDARDS USED IN POTOSIITE ANALYSES

Element	Emission Line	Standard	Analysis number 1	2	3	4	5	6	7
Pb	Lα	syn PbS			X				
Pb	Mα	syn PbS	X	X					
Pb	Mα	jamesonite				X			
Pb	Mα	meneghenite					X		X
Pb	Mα	boulangerite						X	
Ag	Lα	silver	X	X	X	X	X	X	X
Fe	Kα	syn Cu_2FeSnS_4	X	X	X			X	
Fe	Kα	jamesonite				X			X
Fe	Kα	syn $Cu_{11}FeSb_4S_{13}$				X			
Sb	Lα	syn $Cu_{11}FeSb_4S_{13}$	X		X				
Sb	Lα	syn Sb_2S_3		X					
Sb	Lα	jamesonite				X			
Sb	Lα	meneghenite					X		X
Sb	Lα	boulangerite						X	
Sn	Lα	Cu_2FeSnS_4	X	X	X	X		X	X
Sn	Lα	syn SnS					X		
In	Lα	syn InAs	X	*	*	X	X	X	X
S	Kα	meneghenite					X		X
S	Kα	boulangerite						X	
S	Kα	jamesonite				X			
S	Kα	syn $AgBiS_2$	X		X				
S	Kα	syn Bi_2S_3		X					

*Indium not determined in these analyses.