Ag- AND Bi-RICH HEYROVSKYITE FROM THE Bi–W–Mo MINERALIZATION AT CASTLEGAR, BRITISH COLUMBIA

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ABSTRACT

The Bi–W–Mo mineralization in a mylonite zone at Castlegar, British Columbia, contains Ag–Bi-rich heyrovskyite, galena with exsolved lamellae of lillianite homologues, scheelite, molybdenite, pyrite and chalcopyrite. The heyrovskyite, with idealized formula $Pb_{2.45}Ag_{1.78}Bi_{3.78}S_9$, contains 28.9 mol. % of the Pb–Bi end-member $Pb_6Bi_2S_9$ and 71.1 mol. % of the Ag–Bi end-member $Pb_{1.0}Ag_{2.5}Bi_{4.5}S_9$. Crystallographic data: orthorhombic, a 13.583(5), b 30.533(10), c 4.129(10) Å, space group $Bbmm$ or $Bb2_1m$. The exsolved lamellae degrees of Ag–Bi substitution similar to that in heyrovskyite and give averaged empirical formulae $Pb_{2.4}Ag_{1.7}Bi_{1.7}S_{8.8}$ and $Pb_{2.7}Ag_{2.2}Bi_{4.2}S_{10.1}$. After exsolution, galena contains 12.1 to 17.3 mol. % $Ag_{0.5}Bi_{0.5}S$, with an average a of 5.914(7) Å. This occurrence shows similarities to the late phase at the Darwin deposit. California and illustrates dimorphism of heyrovskyite with eskimoite.

Keywords: Bi–W–Mo mineralization, heyrovskyite, lillianite homologues, Castlegar, British Columbia.

SOMMAIRE

On trouve, dans la minéralisation Bi–W–Mo de la zone mylonitisée de Castlegar (Colombie-Britannique): heyrovskyite à haute teneur en Ag et Bi, galène à lamelles exsolvées (homologues de lillianite), schéelite, molybdénite, pyrite et chalcopyrite. La heyrovskyite, qui répond à la formule idéalisée $Pb_{2.45}Ag_{1.78}Bi_{3.78}S_9$, contient 28.9 % (mol.) du pôle $Pb_6Bi_2S_9$ et 71.1 % du pôle riche en Ag et Bi, $Pb_{1.0}Ag_{2.5}Bi_{4.5}S_9$. Elle est orthorhombique, a 13.583(5), b 30.533(10), c 4.129(10) Å, groupe spatial $Bbmm$ ou $Bb2_1m$. Les lamelles exsolvées, dans la galène, montrent des degrés d'enrichissement en Ag–Bi semblables à celui de la heyrovskyite et possèdent les compositions moyennes empiriques $Pb_{2.4}Ag_{1.7}Bi_{1.7}S_{8.8}$ et $Pb_{2.7}Ag_{2.2}Bi_{4.2}Si_{10.1}$. Après démixtion, la galène contient de 12.1 à 17.3 % (mol.) de $Ag_{0.5}Bi_{0.5}S$; son paramètre réticulaire moyen a est de 5.914(7) Å. On signale les ressemblances aux stades tardifs de l'évolution du gîte Darwin (Californie) et on note le dimorphisme heyrovskyite–eskimoite.

(Traduit par la Rédaction)

Mots-clés: minéralisation Bi–W–Mo, heyrovskyite, homologues de la lillianite, Castlegar, Colombie-Britannique.

INTRODUCTION

In 1977 the authors obtained from Dr. J.D. Scott (then at CANMET, Ottawa) several ore samples that contained an unspecified lillianite homologue. The samples were collected by the late Dr. R.M. Thompson in 1959, from a small trench just north of Highway 3, at a point 27.2 km west of Castlegar, British Columbia, in what appeared to be a mylonite zone.

MICROSCOPIC DESCRIPTION

The character of the ore suggests that mineralization occurs along a mylonite zone. Sulfides occur disseminated in a heterogeneous, very fine grained mixture of chlorite, calcite, muscovite and quartz that developed along fracture zones in granular quartz. Associated with this mixture are subhedral crystals of scheelite up to several millimetres in size. The sulfides also occur along the boundaries of quartz and scheelite as well as along fractures in scheelite.

Galena and Ag–Bi-rich heyrovskyite represent the principal sulfide phases. They are accompanied by minor amounts of pyrite, chalcopyrite and molybdenite.

The small, polycrystalline galena aggregates display exsolution lamellae of one or more lillianite homologues. These occur as thin, straight lamellae up to 0.02 mm thick on two or three distinct systems of planes of the parent galena grains. They end rather abruptly, commonly on the boundary with the adjacent grain of galena or on a lamella from the other system of planes. Anisotropy effects reveal different orientations of the exsolved mineral in distinct systems of lamellae of the same galena grain; rarely one orientation "overgrows" the other (Fig. 1). Optically the lamellae are indistinguishable from
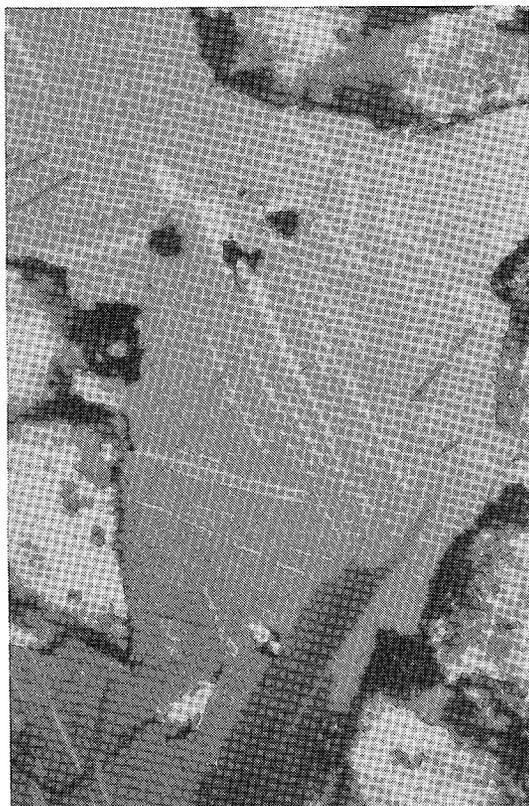
FIG. 1. Aggregate of galena from Castlegar, B.C. with exsolution lamellae up to 0.02 mm thick of a lillianite homologue. Mutual overgrowths of the latter phase, formed on two distinct sets of planes in galena, are shown in the upper part of the photograph. Lamellae of Ag–Bi-rich heyrovskyite may be observed in the lower portions of the figure.

the associated crystals of heyrovskyite. Miller indices of the planes in galena on which the exsolution took place could not be determined.

The Ag- and Bi-rich heyrovskyite occurs primarily as randomly oriented crystals in galena. They range in thickness from 0.05 to 0.5 mm. In other portions of the ore they form aggre-

gates in silicate minerals, with only minor amounts of interstitial galena present.

Subhedral pyrite occurs alone in gangue minerals or is associated with galena and heyrovskyite. Grains of chalcopyrite in the gangue are rare and partly altered. Minor aggregates of very fine grained lamellar molybdenite occur in the fine grained gangue as well. Molybdenite was determined optically, whereas scheelite was confirmed by an X-ray powder diffractogram.

CHEMICAL DATA

Galena and the Pb–Bi–Ag sulfosalts were analyzed on a Hitachi XMA–5B microprobe at the Institute of Mineralogy, University of Copenhagen, using the following analytical wavelengths and standards: Ag $L\alpha$ (pure Ag), Cu $K\alpha$ (pure Cu), Bi $L\alpha$ (pure Bi), Pb $L\alpha$ and S $K\alpha$ (natural galena). No Sb was detected. Springer's (1967) correction program modified after Sweatman & Long (1969) by J. Rønsbo was used. The results of analyses are given in Tables 1 and 2.

The analyses of the large sulfosalt lamellae cluster tightly around the composition line for the homologues of lillianite with the order number N equal to 7 (cf., Makovicky & Karup-Møller 1977a). The N value for the average of all analyses is 6.83. The phase contains 71.1 mol. % of the Ag–Bi-rich end-member and 28.9 mol. % of the Ag-unsubstituted, Pb–Bi end-member with this value of N. Its empirical formula is $Pb_{2.40}Ag_{1.72}Bi_{3.72}S_{8.83}$. If the value of N is idealized to 7, in agreement with the X-ray-diffraction results, and if the same molar percentages of the unsubstituted ($Pb_6Bi_2S_9$) and fully Ag–Bi-substituted ($Pb_{1.0}Ag_{2.5}Bi_{4.5}S_9$) heyrovskyite-type end-members ($N = 7$) are assumed, the idealized formula is $Pb_{2.45}Ag_{1.78}Bi_{3.78}S_9$.

The spread of individual analyses (Fig. 2) is best expressed by the range of observed N values, from 6.47 to 7.29, and by the range of empirical percentages of the substituted (Ag–Bi-rich) end-member, from 69.4 to 72.3 mol. %. Both ranges suggest considerable compositional homogeneity of the phase.

TABLE 1. AVERAGED MICROPROBE DATA FOR SULFOSALTS FROM CASTLEGAR, BRITISH COLUMBIA

Mineral	Ag*	Pb*	Bi*	S*	Total	Ag†	Pb†	Bi†	S†
Heyrovskyite	10.5(3)	28.2(6)	44.1(5)	16.6(4)	99.2	21.9(6)	30.6(6)	47.5(5)	116.5(3)
Exsolved lamellae 1	10.6(3)	28.4(5)	44.6(8)	17.0(3)	100.6	21.8(6)	30.6(6)	47.6(9)	118.2(21)
Exsolved lamellae 2	12.0(6)	27.5(6)	44.2(8)	16.8(3)	100.5	24.5(12)	29.1(7)	46.4(8)	114.8(17)

Standard deviations are indicated in parentheses in terms of the last digit. Cu, Sb not detected.
* Data expressed in weight %. † Data expressed in atomic proportions, ΣMe = 100.

TABLE 2. RESULTS OF MICROPROBE ANALYSES OF GALENA FROM CASTLEGAR

Ag (wt. %)	Bi (wt. %)	Ag (wt. %)	Bi (wt. %)
2.6	5.7	3.7	7.5
2.8	5.9	4.0	7.2
2.9	5.3	4.2	7.6
3.3	6.6		

Although all the thin lamellae of the lillianite homologue exsolved from galena look identical optically, in distinct galena grains they exhibit somewhat different compositions (Fig. 2, Table 1). The main trend of values in the Pb–Ag–Bi compositional plot suggests that their compositional variations cannot be ascribed to the analytical errors arising from the small thickness of lamellae. The choice of analytical points was directly influenced by the size of the lamellae. Two principal averages could be constructed for two galena grains that are situated only several millimetres apart (Fig. 2). The remaining compositional points lie close to or within the two groups. The averages are: (1) Chemically estimated $N = 6.76$; 71.2 mol. % of the Ag–Bi-rich end-member. The resulting formula is $Pb_{2.37}Ag_{1.70}Bi_{3.70}S_{8.76}$. This phase appears to be closely related chemically to the large heyrovskyite crystals. (2) Average $N = 8.11$; 72.9 mol. % of the Ag–Bi-rich end-member, and

the formula is $Pb_{2.66}Ag_{2.23}Bi_{4.23}S_{10.11}$. In the absence of structural data it is not possible to determine whether these data represent a single phase or a mixture of distinct lillianite homologues. The lower and upper limiting values of N for all the analyses of the exsolved lamellae are 6.3 and 9.4, and the range in molar percentages of the substituted end-member is 70.2–74.4%.

For galena, only the Ag and Bi values were measured (Table 2). The calculated compositions do not deviate from the PbS–$AgBiS_2$ tie-line. The lower limit of the compositional range represents 12.14 mol. % $Ag_{0.5}Bi_{0.5}S$, whereas the upper limit is 17.3 mol. % $Ag_{0.5}Bi_{0.5}S$.

X-RAY-DIFFRACTION DATA

Single crystal photographs of a crystal of Ag–Bi-substituted heyrovskyite show that the phase is orthorhombic, with the weighted reciprocal lattice typical of lillianite homologues (Makovicky & Karup-Møller 1977a). Lattice constants determined from Weissenberg and rotation photographs (calibrated with quartz) are a 13.583(5), b 30.533(10), c 4.129(10) Å. No doubling of the 4 Å axis was detectable on overexposed rotation photographs.

From the three space groups allowed by systematic extinctions, $Bbmm$, $Bb2_1m$ and $Bbm2$,
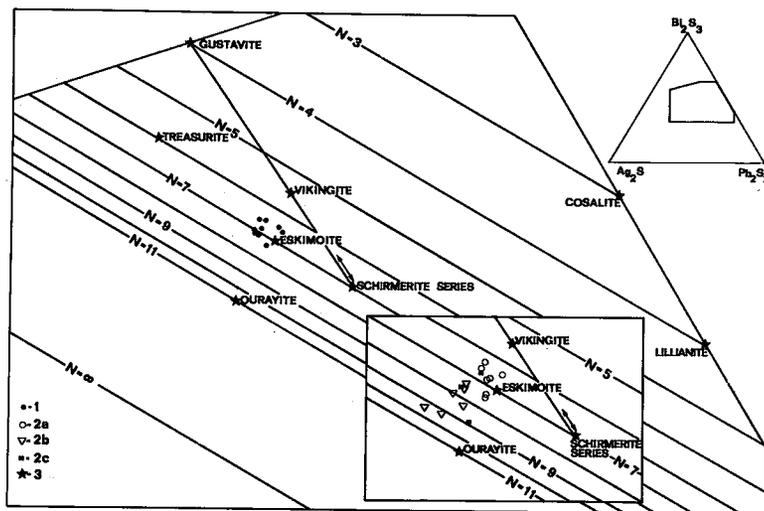
FIG. 2. Portion of the compositional triangle Ag_2S–Bi_2S_3–Pb_2S_2 (i.e., Ag–Bi–Pb), with the compositions of the phases studied plotted on the background of the appropriate N values of the lillianite homologous series. Symbols: 1. Ag–Bi-rich heyrovskyite; 2a, 2b represent the two sets of exsolution lamellae discussed in the text; 2c represents the remaining measurements on the lamellae; 3. the idealized compositions of the known lillianite homologues and cosalite.

the last is excluded because of the identical distribution of X-ray intensities in the $hk0$ and $hk2$ sections of the reciprocal lattice. Weak, diffuse streaks underlie the reciprocal lattice rows parallel to $[010]^*$, indicating a certain amount of disorder in the b direction. The measured lattice parameters compare favorably with those obtained by Erd (in Czamanske & Hall 1975) for Ag–Bi-rich selenian heyrovskyite from Darwin, California. They indicate a significant negative change in the unit-cell parameter b with increasing $(Ag+Bi)$-for-2Pb substitution.

No usable X-ray-diffraction data could be obtained from the sulfosalt lamellae in galena. A powder-diffraction photograph of galena shows very diffuse lines that indicate its compositional inhomogeneity. From nine diffraction lines on a quartz-calibrated Guinier photograph, the average value of a is 5.914(7) Å. Using the data of Craig (1967) and a linear model, these data indicate an average of 7.6 mol. % matildite in solid solution. However, the linearity of change in a with composition was established by Craig (1967) in the reference system mol. % AgBiS₂ vs. mol. % PbS. In the reference system mol. % $Ag_{0.5}Bi_{0.5}S$ vs. mol. % PbS, which is more consequent in terms of crystal chemistry, the average becomes 14.1 mol. % matildite, in very good agreement with microprobe data. No lines of matildite were detected in the powder pattern.

DISCUSSION

The sulfosalts examined occur with two morphologies: either as an obviously primary, hydrothermal phase, often with only minor amounts of interstitial galena, or as systems of thin lamellae, apparently exsolved from the predominant galena component. The mineralogical composition of the ore varies substantially as also do the Pb:Bi:Ag proportions. The presence of exsolution products in galena suggests that the original galena composition was situated on the Bi_2S_3-richer side of the PbS–AgBiS₂ join, at some distance from it. During exsolution, the compositions of galena altered into those on the above join, at variable and generally lower Ag and Bi contents, by exsolving one or more lillianite homologues.

The microprobe composition of Ag–Bi-substituted heyrovskyite, $^{6.83}L_{71.1}$, from the locality studied is close to that of selenian, Ag–Bi-substituted heyrovskyite from Darwin, California (Czamanske & Hall 1975), which can be described as $^{7.53}L_{58.2}$ to $^{6.73}L_{66.2}$ (for notation, see Makovicky & Karup-Møller 1977a). The phase

from Darwin is associated with interstitial selenian galena with up to 4.6 wt. % Ag and 10.8 wt. % Bi, i.e., it is slightly more substituted than the Castlegar material. The late heyrovskyite- and galena-bearing assemblage at Darwin is also distinguished by the presence of homologues with N higher than 7 and with the percentages of the Ag–Bi-rich end-member similar to those in the associated heyrovskyite $(^{8.7-10.2}L_{65.9-66.4})$, i.e., again a situation analogous to our occurrence. There are differences between the two localities: (1) the more extensive role of galena, (2) the higher percentages of Ag–Bi-substitution in the lillianite homologues, and (3) the absence of Se in the mineralization at Castlegar. Furthermore, the microprobe data indicate that the heyrovskyite compositions at Darwin start at rather low percentages of Ag–Bi-substitution ($\sim$ 48 mol. %: Czamanske & Hall 1975; for cross-references, see Karup-Møller 1977).

Comparison of the idealized composition of substituted heyrovskyite ($^{7.7}L$) from the present study ($Pb_{2.45}Ag_{1.78}Bi_{3.78}S_9$) with that of eskimoite ($^{5.9}L$) from Ivigtut, Greenland ($Cu_{0.06}Pb_{2.44-2.60}$ $Ag_{1.78-1.70}Bi_{3.78-3.70}S_9$; data and notation in Makovicky & Karup-Møller 1977a, b) shows that, except for traces of Cu, the two minerals can be considered as *dimorphs* with practically identical compositions. Whether the above minor chemical differences, the extent of structural errors (average chemical N based on the proportion of Ag, Bi and Pb is lower for eskimoite than for heyrovskyite, i.e., between 6.0 and 6.5 as opposed to 6.8), the kinetics of crystallization or different P–T conditions determined the formation of the two homologues remains unknown.

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