

Assemblage of Ag–Pb–Bi±Cu sulfosalts from the Bieber vein, Banská Štiavnica deposit, Slovakia

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Abstract: An interesting assemblage of Ag–Pb–Bi±Cu-sulfosalts was found at the Bieber vein in Banská Štiavnica. Their occurrence is related to the deepest part of the vein, characterized by a high copper content and the predominance of chalcopyrite over other base metals sulfides. Rare members of lillianite series (ourayite, eskimoite and “schirmerite”) are associated with schapbachite and matildite – galena exsolutions. Berryite, arcubisite and acanthite, polybasite and unnamed phase (Cu₃AgPbBi₂S₆) were also rarely found as inclusions in galena. Bi sulfosalts of the lillianite homologous series (ourayite, eskimoite, “schirmerite”) and schapbachite probably formed at temperatures around 350 °C. When the temperature was reduced below 215 °C, the sulfosalts were unstable and below 144 °C the solid solution exsolved to pure AgBiS₂ and PbS.

Key words: Western Carpathians, Štiavnické vrchy Mts., sulfosalts, lillianite homologous series, eskimoite, ourayite, “schirmerite”, matildite-galena exsolution

1. INTRODUCTION

Bismuth sulfosalts from the horst-related epithermal veins in Banská Štiavnica were often the subject of studies by mineralogists. Their occurrence is rare but characteristic for deeper levels of veins, which correspond to the lowermost, so-called copper zone. The ore minerals are represented mostly by chalcopyrite, with smaller amounts of galena and sphalerite. Pyrite may be locally abundant, bornite and scheelite are less common, and Bi sulfosalts are encountered frequently (Koděra et al., 1986). The succession scheme of Kovalenker et al. (1991) assigns this mineralization to the fourth stage and to the seventh paragenetic association, which includes quartz, hematite, sericite, pyrite, predominant chalcopyrite, rare bornite, scheelite, and rare sphalerite. Galena with elevated Ag and Bi was reported in paragenesis with matildite, wittichenite, emplectite, aikinite and an unnamed Ag–Cu–Pb–Bi-sulfosalt. Ag-tetrahedrite, polybasite, naumanite, acanthite and gold are also present. Jeleň (in Chovan et al., 1994) described typical exsolution textures of the unnamed sulfosalts Ag–Bi–Pb–Cu. Bi sulfosalts from the Banská Štiavnica and Hodruša deposit were described by Jeleň & Háber (1995), ourayite and schapbachite were reported by Jeleň & Pršek (2008) and Ďuda & Ozdín (2012). Bi sulfosalts of the cuprobismuthite, pavonite and aikinite series as well as berryite from Rozália mine were described by Jeleň et al. (2012). Bi sulfosalts of matildite, schapbachite and arcubisite as well as Ag sulfosalts of polybasite/pearceite, acanthite, cervelleite, jalpaite, Ag-tetrahedrite/tennantite were described by Chovan et al. (2019) from the horst-related Amália vein in the Rozália mine. In the copper zone at the Rozália vein, a new Bi sulfosalt hodrušite (as “hodrushite”) was described in association with hematite chalcopyrite and galena (Koděra et al., 1970). Two morphological forms of hodrušite in bismuthite-kupčikite aggregates from

deeper parts of the Rozália veins were described. Bi sulfosalts are intensively pushed back by zoned W- and Al- rich hematite (Sejkora et al., 2015).

In this article, we present the results of a study of Ag–Pb–Bi sulfosalts in samples taken from the Bieber vein. The ore samples in this part of the Bieber vein are rich in gold, silver as well as copper, lead and zinc. We present the mineralogical and chemical characteristics of the ore minerals, their spatial association, and the definition of mineral assemblages.

2. GEOLOGICAL SETTINGS

The studied area is hosted by the central zone of the large andesite Miocene Štiavnica stratovolcano, located in the Central Slovakia Volcanic Field on the inner side of the Carpathian arc. The characteristic features of the stratovolcano include an extensive caldera (ca. 20 km in diameter), a late-stage resurgent horst in the caldera centre and an extensive subvolcanic complex (Konečný et al., 1995). The epithermal system of relatively steep dipping post-caldera veins in the central zone of the stratovolcano includes 120 veins, covering an area of almost 100 km² (Lexa et al., 1999). The horst-related mineralization was the most important in terms of metal mining in the past. This mineralization belongs to the extensive system of the NE–SW inclined veins with the average dip of 50–70°. It represents the final stages of hydrothermal activity related to the resurgent horst uplift during the post-caldera evolution of the stratovolcano. The Bieber vein is more than 5 km long and up to 40 m thick and is one of the longest Štiavnica horst-related veins. The upper parts of the vein consist of quartz, hematite, Pb–Zn and Cu sulfides. These parts belong to the precious-metal (Ag–Au) and base-metal (Pb–Zn) paragenetic zones. In the deeper parts, the vein passes into the copper paragenetic zone with dominant chalcopyrite and pyrite

(Koděra, 1963; Koděra et al., 1986). The vein in the central part is hosted by quartz-diorite porphyries and Mesozoic sediments (Gargulák et al., 2010).

3. METHODS

Samples from the Bieber vein on the 12th horizon of the Štiavnica mine, which are accessible from the 14th horizon of the Rozália mine, were taken in the central part between Michal and Alžbeta cross adit by staff of Slovenská Banská Ltd. These samples were analyzed for their Au, Ag, Cu, Pb, Zn content. A total of 13 samples were selected for further mineralogical analysis on 19 polished sections. Reflected (RPL) and transmitted (TPL) polarized light microscopy and photographic documentation was done on Leica and Olympus microscopes at the Comenius University in Bratislava. The chemical composition of sulfides and sulfosalts was determined by wavelength-dispersive spectrometry (WDS) on an electron probe microanalyzer (EPMA) JEOL JXA 8530FE (at Earth Sciences Institute of Slovak Academy of Sciences in Banská Bystrica) with the following conditions: accelerating voltage 20 kV, probe current 15 and 20 nA, beam diameter 2–3 μm , ZAF correction, counting time 20 s on peak, 10 s on background. For WDS analyses the following emission lines and standards were used: Ag(L α) - pure Ag, S(K α) - pyrite, Cu(K α) and Fe(K α) - chalcopyrite, As(L β) - GaAs, Se(L β) - Bi₂Se₃, Cd(L α) and Te (L α) - CdTe, Sb(L α) - stibnite, Hg(M α)

- cinnabar, Bi(L α) - Bi₂S₃, Pb(M α) - galena, Ni(K α) - gersdorffite, Co(K α) - pure Co, Zn (K α) - sphalerite, Mn (K α) - rhodonite, Au (M α) - pure Au.

4. RESULTS

4.1 Ore textures

Samples from the Bieber veins have massive, banded, and brecciated textures. They consist of coarse-grained aggregates of pyrite, chalcopyrite and galena, more rarely sphalerite, which often forms large isolated aggregates (Fig. 1). Overgrowth of fine-grained quartz with hematite is present. The gangue minerals are dominated by quartz; carbonates and K-feldspar are less common. The following assemblages (from the oldest to the youngest) have been identified: 1. *Altered argillitized* rocks, often forming fragments in breccias in base-metal sulfides (BMS), with common pyrite impregnations. 2. Quartz, carbonate, adularia, pyrite, sphalerite, galena, chalcopyrite. This assemblage is typical for the horst-related veins. 3. Quartz-chalcopyrite, pyrite, less sphalerite, galena, rare Ag sulfides mostly in galena (acanthite, polybasite, arcubisite). 4. Fine-grained quartz with finely dispersed hematite, Bi sulfosalts (matildite, schapbachite, ourayite, eskimoite, berryite and other rare minerals), galena, gold, rare chalcopyrite, pyrite. This article describes sulfosalts and gold from the 4th (sulfosalts) assemblage.



Fig. 1. Bieber vein. Altered rock contain galena zone (gray), chalcopyrite – pyrite (yellow) zone and hematite association (brown). Vein thickness is 40 cm.

4.2 Minerals of the sulfosalt assemblage.

Gold

Gold frequently occurs with galena–matildite myrmekites (Fig. 2a). It forms particles in size between 10–70 μm. Only rarely are gold grains smaller than 10 μm. Gold is homogeneous and its composition is showed in Fig. 3. It contains in average (19 points) 0.38 apfu of Ag (25.00 wt %) and 0.61 apfu of Au (73.73 wt %). Content of Te is slightly elevated (up to 0.05 apfu), average content is 0.03 apfu. Selected microprobe analyses of gold from the Bieber vein are given in Tab. 1.

Ag-Pb-Bi-Cu sulfosalts

Druses in quartz are filled with Bi sulfosalts, gold and galena and overgrown with younger hematite. Sulfosalts are more abundant than gold and occur in more samples.

Matildite (AgBiS₂)

Matildite is a common phase and was usually found with galena and sulfosalts of the lillianite homologous series

(Fig. 2a, 2c, 4a, 4b, 4d). It forms typical myrmekitic exsolutions (Fig. 4b). Matildite is a part of myrmekites with galena, often intergrown with gold (Fig. 2a), and replaced by ourayite and eskimoite. Chemical composition of matildite and corresponding chemical formula are given in Tab. 2. Average ($n = 12$) crystal chemical formula based on 4 apfu is $Ag_{0.97}Pb_{0.04}Bi_{0.99}(S_{1.93}Se_{0.01})_{\Sigma 1.94}$. Most

Tab. 1 Chemical composition of gold (wt. %) from the Bieber vein in Banská Štiavnica.

sample	BP-5B	BP-5B	BP-30	BP-5B	BP-5	BP-5	BP-5
Ag	22.45	20.66	27.76	23.53	27.80	27.35	27.10
Fe	0.08	0.23	0.98	0.24	0.26	0.08	0.14
Au	75.33	77.12	69.94	74.23	70.90	70.72	71.13
Cu	0.06	0.02	0.03	0.00	0.02	0.01	0.02
Te	0.04	0.21	0.11	0.35	0.23	0.31	0.28
Bi	0.26	0.22	0.17	0.15	0.05	0.13	0.14
Hg	0.00	0.12	0.00	0.00	0.10	0.00	0.00
S	0.03	0.04	0.08	0.04	0.12	0.10	0.08
total	98.26	98.63	99.08	98.54	99.48	98.70	98.89

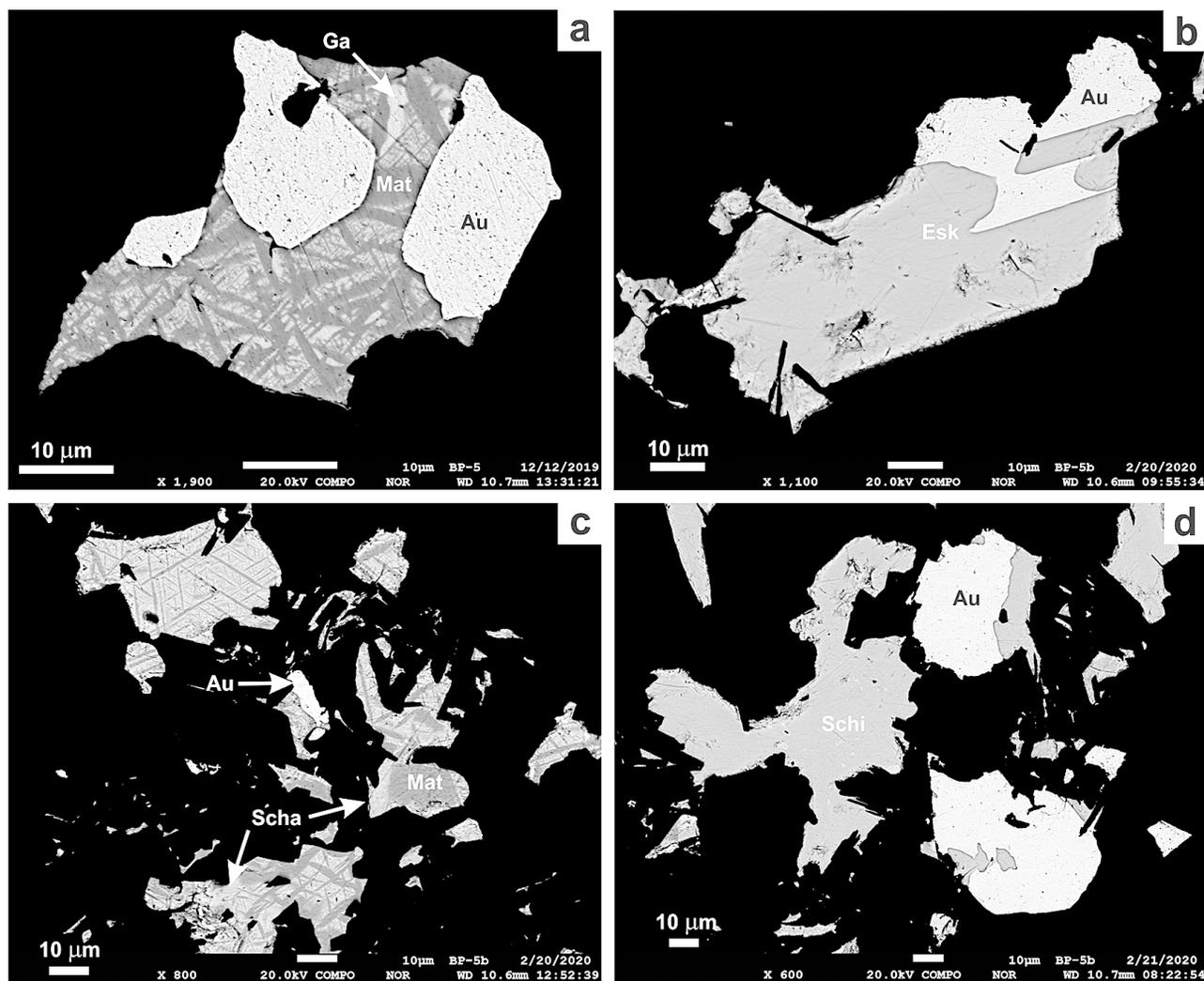


Fig. 2. a – Gold particles (Au) associated with matildite (Mat) and galena (Ga) exsolutions; b – Eskimoite (Esk) grain overgrown with gold (Au); c – Matildite (Mat) – galena exsolutions associated with schapbachite (Scha) and gold (Au); d – Gold grains associated with schirmerite. All pictures are back-scattered images (BSE).

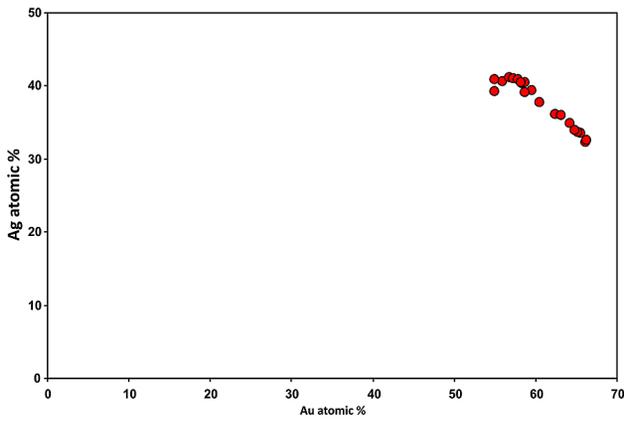


Fig. 3. Chemical composition of gold from the Bieber vein.

of the points lie near the theoretical composition of matildite (Fig. 5). Some analyses show increased Pb content 0.02–0.14 apfu (1.29–7.26 wt. %) what correspond to 1.21–6.72 mol. % PbS, suggesting a limited solid solution between matildite and galena.

Myrmekitic galena has increased content of Ag (up to 0.09

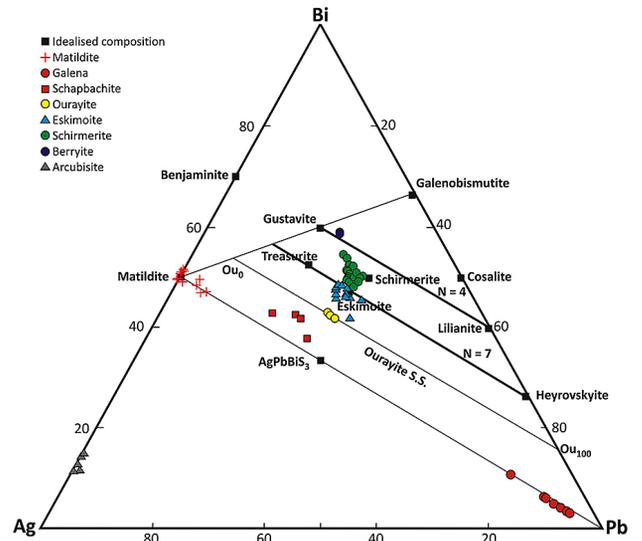


Fig. 5. Microprobe analyses of sulfosalts from the Bieber vein showing the atomic proportions for minerals in the ternary Ag-Pb-Bi system. End-member compositions (filled squares) from Foord et al. (1988).

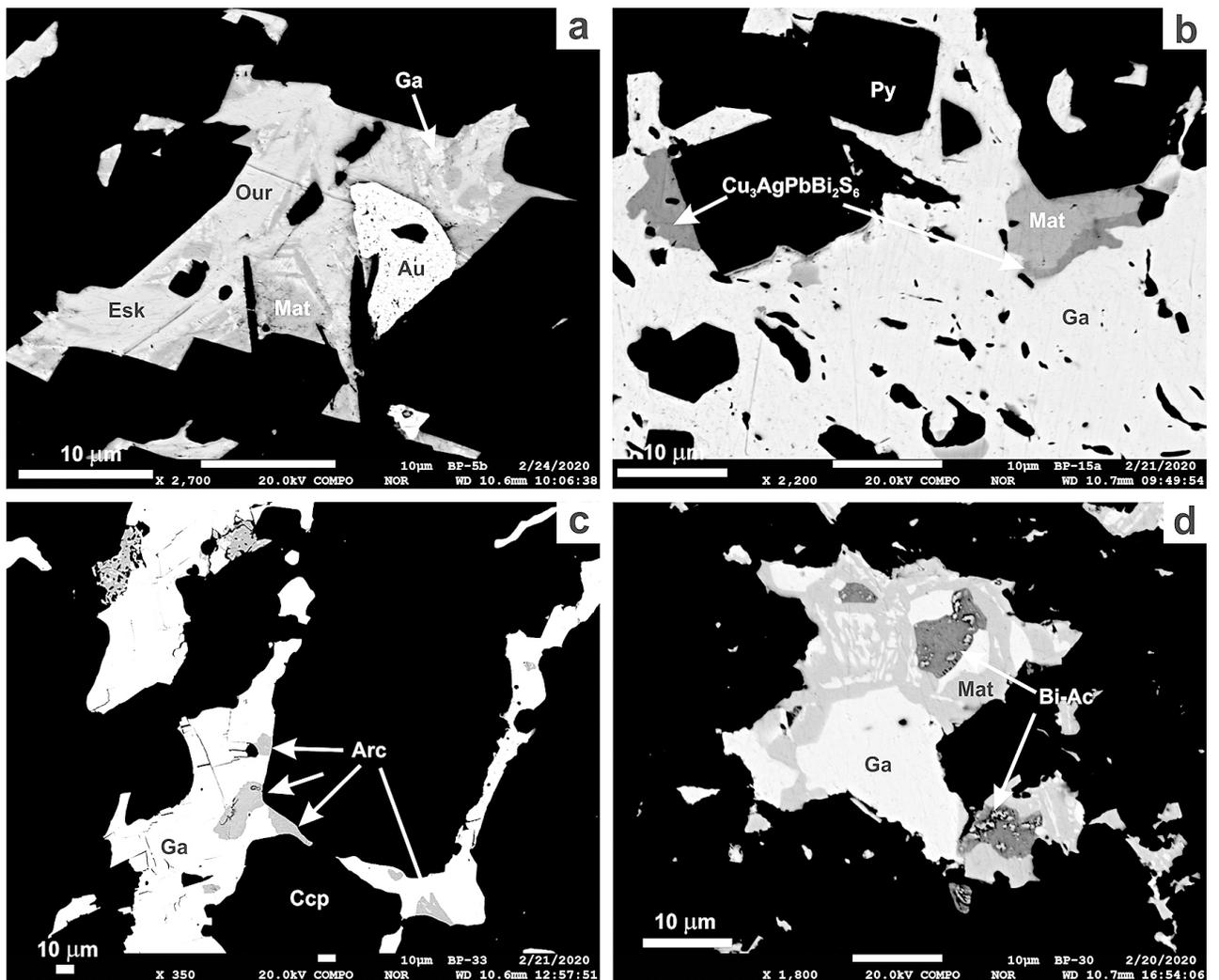


Fig. 4. a – Association of eskimoite (Esk), ourayite (Our), matildite (Mat), galena (Ga) and gold (Au); b – Anhydrous aggregates of unnamed phase $Cu_3AgPbBi_2S_6$ in galena associated with matildite (Mat) and pyrite (Py); c – Anhydrous aggregates of arcubisite (Arc) in galena (Ga); d – Bi-bearing acanthite (Bi-Ac) associated with galena (Ga) and matildite (Mat). All pictures are back-scattered images (BSE).

Tab. 2 Chemical composition of matildite, schapbachite and ourayite from the Bieber vein in Banská Štiavnica (*apfu* – the basis for calculation of empirical formula).

phase	matildite				schapbachite		ourayite	
sample	BP-30	BP-15a	BP-5	BP-5	BP-5	BP-5b	BP-5b	BP-5b
point	2	4	2	1	18	16	18	29
Ag	27.73	28.27	27.80	26.04	26.44	17.84	15.25	12.24
Fe	0.14	0.32	0.39	0.23	0.15	0.98	0.34	0.95
Cu	0.26	0.20	0.01	0.01	0.01	0.38	0.52	0.45
Pb	0.02	0.11	1.30	7.26	6.16	21.64	25.43	30.59
Bi	55.11	53.66	53.15	51.28	50.48	44.69	42.47	41.09
As	0.00	n.a.	0.43	0.52	0.50	0.00	0.00	0.00
S	16.37	16.83	16.17	14.91	15.02	15.62	15.61	15.62
Se	0.78	0.06	0.05	0.00	0.00	0.00	0.60	0.15
Te	0.02	0.25	0.09	0.14	0.18	0.15	0.19	0.17
total	100.42	99.71	99.38	100.40	99.02	101.29	100.24	101.27
apfu	4	4	4	4	4	2	2	25
Ag	0.98	0.99	0.99	0.97	0.98	0.33	0.29	2.92
Fe	0.01	0.02	0.03	0.02	0.01	0.04	0.01	0.44
Cu	0.02	0.01	0.00	0.00	0.00	0.01	0.02	0.18
Pb	0.00	0.00	0.02	0.14	0.12	0.21	0.25	3.80
Bi	1.01	0.97	0.98	0.98	0.97	0.43	0.42	5.06
As	0.00	0.00	0.02	0.03	0.03	0.00	0.00	0.00
S	1.95	1.99	1.95	1.86	1.88	0.98	1.00	12.52
Se	0.04	0.00	0.00	0.00	0.00	0.00	0.02	0.05
Te	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.03

apfu) and Bi (up to 0.11 *apfu*). Representative microprobe analyses of galena are given in Tab. 3. Average ($n = 7$) crystal chemical formula based on 2 *apfu* is $(\text{Pb}_{0.91}\text{Bi}_{0.05}\text{Ag}_{0.05})_{\Sigma 1.01}\text{S}_{0.96}$.

Schapbachite ($\text{Ag}_{0.4}\text{Pb}_{0.2}\text{Bi}_{0.4}\text{S}$)

Schapbachite occurs only rarely as irregular grains up to 10 μm in size (Fig. 2c). It is associated with matildite, galena, ourayite, and eskimoite. Representative microprobe analyses of schapbachite are given in Tab. 2. From the minor elements, only Cu and Fe are slightly elevated. Average ($n = 4$) crystal chemical formula is: $(\text{Ag}_{0.30}\text{Fe}_{0.07}\text{Cu}_{0.01})_{\Sigma 0.38}\text{Pb}_{0.25}\text{Bi}_{0.40}(\text{S}_{0.97}\text{Se}_{0.01})_{\Sigma 0.98}$.

Lillianite homologous series

Ourayite ($\text{Ag}_3\text{Pb}_4\text{Bi}_5\text{S}_{13}$)

Ourayite was identified only rarely, associated with matildite and galena (Fig. 4a). It belongs to the lillianite homeotypic series and represents the homeotypic pair ($^{11,11}\text{L}$, $N_{\text{chem}} = 11$). The calculated order number N_{chem} is 11.27. Representative EPM analyses are given in Tab. 2 and document slightly increased Fe and Cu content. The empirical formula ($n = 3$, based on 25 *apfu*) for ourayite is $(\text{Ag}_{2.94}\text{Fe}_{0.26}\text{Cu}_{0.12})_{\Sigma 3.32}\text{Pb}_{3.82}\text{Bi}_{5.04}(\text{S}_{12.66}\text{Se}_{0.14}\text{Te}_{0.02})_{\Sigma 12.82}$.

Eskimoite ($\text{Ag}_7\text{Pb}_{10}\text{Bi}_{15}\text{S}_{36}$)

Eskimoite occurs together with other lillianite homologues (ourayite and schirmerite) and is associated with matildite, galena and gold. It forms irregular grains up to 100 μm (Fig. 2b). It belongs to (^5L , $N_{\text{chem}} = 7$) dimorph of lillianite homologous

Tab. 3 Chemical composition of galena, arcubisite, Bi-acanthite and unnamed phase from the Bieber vein in Banská Štiavnica.

phase	galena			arcubisite			$\text{Cu}_3\text{AgPbBi}_2\text{S}_6$ Bi-acanthite			
sample	BP-5	BP-30	BP-5b	BP-33	BP-33	BP-30	BP-15a	BP-15a	BP-30	BP-30
point	6	4	14	4	5	5	1	3	11	8
Ag	2.27	1.34	2.45	58.23	57.15	57.27	8.13	8.46	73.55	72.08
Fe	0.09	0.06	0.25	0.21	0.70	0.53	0.64	0.17	0.68	1.61
Cu	0.02	0.12	0.03	7.83	7.25	6.32	17.52	16.71	0.84	0.07
Pb	79.02	84.17	80.42	0.07	0.05	1.76	18.08	19.10	0.05	0.08
Bi	4.89	2.27	5.08	17.11	18.90	14.74	36.94	37.97	9.50	10.81
As	0.00	0.00	0.01	0.14	0.06	1.08	0.00	0.09	0.06	0.15
S	13.41	13.21	13.14	12.69	14.53	14.54	17.28	17.04	12.30	12.68
Se	0.22	0.00	0.00	0.00	0.85	2.52	0.19	0.07	1.73	1.82
Te	0.05	0.03	0.04	4.29	0.92	0.65	0.00	0.00	1.10	1.24
total	99.97	101.20	101.41	100.55	100.40	99.97	98.79	99.60	99.81	100.63
apfu	2	2	2	12.2	12.2	12.2	13	13	3	3
Ag	0.05	0.03	0.05	5.58	5.30	5.27	0.84	0.89	1.75	1.70
Fe	0.00	0.00	0.01	0.04	0.13	0.09	0.13	0.03	0.03	0.07
Cu	0.00	0.00	0.00	1.27	1.14	0.99	3.07	2.97	0.03	0.00
Pb	0.90	0.96	0.91	0.00	0.00	0.08	0.97	1.04	0.00	0.00
Bi	0.06	0.03	0.06	0.85	0.91	0.70	1.97	2.05	0.12	0.13
As	0.00	0.00	0.00	0.02	0.01	0.14	0.00	0.01	0.00	0.00
S	0.98	0.98	0.96	4.09	4.53	4.50	6.00	6.00	0.99	1.00
Se	0.01	0.00	0.00	0.00	0.11	0.32	0.03	0.01	0.06	0.06
Te	0.00	0.00	0.00	0.35	0.07	0.05	0.00	0.00	0.02	0.02

Tab. 4 Chemical composition of eskimoite, schirmerite and berryite from the Bieber vein in Banská Štiavnica.

phase	eskimoite			schirmerite			berryite	
sample	BP-5b	BP-5b	BP-5b	BP-5b	BP-5b	BP-5b	BP-5b	BP-5b
point	30	21	45	25	34	51	49	50
Ag	10.77	10.46	10.29	9.07	9.35	8.86	6.91	7.02
Fe	0.36	0.19	0.09	0.19	0.04	0.09	0.23	0.29
Cu	0.37	0.75	0.31	0.71	0.58	1.10	6.42	6.12
Pb	27.87	27.20	28.05	28.95	28.65	28.20	20.95	21.21
Bi	44.48	44.14	44.62	45.50	44.79	45.04	48.75	49.42
S	16.18	15.97	15.90	15.73	15.84	15.71	16.53	16.52
Se	0.44	0.22	0.51	0.05	0.59	0.42	0.33	0.22
Te	0.10	0.23	0.18	0.10	0.13	0.21	0.16	0.03
total	100.55	99.15	99.95	100.30	99.98	99.67	100.28	100.83
apfu	68	68	68	34	34	34	31	31
Ag	7.00	6.89	6.80	3.01	3.10	2.94	1.94	1.97
Fe	0.45	0.22	0.11	0.12	0.03	0.06	0.12	0.16
Cu	0.40	0.84	0.34	0.39	0.33	0.62	3.05	2.91
Pb	9.43	9.34	9.67	5.01	4.94	4.87	3.06	3.10
Bi	14.92	15.00	15.19	7.81	7.66	7.71	7.06	7.16
S	35.36	35.39	35.33	17.59	17.65	17.54	15.60	15.60
Se	0.39	0.19	0.46	0.02	0.27	0.19	0.13	0.09
Te	0.05	0.13	0.10	0.03	0.04	0.06	0.04	0.01

series. The calculated N_{chem} is 7.61 and the crystal chemical formula ($n = 9$, on 68 *apfu*) is: $(\text{Ag}_{6.90}\text{Fe}_{0.64}\text{Cu}_{0.59})_{\Sigma 8.14}\text{Pb}_{9.99}\text{Bi}_{14.80}(\text{S}_{34.55}\text{Se}_{0.42}\text{Te}_{0.10})_{\Sigma 35.07}$. Representative microprobe analyses are given in Tab. 4.

“Schirmerite” $Ag_3Pb_3Bi_9S_{18}$ to $Ag_3Pb_6Bi_7S_{18}$

Beside matildite, “schirmerite” is the most common sulfosalts. It occurs together with gold, forming irregular grains larger than 100 μm (Fig. 2d). It is classified as lillianite homologue - disordered phase. The calculated N_{chem} is 6.09 and the empirical formula ($n = 22$, based on 34 *apfu*) is $(Ag_{2.79}Cu_{0.42}Fe_{0.33})_{\Sigma 3.54}Pb_{4.93}Bi_{7.71}(S_{17.55}Se_{0.23}Te_{0.05})_{\Sigma 17.83}$. Representative EPM analyses are given in Tab. 4. Reexamination of “schirmerite” (Type 2) from the type locality (Karup-Møller, 1977; Makovicky & Karup-Møller, 1977b) proved it to be a disordered intergrowth of different proportions of slabs ^4L and ^7L , with composition intermediate between gustavite and (Ag, Bi)-rich heyrovskýite. Such a disordered intergrowth is not a valid mineral species. “Schirmerite” (Type 1 - $Ag_4PbBi_4S_9$) is very close to the stable form of schapbachite. In the absence of crystallographic data, it is not possible to conclude whether “schirmerite” is equivalent to schapbachite or corresponds to an ordered dimorph (Moëlo et al., 2008).

Other sulfosalts

Berryite ($Cu_3Ag_2Pb_3Bi_7S_{16}$)

Berryite occurs only rarely. It forms irregular inclusions up to 10 μm and was found intergrown with matildite-galena exsolutions. EPM analyses are given in Tab. 4 and the crystal chemical formula ($n = 2$, based on 31 *apfu*) is: $Cu_{2.98}(Ag_{1.95}Fe_{0.14})_{\Sigma 2.09}Pb_{3.08}Bi_{7.11}(S_{15.60}Se_{0.11}Te_{0.02})_{\Sigma 15.73}$.

Arcubisite ($CuAg_6BiS_4$)

Arcubisite occurs as irregular grains or inclusions intergrown with galena. Their size is up to 60 μm . The empirical formula ($n = 6$, based on 12.2 *apfu*) for arcubisite is $(Cu_{1.17}Fe_{0.08})_{\Sigma 1.25}Ag_{5.53}Bi_{0.79}Pb_{0.02}(S_{4.34}Te_{0.13})_{\Sigma 4.47}$. Representative EPM analyses are given in Tab. 3. Its composition is similar to that reported for arcubisite from Ivigtut, Greenland (Karup-Møller, 1976).

Bi-bearing polybasite $Cu(Ag,Cu)_6Ag_9Sb_2S_{11}$

Just like acanthite and arcubisite, it forms tiny (up to 10 μm) inclusions in galena. Its composition deviates from those usually reported because of elevated Bi content, most likely substituting for Sb and As. Additionally, the Te content is also elevated. The crystal chemical formula (based on 29 *apfu*) is $Cu_{1.00}(Cu_{2.02}Ag_{3.98})_{6.00}Ag_{9.75}(Sb_{1.26}Bi_{0.50}As_{0.18})_{1.94}(S_{9.94}Te_{0.33})_{\Sigma 10.27}$.

Acanthite (Ag_2S)

Acanthite was found associated with chalcopyrite, quartz, and carbonates as aggregates up to 20 μm . The WDS microprobe analyses correspond to the theoretical composition.

Bi-bearing acanthite (Ag,Bi) $_2S$

This type of acanthite forms irregular grains up to 10 μm associated with matildite-galena myrmekites. Its chemical composition is unusual for the Bi content (up to 0.14 *apfu*) and small amounts of Te and Se. The quality of the EPM analyses may have been compromised by the instability of the mineral under the electron beam, where it appears as if it was “boiling” (Fig. 4d). Selected microprobe analyses are given in Tab. 3 and the crystal-chemical formula ($n = 3$, based on 3 *apfu*) is: $Ag_{1.70}Bi_{0.13}(S_{0.98}Se_{0.07}Te_{0.03})_{\Sigma 1.08}$.

Unnamed phase ($Cu_3AgPbBi_2S_6$)

This mineral forms inclusions in galena up to 10 μm and is associated with matildite (Fig. 4b). Selected EPM analyses are given in Tab. 3. Average ($n = 3$) crystal chemical formula fixed on 13 *apfu* can be written as: $Cu_{3.06}Ag_{0.83}Fe_{0.07}Pb_{1.01}Bi_{2.02}S_{6.00}$.

5. DISCUSSION

Lillianite homologues (eskimoite, ourayite, “schirmerite”), schapbachite and berryite are relatively rare in nature. Similar associations of sulfosalts were described from the cryolite deposit in Ivigtut, Greenland (Karup-Møller & Pauly 1979) where matildite appears as fine-grained exsolution in galena, with variable proportions of both minerals. Other sulfosalts at this locality are berryite, gustavite, cosalite, eskimoite, ourayite, and vikingite. In Schwarzwald (Germany), the sequence of mineralization starts with gustavite, ourayite and eskimoite, followed by native bismuth and bismuthinite. These assemblages are overgrown or replaced by a cubic solid solution of the Ag–Bi–Pb sulfosalts schapbachite, which later exsolved into galena and matildite. Subsequently, these aggregates were overgrown by berryite, benjaminite, chalcopyrite, and tennantite (Staude et al., 2010). Similar Pb content (6.25 mol. % PbS) in matildite were reported by Pažout et al. (2017) from the Kutná Hora deposit (Czech Republic). Ertl et al. (1994) published X-ray data of eskimoite and heyrovskýite from “Raurischer Goldberg” in Austria. Ourayite in the decomposed PbS–AgBiS₂ aggregates and aggregates in which the composition of lillianite homologues varies along the vikingite-heyrovskýite line, similar to the “schirmerite”, were described together with rare dantopaite in the Erzweis deposit in Austria (Makovicky et al., 2010). Ford & Shawe (1989) reviewed the occurrence and chemical composition of galena and Pb–Bi–Ag–Cu sulfosalts in Colorado, California, and Pennsylvania. Occurrence of a number of rare minerals, including berryite, and “schirmerite” in association with felbertalite were confirmed in the Funiushan copper skarn deposit, near Nanjing, in eastern China (Gu et al., 2001). Very fine grained (<50 μm) acicular and prismatic Ag–Bi, Ag–Pb–Bi, Pb–Bi sulfosalts including ourayite are present in low sulfidation In-bearing polymetallic vein Pingüino deposit in Patagonia, Argentina. Jovic et al., (2011) assume genetic relation between the polymetallic mineralization and dioritic intrusions that could have been the source of metals and hydrothermal fluids.

Consideration of the available experimental data on lillianite homologues point to crystallization temperatures more than 350 °C (Cook, 1997). Moëlo et al. (1987) have suggested formation of various lillianite homologues at temperatures of 350–400 °C and showed them to be metastable at lower temperatures. Lillianite homologues (eskimoite, ourayite, “schirmerite”) and schapbachite from the Bieber vein are most likely metastable precursors and are breaking down to lower temperature phases - matildite and galena that form the observed myrmekitic textures. These exsolution textures of galena and matildite form upon cooling. Matildite and galena can form contemporaneously, though, when temperature of the precipitating fluid is below 215 °C or can form as a product of decomposition of a

high-temperature PbS- α AgBiS₂ solid solution (Karup-Møller & Pauly, 1979). Heating experiments by Craig (1967) showed that matildite and galena are completely miscible above 215 ± 15 °C and tend to exsolve below this temperature. Van Hook (1960) determined the inversion temperature experimentally to be 195 ± 5 °C. Wang (1999) showed that there are two miscibility gaps, between about 8 and 31 mol. % AgBiS₂, and between 67 mol. % and pure AgBiS₂ at 144 °C. Between these two distinct gaps, phases exist without a structural change from high temperatures down to 144 °C. Below this temperature, the solid solution exsolves to pure AgBiS₂ and PbS that can contain up to 8.5 mol. % AgBiS₂ (Wang 1999).

In a recent study of galena–matildite exsolution assemblages from the epithermal Baia Mare district of Romania, Damian et al. (2008) argued for a temperature of formation between 175 and 230 °C. The temperature of formation of the sulfosalt assemblages corresponds to the conversion of schapbachite (cubic AgBiS₂) to matildite (hexagonal AgBiS₂). The upper limit based on untwinned acanthite is 179 °C, whereas recalculated compositions of schapbachite–galena intergrowths from various localities indicate a formation temperature above 144 °C (Staupe et al., 2010).

6. CONCLUSIONS

– Ag-Pb-Bi-Cu sulfosalts occur in the Bieber vein in Banská Štiavnica in quartz-hematite gangue together with gold, electrum and rare chalcopyrite, pyrite and galena.

– Their occurrence is related to the deepest parts of the vein, characterized by high copper grades and the predominance of chalcopyrite over other base-metal sulfides.

– Bi sulfosalts of the lillianite homologous series (ourayite, eskimoite, “schirmerite”) and schapbachite probably formed at temperatures around 350 °C. When the temperature dropped below 215 °C, the sulfosalts became unstable and exsolved below 144 °C to pure AgBiS₂ and PbS. The presence of Bi-acanthite and an unnamed phase (Cu₃AgPbBi₂S₆) was also detected in this lowest temperature association.

– Other Ag-bearing sulfides (arcubisite, acanthite, polybasite) occur in coarse-grained chalcopyrite, most often as inclusions in galena.

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