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MINERALS OF THE SYSTEM Ag-Cu-Pb-Bi-S FROM THE POLYMETALLIC VEINS OF THE ŠTIAVNICA-HODRUŠA ORE FIELD (SLOVAKIA)

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Abstract: In deep-seated parts of the Štiavnica-Hodruša ore field veins in quartz-hematite-chalcopyrite ores associated with gold the assemblage of bismuth minerals was identified represented by aikinite, emplectite, wittichenite, hodrushite, matildite, vikingite, paděraite, galena solid solution (PbS_{ss}) and a number of mineral phases of the system Ag-Cu-Pb-Bi-S. Presumable examples of the variability of the bismuth minerals - forming processes in the Banská Štiavnica (temperature, deep-seated temperature source, the role of the minor elements in the chemical composition of the natural mineral phases) has been investigated.

Key words: galena, PbS_{ss}, matildite, vikingite, ourayite, hodrushite, Banská Štiavnica.

Introduction

The largest and most famous of the Central Slovak Neovolcanics, the Štiavnica-Hodruša ore field is one of main gold-silver-polymetallic-bearing epithermal areas in the Inner Carpathian volcanic belt. The ore field occurs in the central upwelled part of the vast polygenetic Štiavnica stratovolcano extending 1000 km^2 (Burian et al. 1985).

More than 120 ore veins, majority of them being exploited already, is known in the Štiavnica-Hodruša ore field with main ore deposits in Banská Štiavnica and Hodruša. The veins occur mainly in propylitized pyroxene andesites, diorites and quartz diorite porphyries. The length of main ore veins ranges from about 3 km (the Brenner, Mikuláš, Štefan Vein) to 5 - 7 km (the Bieber, Grüner, Rozália, Terézia Vein), the width from decimeters to several meters and the depth reaches more than 1000 m (Böhmer & Štohl 1971; Burian et al. 1985).

The ores of the Banská Štiavnica deposit belong to the gold -silver-polymetallic epithermal mineralization with lead and zink prevailing over copper. The sulphide concentration varies in veins and their segments from 3 - 5 to 40 - 60 % (with average 5 - 10 %) of total ores (Gazdík et al. 1986). The leading ore minerals are galena, sphalerite, chalcopyrite, pyrite, subordinate - hematite, marcasite, tetrahedrite, polybasite, acanthite, rare - pyrargyrite, proustite, stephanite, pyrhotite, tennantite, bornite, scheelite, gold, *electrum*, and in some veins also antimonite, realgar, cinnabarite, bournonite, plumosite and others. Among the vein minerals prevails quartz (including amethyst, chalcedony and opal), in lesser amounts are present barite, rodonite and various carbonates - calcite, dolomite, kutnahorite, manganocalcite, ankerite, rhodochrosite, oligonite, siderite. Rare are adularia and fluorite.

The first information on bismuth mineralization at the Banská Štiavnica deposit is in the works of Koděra (1965, 1981).

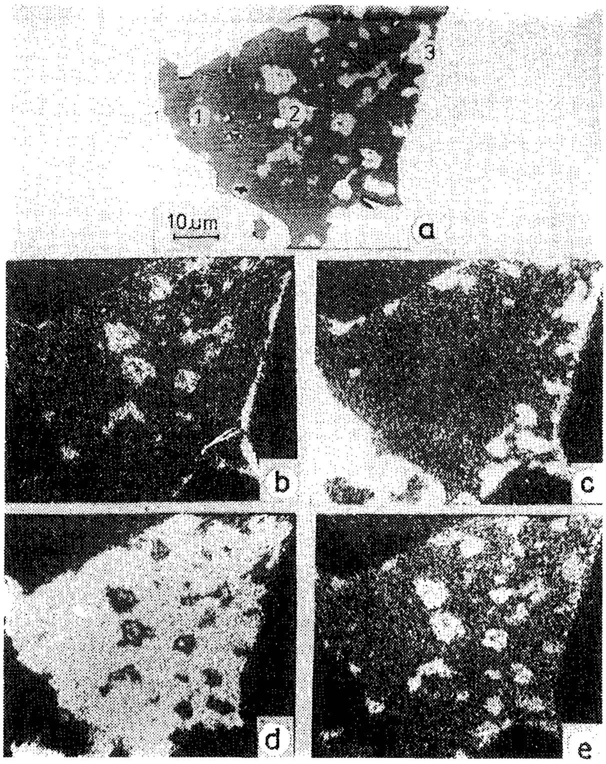

Fig. 1. Photomicrographs of PbS_{ss} - 1, matildite - 2, and wittichenite - 3intergrowths in the centre of quartz in characteristic X-rays: **a** - e^+; **b** - Ag Lα; **c** - Cu Kα; **d** - Pb Lα; **e** - Bi Lα. Sample Bi-55/88-1c.

Table 1: Chemical compositions of the galena matildite series minerals from the Bieber, Bakali and Rozália Veins. The Bieber Vein, IInd deep horizon, samples Bi-55/88, Bi-56/88, Bi-57/88, Bi-hbo-II-4, Bi-hbo-IIa, Sch-23; the Bakali Vein, XIVth deep horizon, sample Ba-19/88; the Rozália Vein , XIVth deep horizon, sample Ro-8.

No	sample	phase	min.	weight %						Total	mol. %		
				Ag	Cu	Pb	Bi	Se	S		Ag_2S	Pb_2S_2	Bi_2S_3
01	Bi-55/88	5	gn	0.00	0.00	85.70	0.76	0.00	13.46	99.92		99.00	1.00
02	Bi-55/88	3a-1	gn	1.34	0.12	81.81	3.50	0.15	13.26	100.18	2.97	93.07	2.96
03	Bi-56/88	1-1	gn	1.41	0.00	82.18	2.85	0.34	13.64	100.42	3.00	94.00	3.00
04	Ba-19/88	2b-3	gn	0.97	0.00	81.95	1.92	0.00	14.16	99.00	2.06	95.88	2.06
05	Ba-19/88	3-1c	gn	1.59	0.00	81.14	3.10	0.00	13.82	99.65	3.03	93.94	3.03
06	Bi-55/88	1d-1	gn	1.04	0.58	81.22	3.49	0.15	13.50	99.98	4.00	92.00	4.00
07	Bi-55/88	1c-1	gn	1.88	0.00	81.12	4.17	0.15	13.58	100.90	4.00	92.00	4.00
08	Bi-55/88	1b-1	gn	2.21	0.19	78.82	4.45	0.20	13.52	99.39	6.05	89.10	5.05
09	Bi-55/88	2b-1	gn	2.80	0.21	77.64	5.55	0.31	13.64	100.15	7.00	87.00	6.00
10	Bi-55/88	2a-5	gn	2.63	0.00	77.47	6.00	0.26	13.60	99.96	6.00	87.00	6.00
11	Bi-55/88	1a	gn	2.90	0.00	77.85	5.67	0.00	13.78	100.20	6.06	87.88	6.06
12	Bi-56/88	2-1	gn	2.32	0.00	75.88	6.77	0.34	13.47	98.78	5.00	87.00	8.00
13	Bi-56/88	3-1	gn	2.32	0.00	77.29	6.41	0.18	13.65	100.05	5.05	87.88	7.07
14	Bi-55/88	2a-1	gn	2.86	0.00	76.10	5.74	0.18	13.50	98.38	7.00	86.00	7.00
15	Sch-23	4b	gn	3.72	0.00	73.89	7.21	0.00	14.17	98.99	8.20	83.60	8.20
16	Bi-hbo-IIa	1-1	gn	4.54	0.00	72.40	9.10	0.25	13.78	100.07	10.00	80.00	10.00
17	Bi-57/88	1		7.17	0.00	60.60	16.97	0.00	13.56	98.30	15.10	66.40	18.50
18	Bi-57/88	2c		9.81	0.00	55.65	18.96	0.00	14.49	98.91	20.30	59.70	20.00
19	Sch-23	1b-5b		16.10	0.48	33.70	34.00	0.00	15.64	99.92	32.40	33.80	33.80
20	Bi-57/88	2b		17.12	0.00	32.93	33.68	0.00	15.40	99.13	33.10	33.10	33.80
21	Bi-56/88	2-2		18.10	0.16	29.83	38.99	0.65	15.57	99.98	35.00	29.60	35.40
22	Bi-56/88	3-2		17.20	0.53	29.85	35.46	0.43	15.32	98.79	34.80	30.00	35.20
23	Sch-23	1b-5a		21.37	0.00	20.33	41.02	0.00	15.83	98.55	40.10	19.90	40.00
24	Bi-57/88	1a		21.73	0.00	18.02	43.55	0.00	15.58	98.88	40.60	17.30	42.10
25	Bi-55/88	2b-2	mat	26.00	0.76	2.60	53.49	1.32	16.30	100.47	48.50	2.50	49.00
26	Bi-55/88	1b-2	mat	27.10	0.45	1.50	53.97	0.58	16.56	100.16	49.50	1.00	49.50
27	Bi-55/88	2a-3	mat	26.50	0.55	1.06	53.50	0.55	16.50	98.66	49.25	1.00	49.75
28	Bi-hbo-II-4	3	mat	25.75	0.74	0.88	55.15	1.27	16.33	100.12	48.25	1.00	50.75
29	Bi-55/88	3a-2	mat	26.80	0.47	0.63	55.27	1.30	16.19	100.66	49.25	0.50	50.25
30	Bi-55/88	1b-2	mat	26.66	0.23	0.51	54.55	0.75	17.00	99.70	49.00	0.50	50.50
31	Bi-hbo-II-4	2	mat	26.87	0.34	0.30	54.43	0.80	16.24	98.98	49.00	0.50	50.50
32	Bi-56/88	1-2	mat	27.87	0.00	0.00	54.42	0.65	16.50	99.94	49.50		50.50
33	Bi-56/88	2-3	mat	28.20	0.00	0.00	54.42	0.33	16.66	99.61	50.25		49.75
34	Bi-57/88	2a	mat	28.62	0.00	0.00	53.85	0.00	17.25	99.72	50.75		49.25
35	Sch-23	4a	mat	27.93	0.00	0.00	54.12	0.00	16.61	98.66	50.00		50.00
35a	Ro-8	4a-2	mat	27.10	1.37	0.00	54.36	0.00	17.23	100.72	50.00		50.00

Phase numbers: 1st is intergrowth number, 2nd is a phase number.

Analyses: 1 - 16 (gn): galena solid solution (PbS_{ss}), 17 - 24: the empirical formulae of unnamed sulfosalts:

17 - $Ag_{0.92}Pb_{4.06}Bi_{1.13}S_{5.88}$
18 - $Ag_{1.01}Pb_{2.98}Bi_{1.00}S_{5.01}$
19 - $Ag_{0.92}Pb_{0.05}Pb_{1.01}Bi_{1.01}S_{3.01}$
20 - $Ag_{0.99}Pb_{0.99}Bi_{1.01}S_{3.01}$
21 - $Ag_{5.88}Cu_{0.09}Pb_{5.05}Bi_{6.03}S_{16.67}Se_{0.28}$
22 - $Ag_{5.62}Cu_{0.29}Pb_{5.08}Bi_{5.98}S_{16.84}Se_{0.17}$
23 - $Ag_{2.00}Pb_{0.99}Bi_{1.99}S_{5.02}$
24 - $Ag_{4.92}Pb_{2.10}Bi_{5.10}S_{11.88}$
25-35a (mat): matildite.

He reports aikinite, rezbanyite (the mineral now discredited), matildite, wittichenite in the so-called "copper paragenetic zone" (Koděra 1963), i.e. in deep-seated veins enriched in chalcopyrite. Also, a new copper-bismuth sulfosalt $Cu_8Bi_{12}S_{22}$ - hodrushite, was identified by Koděra et al. (1970) at the Rozália Vein. Recently, Rojkovičová (in Brlay et al. 1989) reported bismutite and tetradymite in the samples from drillings B-2 and BBR-1 near Banská Belá, and aikinite and wittichenite in drilling B-1 near Horná Roveň (Rojkovičová & Štohl 1993).

A detailed study of mineral composition in the Terézia, Bieber, Špitaler, Rozália and Bakali Vein systems over the entire accessible vertical interval confirmed that the mineral associations containing bismuth sulfosalts, in accord with Koděra's data, occur preferably in deep horizons of both deposits, in the vein parts enriched in copper, gold, silver and often in tungsten (Kalinaj 1992).

However, the composition of the bismuth mineralization proved to be much more complicated than was supposed. X-ray microprobe study has not only confirmed the chemical composition of wittichenite, hodrushite and matildite but revealed the presence of emplectite, galena solid solution (PbS_{ss}), and a new, unnamed, mineral $AgPbBiS_3$. A number of natural phases was found which have not now been identified up to now among the mineral phases of the system Ag-Cu-Pb-Bi-S. Compositions of the phases can be expressed by the following formulae:
$(Cu,Ag)_{7.2}Pb_{1.3}(Bi,Fe)_{11.5}S_{22}$, $AgPb_3BiS_5$, $(Cu,Ag)_4PbBi_2S_6$, $Ag_6Pb_5Bi_6S_{17}$, $Cu_5AgPb_2Bi_4S_{11}$, $Ag_2PbBi_2S_5$, $Cu_2AgPbBiS_4$, $Ag_5PbBi_5S_{12}$, $Ag_5CuPbBi_2S_7$, $AgPb_2Bi_3S_7$, $AgPb_4BiS_6$, $Ag_4Pb_4Bi_6S_{15}$

They represent either new species or new varieties of known minerals. Moreover, matildite and wittichenite, similarly as galena, was found to be characteristic by considerable variations in chemical compositions and to form solid solutions in the system Ag-Cu-Pb-Bi-S.

In this paper we focus our attention to the chemical composition, conditions of occurrence, assemblages of determined minerals, the comparison with Ag-Cu-Pb-Bi-S sulfosalts of other deposits (they are known in two tens of world deposits only) and we speculate about possible causes of the unique diversity of the Štiavnica bismuth mineralization which exceeds the number of known natural and synthetic phases in the system.

Minerals of the galena - matildite series

The chemistry of galena - matildite series minerals and other Ag-Cu-Pb-Bi-S sulfosalts found in the Banská Štiavnica deposit was studied by X-ray microanalyser Camebax at following conditions: accelerating voltage 20 kV, current ≈ 10 nA, analytical lines $L\alpha$ for Ag, Pb, Bi, Sb, $K\alpha$ for Cu, S, Se, Fe. The used standards were: $CuFeS_2$ (Fe), $CuSbS_2$ (Cu,S), PbS (Pb), CdSe (Se) and analytically pure Ag, Bi.

Minerals of the *galena - matildite series* occur in deeper levels of the Bieber Vein, in the copper, gold and silver enriched parts with widespread mineral associations of the IVth, galena - chalcopyrite, mineralization period (Kovalenker et al. 1991). They usually form tight intergrowths containing 3 - 4, or more, minerals of the Ag-Cu-Pb-Bi-S system.

Since the optical properties of these minerals in reflected light are similar to those of galena they can easily be confused with this mineral. A heterogeneous structure can be observed under crossed nicols in the minerals. Even more distinct is the polyphase structure of the intergrowths in absorbed electrons and in the characteristic X-rays in microprobe. In Fig. 1 are shown photomicrographs of a Ag-Bi bearing galena containing inclusions of matildite and the wittichenite rim growing over the galena.

The chemical compositions of the galena - matildite series minerals is given in Tab. 1. Their position in the diagram $(Ag,Cu)_2S$ - Bi_2S_3 - Pb_2S_2 is illustrated in Fig. 2 (the numbers are the same as in Tab. 1). 36 analysed phases show splitting into: the galena solid solution (PbS_{ss}) containing more than 0.5 wt.% of total metals other than lead (Foord & Shawe 1989); matildite and six other distinct natural phases occurring at the join galena - matildite and characteristic by the steadily increasing ratio $AgBiS_2$/PbS from galena to matildite: *$AgPb_4BiS_6$, $AgPb_3BiS_5$, $AgPbBiS_3$, $Ag_6Pb_5Bi_6S_{17}$, $Ag_2PbBi_2S_5$, $Ag_5Pb_2Bi_5S_{12}$.*

Silver and bismuth contents attain 4.54 and 9.1 wt.% respectively in the studied grains of galena solid solution. The ratio Ag(Cu) : Bi is approximately equal 1 : 2 (wt.%), or 1 : 1 (at.%), what is in accord with the "gustavite" type of substitution: $2Pb^{2+} = Bi^{3+} + Ag^+$ in PbS_{ss} typical for both the lillianite - gustavite ($Pb_3Bi_2S_6$ - $AgPbBi_3S_6$) series and heyrovskite ($Pb_{12}Bi_4S_{18}$ - $Ag_5Pb_2Bi_9S_{18}$) series (Makovický & Karup-Møller 1977 a,b; Chang et al. 1988). The majority of points in the diagram $(Ag,Cu)_2S$ - Bi_2S_3 - Pb_2S_2 corresponding to PbS_{ss} plot at, or close, to the galena - matildite series.

The samples of PbS_{ss} contain usually numerous inclusions of matildite, wittichenite and minerals of the system Ag-Cu-Pb-Bi-S enriched in copper. Some points (analyses 12, 13), however, fall off the line galenite - matildite towards relatively higher bismuth contents. Unlike the first case, here the grains occur in intergrowths mainly with Ag-Pb-Bi sulfosalts of galena - matildite series enriched in bismuth relative to silver, with matildite either lacking or being subordinate. According to Foord & Shawe (1989) such an excess of bismuth in PbS_{ss} may be a result of vacant sites, the presence of a Bi-rich phase according {111}, or dubling of unit cell according (131). Based on this phenomenon Karup-Møller (1977) suggested that the excess of bismuth may result from the domain type of structure of this mineral similarly as in the lillianite homologous series.

The wide extent of the $AgBiS_2$ solid solution in galena which reaches up to 20 mol.% is very rare in nature: according to recent data (Foord & Shawe 1989) the most characteristic chemical compositions of natural PbS_{ss} do not exceed 10 mol.% and only the PbS_{ss} from the Fairview mine in the Round Mountain (Nevada) coexisting with ourayite contains 25 mol.% $AgBiS_2$.

After experimental data (Craig 1967; Nenasheva 1975) a continuous solid solution exists between galena and matildite, at the temperatures higher than 220 °C, due to the isostructural relationship of high temperature cubic α-$AgBiS_2$ and galena. For example, at 200 °C the galena solid solution contains only 8 % of matildite molecule (Craig l.c.) while at 210 - 150 °C the unmiscibility area of the cubic solid solution ranges between 40 - 0.3 % PbS (Nenasheva l.c.). However, the existence of only one phase is proved experimentally in this area, the synthetic "schirmerite" $Ag_4PbBi_4S_9$ which at 184 °C forms eutectoid with -matildite and at 150 °C with galenite solid solution (Nenasheva l.c.). No other mineral phases in the system $AgBiS_2$ - PbS have been obtained in experimental conditions. Moreover, Boldyreva (1985) presumes that the synthetic phase $Ag_4PbBi_4S_9$ cannot exist in nature. On the contrary, when studying the Kuraminske Mountains ore field (Tadjikistan), Bortnikov et al. (1985, 1986) reported four new, unknown natural sulfosalts ($Ag_3Pb_7Bi_3S_{13}$, $Ag_2Pb_3Bi_2S_7$, $AgPbBiS_3$, $Ag_4PbBi_4S_9$) in assemblage with gustavite, berryite, matildite and the PbS_{ss} containing up to 10 - 14 % $AgBiS_2$. Too small grain size ($<20 \mu m$) and very close mutual intergrowing of the galena - matildite series minerals with other sulfosalts made the identification by X-rays impossible, so they were identified by microprobe only as their optical properties are practically indistinguishable from those of matildite. As shows Fig. 2, the chemical compositions of these sulfosalts plot on the galena - matildite series.

The results of bismuth mineralization study at the Banská Štiavnica deposit augmented considerably the group of natural mineral phases of the galenite - matildite series (Tab. 1, Fig. 2), and confirmed that the finding of natural phases in the system $AgBiS_2$ - PbS, among which only one, $Ag_4PbBi_4S_9$, has a synthetic analogue, was not fortuitous. One phase, a silver analogue of aikinite - $AgPbBiS_3$, has been found both in Kanimansur and Banská Štiavnica. Five other sulfosalts are spread evenly along the galena - matildite join both at the PbS-rich and $AgBiS_2$-rich ends.

The discrepance between phase relations observed in the natural system $AgBiS_2$ - PbS and experimental data was explained either by the assumption that natural sulfosalts precipitate at lower temperature conditions compared to those in experiments (Czamanske & Hall 1975), or by the stabilizing role of minor elements in natural phases (Bortnikov et al. 1985). The latter assumption is in part confirmed by the chemical compositions of the galena - matildite series sulfosalts from the Banská Štiavnica deposit (Tab. 1): low copper and/or selenium concentrations (0.16 - 0.53 and 0.43 - 0.65 wt.%, respectively) were determined in the half of analysed phases. Nevertheless, the formation of discrete phases having compositions between PbS_{ss} and matildite results most probably from a combination of many factors including above mentioned.

Another group of minerals of the galena - matildite series in Štiavnica ores is represented by *matildite* (Tab. 1, Fig. 2). This mineral mostly occurs among bismuth sulfosalts of the Bieber Vein, less in the veins Rozália and Bakali. Matildite (along with PbS_{ss}) constitutes often the main part of the Ag-Cu-Pb-Bi-S mineral system intregrowths (Figs. 1, 3 - 5) forming usually anhedral grains within PbS_{ss} which prevails (Figs. 1, 3), or occurs with matildite in eutectoid relation (Figs. 4, 5). In the latter case are in the matildite matrix relatively often observed tabular grains of PbS_{ss} and inclusions of Cu-Ag-Pb-Bi-S sulfosalts enriched in copper.

As shown by analytical data (Tab. 1), the concentrations of copper (to 0.76 wt.%), lead (to 2.6 wt.%) and selenium (to 1.32 wt.%) are often present Štiavnica matildite. Although a "pure" stechiometric composition is typical of matildite, the lead-rich matildites (3.5 - 5.7 wt.%) were found in a number of deposits (Boldyreva 1985; Czamanske & Hall 1975; Gaspar et al. 1987; Foord & Shawe 1989). Experimental data show that almost all the galena exsolves from the matildite composition at its phase

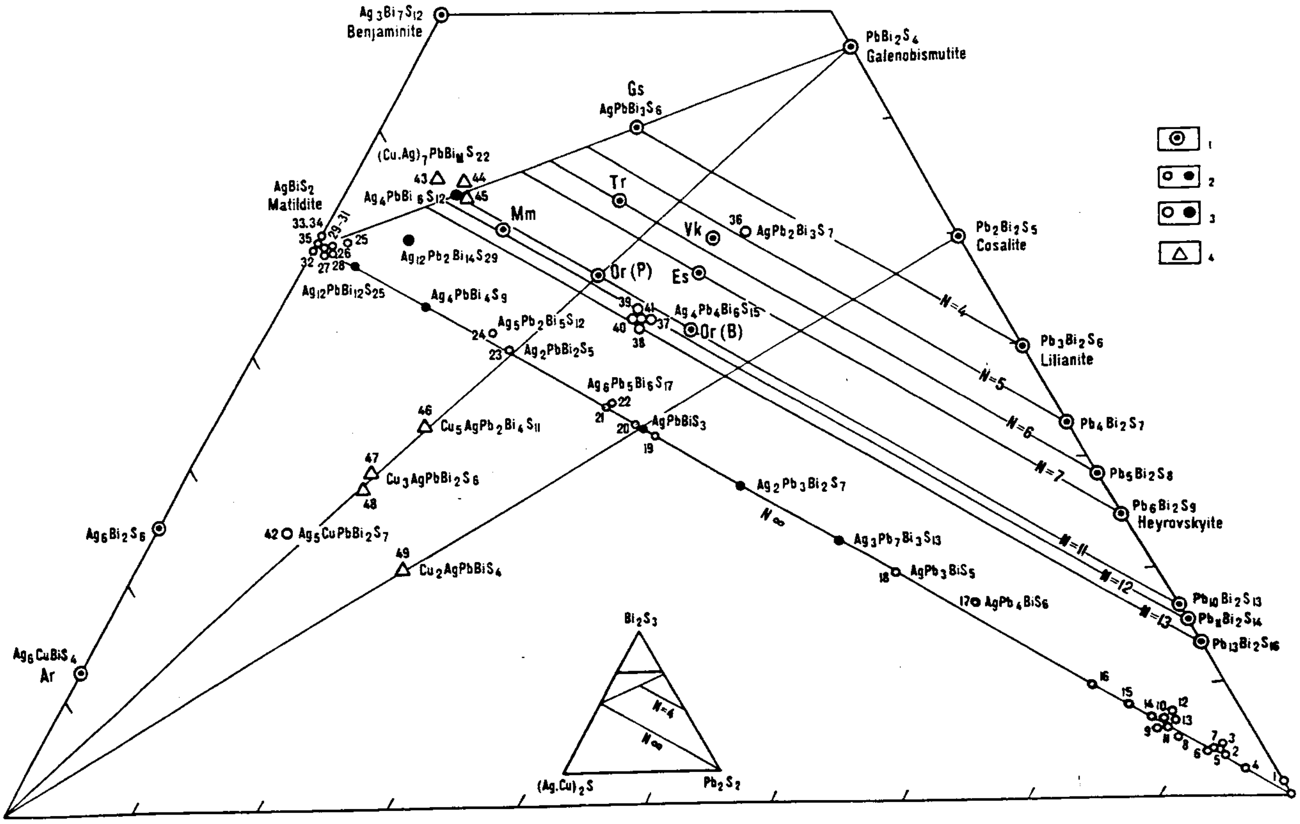

Fig. 2 . Diagram $(Ag, Cu)_2S$ - Bi_2S_3 - Pb_2S_2 of the Banská Štiavnica bismuth sulfosalts.
1 - theoretical compositions of some minerals and synthetic phases; 2 - minerals of the galenite - matildite series; 3 - complex Cu (±Ag) - Pb - Bi sulfosalts. Open symbols - Banská Štiavnica data; closed symbols - Kanimansur ore field data (Bortnikov et al. 1985). Minerals: Ar - arcubisite, Vk - vikingite, Gs - gustavite, Mm - mummeite, Or (P,B) ourayite P, ourayite B, Tr - treasurite, Es - eskimoite. $N = N_{chem}$ - number of octahedrons in galena-similar domains of the unit cell in the plane roughly parallel to (001) and ab projection.
$N_{chem} = -1 + [1/(Bi_i + Pb_i/2 - 0.5)]$ (according to Makovický & Karup-Møller 1977b).

Table 2 : Chemical composition of the Ag-Cu-Pb-Bi-S system sulfosalts enriched in silver and copper, the Banská Štiavnica deposit.

No	sample	phase	min.	Ag	Cu	Pb	Bi	Se	S	Total	N_{chem}	%Gus
36	Bi-55/88	1	vik	5.71	1.22	30.23	46.26	0.00	16.17	99.59	4.9	67
37	Sch-23	1a-2a		13.12	0.57	27.64	42.28	0.00	16.10	99.71	12.2	73
38	Sch-23	1a-2b		13.46	0.63	28.14	41.70	0.00	16.25	100.18	13.6	72
39	Sch-23	1a-2c		13.31	0.56	27.69	42.17	0.00	16.07	99.80	12.5	73
40	Sch-23	1a-2d		13.24	0.62	27.98	41.69	0.00	16.20	99.73	12.9	72
41	Sch-23	1a-2		13.18	0.66	27.56	41.57	0.00	16.04	99.01	13.1	73
42	Bi-56/88	1-3		37.22	3.34	13.45	29.60	0.76	14.42	98.79		
43	Ro-10	11a	pad	2.11	11.01	7.21	62.00	0.60	18.80	102.31		
44	Ro-10	5-1b		1.13	11.60	9.11	59.99	0.00	18.58	100.41		
45	Ro-10	5-2b		1.03	11.70	9.66	59.17	0.16	18.58	100.30		
46	Bi-55/88	2a-7		5.67	15.48	19.95	40.56	1.07	16.78	99.51		
47	Bi-55/88	2b-3		6.70	18.40	18.00	38.49	1.57	16.79	100.37		
48	Bi-55/88	1b-3		9.45	16.59	18.98	35.98	0.85	16.65	98.50		
49	Bi-55/88	3a-3		14.33	15.11	26.89	26.82	1.10	15.84	100.09		

Samples: Ro-10, 10a the Rozália Vein, VIth deep horizon, other samples as in Tab. 1, vik - vikingite, pad - paděraite.

36 - $Ag_{0.72}Cu_{0.27}Pb_{2.01}Bi_{3.05}S_{6.95}$
37 - $Ag_{3.64}Cu_{0.27}Pb_{3.99}Bi_{6.01}S_{15.09}$
38 - $Ag_{3.71}Cu_{0.29}Pb_{4.03}Bi_{5.92}S_{15.05}$
39 - $Ag_{3.69}Cu_{0.27}Pb_{4.00}Bi_{5.98}S_{15.04}$
40 - $Ag_{3.66}Cu_{0.29}Pb_{4.04}Bi_{5.95}S_{15.06}$
41 - $Ag_{3.67}Cu_{0.31}Pb_{4.00}Bi_{5.98}S_{15.04}$
42 - $Ag_{5.19}Cu_{0.79}Pb_{0.98}Bi_{2.13}S_{6.77}Se_{0.14}$
43 - $Cu_{6.41}Ag_{0.73}Pb_{1.24}Bi_{10.99}S_{21.72}$
44 - $Cu_{3.80}Ag_{0.22}Pb_{0.92}Bi_{5.98}S_{12.08}$
45 - $Cu_{3.83}Ag_{0.20}Pb_{0.97}Bi_{5.90}S_{12.07}Se_{0.03}$
46 - $Cu_{4.99}Ag_{1.08}Pb_{1.97}Bi_{3.97}S_{10.71}Se_{0.28}$
47 - $Cu_{3.23}Ag_{0.69}Pb_{0.99}Bi_{2.05}S_{5.82}Se_{0.22}$
48 - $Cu_{2.97}Ag_{1.00}Pb_{1.00}Bi_{1.96}S_{5.91}Se_{0.10}$
49 - $Cu_{1.89}Ag_{1.05}Pb_{1.03}Bi_{1.04}S_{3.91}Se_{0.11}$

transitions. For this reason the above data on relatively higher lead concentrations (Tab. 1, analyses 25 - 28) are likely to be caused by sub-microscopic inclusions of galena in this mineral.

Complex sulfosalts of the Ag-Cu-Pb-Bi-S system

The minerals belonging to the part of the Ag-Cu-Pb-Bi-S system enriched relatively in silver and copper are included in this group of sulfosalts. Along with above mentioned galena - matildite series minerals and wittichenite, they occur in deep horizons of the Bieber Vein samples (IInd deep horizon, Bi-55/88, Bi-56/88, Bi-57/88, Sch-23) in copper, silver and gold enriched ores or in associations with Cu-Bi sulfosalts and matildite in copper ores of the Rozália Vein (IVth horizon, samples Ro-10, Ro-10a). The chemical composition of these minerals is given in Tab. 2 and illustrated in Fig. 2.

A *sulfosalt* $(Ag_{0.72}Cu_{0.27})_{0.99}Pb_{2.01}Bi_{3.05}S_{6.95}$, or in the generalized form $AgPb_2Bi_3S_7$, occurs in quartz in close intergrowths with matildite and wittichenite. The phase shows the inclined extinction and intimate twinning in reflected light and crossed polars. In the diagram $(Ag, Cu)_2S$ - Bi_2S_3- Pb_2S_2 it plots between sulfosalts of the lillianite homologous series (Makovický 1977; Makovický & Karup-Møller 1977a) close to the *vikingite* composition (see Fig. 2), one of the lillianite homologous series monoclinic sulfosalts, having often a variable composition (Makovický & Karup-Møller 1977b). It is confirmed also by closely aproximating values of the calculated N_{chem} for mineral $AgPb_2Bi_3S_7$ (N_{chem} = 4.9, Tab. 2, analysis 36) and vikingite (N_{chem}= 5.09 - 5.23). One of the vikingite empirical formulae is $Ag_{1.04}Cu_{0.05}Pb_{2.02}Bi_{3.05}S_{7.10}$(Makovický & Karup-Møller 1977b). The similar values in studied minerals is characterized by a degree of the "gustavite" substitution ($2Pb^{2+} \rightarrow Ag^{+} + Bi^{3+}$) which is given by equation too:

$$\% \text{ Gus} = 1 - [(2Bi_i - Pb_i - 1)/ 6(Pb_i/2 + Bi_i - 5/6)],$$

where $Pb_i + Ag_i + Bi_i = 1$ (Makovický - Karup-Møller 1977a) and its value for the mineral $AgPb_2Bi_3S_7$ is 67 % (Tab. 2) and for vikingite 67 - 72 % (Makovický & Karup-Møller 1977b). These data, in spite of the absence of X-ray investigation precluded by very small grain-size (15 - 20 μm), allow us to identify this sulfosalt as *vikingite.*

The *sulfosalt* $Ag_4Pb_4Bi_6S_{15}$ was found in the Bieber Vein (IInd deep horizon) in copper-, silver-, gold- and tungsten-enriched ores where it forms relatively large aggregates in chalcopyrite (size up to 150 - 200 μm) in close intergrowths with gold and hematite (Fig. 6). The phase shows white and cream colour, modest reflectance (R ~ 40 %) and a distinct anisotropy in reflected light.

The sulfosalt has a constant chemical composition (Tab. 2, analyses 37 - 41, Fig. 2) which can be approximated by the formula: $Ag_{3.64-3.71}Cu_{0.27-0.31}Pb_{3.99-4.01}Bi_{5.92-6.04}S_{15.00-15.09}$, or, in generalized form $Ag_4Pb_4Bi_6S_{15}$. The calculated values of N_{chem} range between 12.2 - 13.6, averaging 13. Minerals with N_{chem}= 12 -13 are lacking among known sulfosalts LHS the closest minerals in the composition diagram being ourayite-P and ourayite-B (Fig. 2), the rhombic sulfosalts with N_{chem} = 11. The X-ray diffraction pattern of the mineral $Ag_4Pb_4Bi_6S_{15}$ (Tab. 3) displays a number of peaks being, to a certain extent, similar to the powder diffraction patterns of ourayite and other rhombic sulfosalts of the lillianite homologous series. Preliminary interpretation of the diffraction pattern made by T .L. Evstigneeva (IGEM RAS) showed that the mineral crystallizes in the rhombic system having following parameters of the unit cell: a_0= 13.4, b_0= 4.0, c_0= 44.5 . Based on the obtained data, it is posible to suppose that

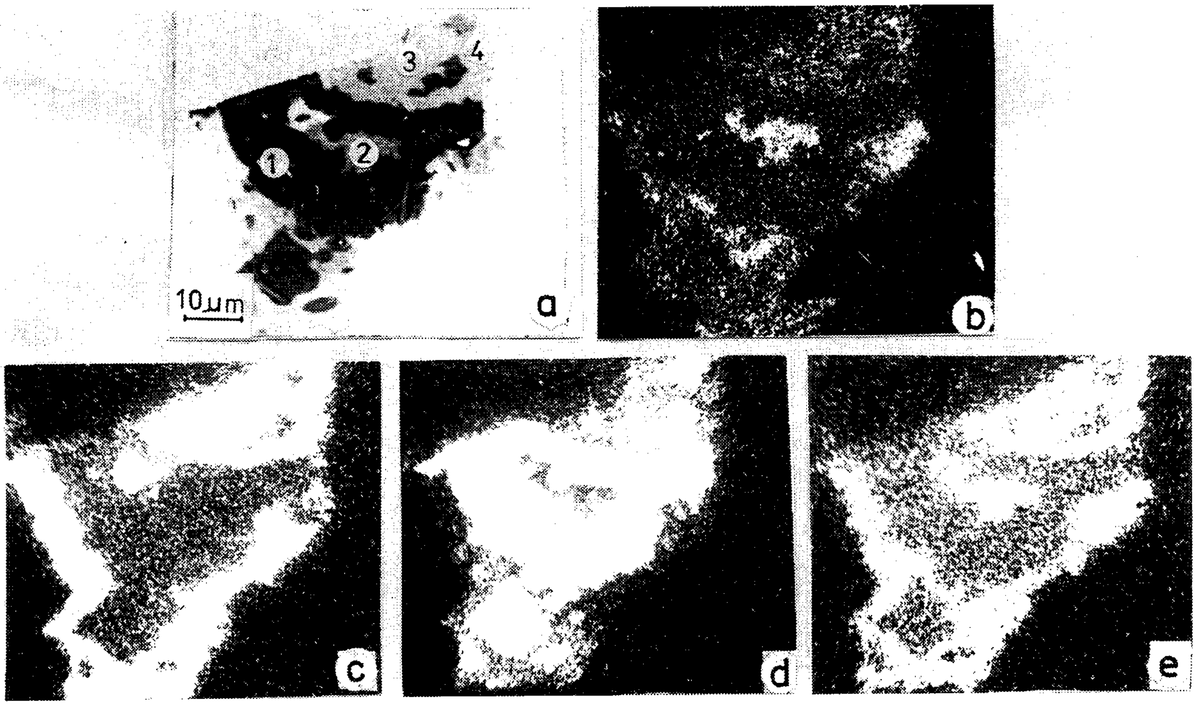

Fig. 3. Photomicrographs of PbS$_{ss}$ - 1, matildite - 2, wittichenite - 3, and sulfosalt $Cu_3AgPbBi_2S_6$ - 4 in the centre of quartz in characteristic X-rays: **a** - e$^+$; **b** - Ag Lα; **c** - Cu Kα; **d** - Pb Lα; **e** - Bi Lα. Sample Bi-55/88-1b.

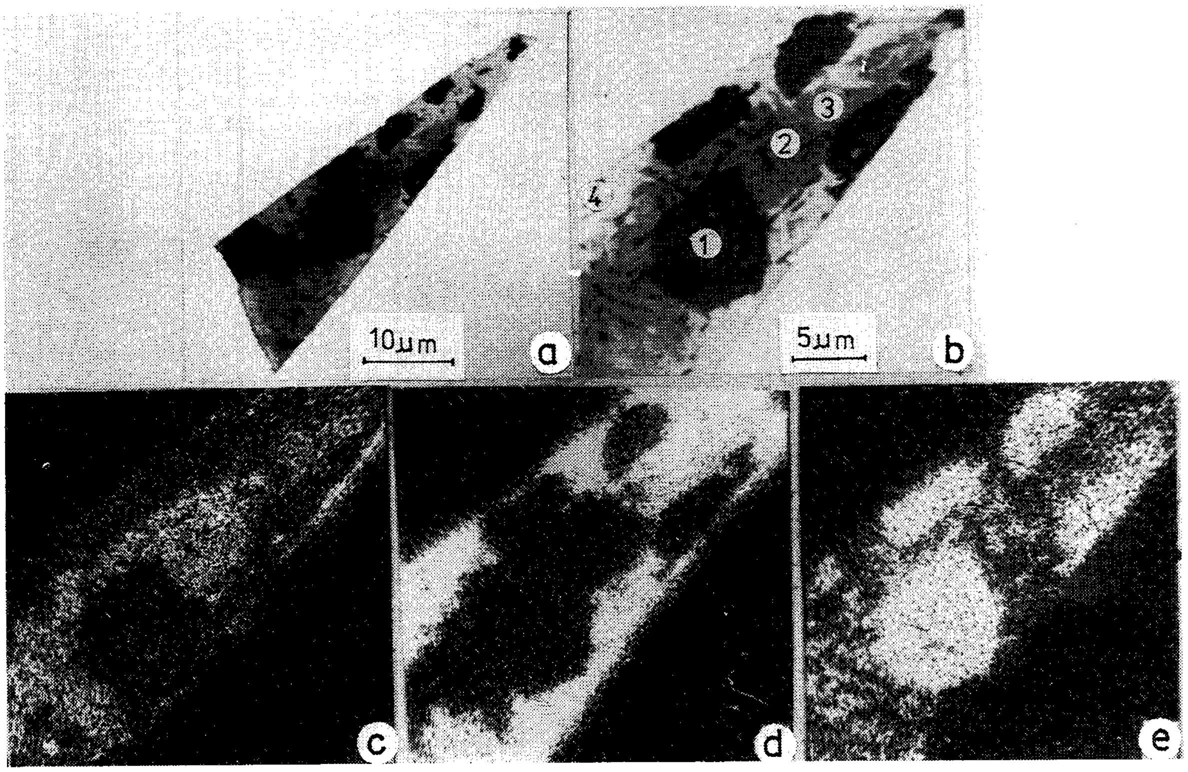

Fig. 4. Photomicrographs of PbS$_{ss}$ - 1; matildite - 2; sulfosalt $Cu_3AgPbBi_2S_6$ - 3; and wittichenite - 4 in the centre of quartz in characteristic X-rays: **a**, **b** - e$^+$; **c** - Ag Lα; **d** - Cu Kα; **e** - Pb Lα. Sample Bi-55/88-2b.

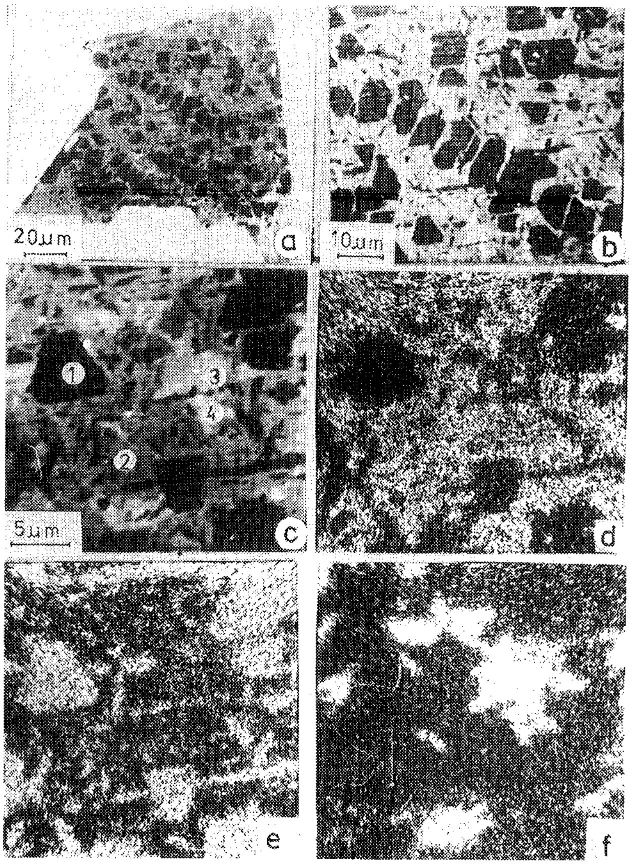

Fig. 5. Photomicrographs of PbS_{ss} - 1, matildite - 2, wittichenite - 3, and sulfosalt $Cu_5AgPb_2Bi_4S_{11}$ (4) in the centre of quartz in characteristic X-rays: **a** , **b**, **c** - e^+; **d** - Ag Lα; **e** - Pb Lα; **f** – CuKα. Sample Bi-55/88-2a.

Table 3: X-ray data of the $Ag_4Pb_4Bi_6S_{15}$ mineral.

No	I	$d_{\alpha meas}$	No	I	$d_{\alpha meas}$
1	1/2	6.20	23	1	1.760
2	1	5.22	24	1b	1.741
3	2	4.90	25	1	1.709
4	1	4.53	26	1	1.591
5	2	4.02	27	1/2	1.570
6	2	3.69	28	1/2	1.546
7	3	3.46	29	1/2	1.526
8	1	3.29	30	1	1.501
9	8	2.99	31	1	1.491
10	10	2.84	32	1	1.372
11	1	2.68	33	1	1.351
12	1/2	2.61	34	1b	1.329
13	1/2	2.49	35	1b	1.301
14	1	2.44	36	1b	1.285
15	1	2.20	37	1b	1.278
16	2	2.17	38	1b	1.238
17	4b	2.10	39	1	1.213
18	5	2.06	40	1	1.194
19	1	2.004	41	1	1.177
20	1	1.973	42	2	1.111
21	1	1.864	43	2b	1.032
22	1	1.800	44	3b	1.020
			45	1b	1.004

Note: X-rayed in the Gandolfi chamber (57.3 mm), Fe, ß - lines filtered by calculation (b - broad line), sample - a caoutchouc ball, d ≈ 0.2 mm, assymetrical position of film.

the sulfosalt $Ag_4Pb_4Bi_6S_{15}$, approaching by its parameters ourayite, may represent a new mineral species in the lillianite homologous series, with $N_{chem} = 13$.

The *sulfosalt* $Ag_5CuPbBi_2S_6$ or $(Ag,Cu)_6PbBi_2S_6$ (Tab. 2, analysis 42) was observed in intergrowths with galena solid solution (3 % $AgBiS_2$) and matildite, having affinity to the quartz-bearing parts of the Bieber Vein deep horizons (IInd deep horizon). In contrast to the known natural and synthetic phases in the system Ag-Pb-Bi-S, situated to the right of the galena - matildite join (N), the salt studied is the bismuth-poor and silver-enriched part of the composition diagram $(Ag,Cu)_2S$ - Bi_2S_3 - Pb_2S_2 (Fig. 2). Composition of this mineral is characterized by the ratios (Ag+Cu)/(Pb+Bi) = 2, Me/S = 1.3, Pb/Bi = 0.5 different from any known bismuth sulfosalts. Since, however, only one grain (with the size 15 - 20 μm) of this sulfosalt has been found so far the chemical data allow to define empirical formula either with independent positions of silver and copper, i.e. $Ag_5CuPbBi_2S_7$, or as $(Ag,Cu)_6PbBi_2S_7$. Without the X-ray diffraction study of mineral structure the problem cannot be unambiguously solved. A significant amount (0.76 wt.%) of selenium was detected, in addition to Cu.

In copper-dominated part of the compositional triangle (Fig. 2) occur still another three unusual sulfosalts discovered in the association with galena solid solution, matildite and wittichenite. The *sulfosalt* $Cu_5AgPb_2Bi_4S_{11}$ or $(Cu,Ag)_6Pb_2Bi_4S_{11}$ (Tab. 2, analysis 46) occurs in close intergorwths with matildite, wittichenite and galena solid solution (Fig. 5) forming usually minute anhedral grains at the boundaries between matildite and wittichenite having maximum size about 10 μm. By optical properties in reflected light the mineral resembles berryite, under crossed polars it is markedly anisotropic.

In a similar association was found another *sulfosalt* $Cu_3AgPbBi_2S_6$ or $(Cu,Ag)_4PbBi_2S_6$ (Tab. 2, analysis 47, 48, Figs. 2 - 4). Anhedral grains, less than 10 μm in size, occur in one case with galena solid solution and wittichenite, and in another case in addition with matildite. The two analyses seem to suggest a mutual substitution between Ag and Cu. If so, the idealized formula of the mineral would be $(Cu, Ag)_4PbBi_2S_6$, its chemical composition forming an intermediate member with hypothetical end-members $Cu_4PbBi_2S_6$ and $Cu_3AgPbBi_2S_6$. The sulfosalt is also characteristic by increased selenium contents (1.07 - 1.57 wt.%) replacing sulphur.

Still one more mineral having a similar composition, *sulfosalt* $Cu_2AgPbBiS_4$ or $(Cu,Ag)_3PbBiS_4$, was identified in the copper ores of the Bieber Vein (IInd deep horizon) associated with matildite and PbS_{ss} (8 % $AgBiS_2$, Tab. 2, analysis 49, Fig. 2). Although the size of its anhedral grains did not allowed an X-ray investigation, similarly as in previous cases the independance of the sulfosalt makes it possible to study it as a potentially new

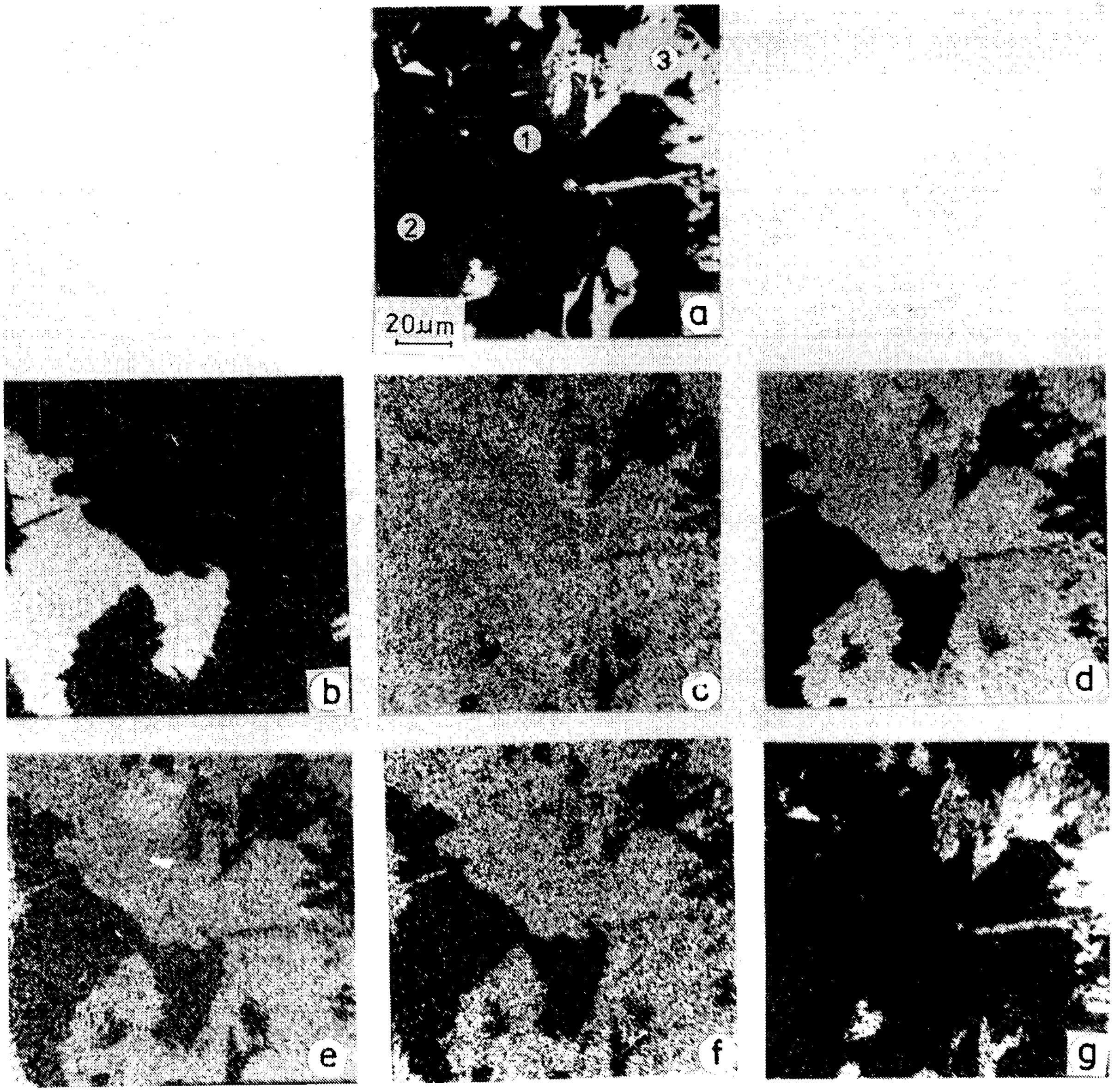

Fig. 6 . Photomicrographs of $Ag_4Pb_4Bi_6S_{15}$ - 1, gold - 2, and hematite - 3 in characteristic X-rays: **a** - e^+, **b** - Au Lα, **c** - Ag Lα, **d** - S Kα, e - Bi Lα, **f** - Pb Mα, **g** - Fe Kα. Sample Sch-23.

mineral. Of interest is that while the chemical compositions of the sulfosalts $(Cu,Ag)_5PbBi_2S_6$ and $(Cu, Ag)_4PbBi_2S_{11}$ plot in compositional diagram (Fig. 2) on the join: $(Cu,Ag)_2S$ and galeno-bismutite (Pb/Bi= 0.5), the sulfosalt $(Cu,Ag)_3PbBiS_4$ lies on the join: $(Cu,Ag)_2S$ - cosalite (Pb/Bi = 1). A possibility cannot be excluded that the discovered group of copper-enriched sulfosalts represents an entirely new mineral group in the system Ag-Cu-Pb-Bi-S being characteristic by their law-like relations between chemical composition and crystal structure, as it is in the lillianite homologous series.

When studying the bismuth mineralization of the Rozália Vein we discovered another two complicated copper sulfosalts of the Ag-Cu-Pb-Bi-S (Tab. 2, analyses 43 - 45). However, unlike the above described bismuth-poorer sulfosalts of this system, they plot to the right of the galenite - matildite join and tend to the intersection of ourayite line (N = 11) with the join matildite - galenobismutite. First of these minerals, a *sulfosalt:* $Cu_{6.4}Ag_{0.73}Pb_{1.24}Bi_{10.99}(S_{21.72}Se_{0.28})_{22}$ is close by its composition to *paděraite:* $Cu_{5.8}Ag_{1.2}Pb_{1.3}Bi_{11.5}S_{22}$

Discovered by Mumme & Žák (1985), this mineral belongs to the cuprobismutite homologous series which includes, after these authors (l.c.) and Makovický (1989), cuprobismutite $Cu_{10.4}Bi_{12.6}S_{24}$ and hodrushite $Cu_{8.4}Bi_{12}S_{22}$. The studied mineral shows in microscope pink to cream-white colour, is distinctly anisotropic with grain size 10-15μm. It occurs in assemblage with chalcopyrite, bornite, highly pure gold, wittichenite, emplectite, hodrushite, Bi-tetrahedrite and mineral $(Cu, Ag)_4PbBi_6S_{12}$.

$(Cu,Ag)_4PbBi_6S_{12}$, or $Cu_4PbBi_6S_{12}$ sulfosalt forms relatively large (50 - 100 μm) anhedral grains in close intergrowths with chalcopyrite. It resembles emplectite by optical properties but differs by pink-brownish colour. The chemical composition is similar to that of *mummeite* or other Cu-Ag-Pb-Bi sulfosalts of the pavonite homologous series (Karup-Møller & Makovický 1992; Bortnikov et al. 1985).

Table 4 : Chemical composition of the Cu ± (Ag) ± (Pb) - Bi - S system minerals.

No	sample	phase	min.	Ag	Cu	Pb	Fe	Bi	Se	S	Total
50	Ro-10A	2	emp	0.00	18.93	0.00	0.00	62.38	0.00	19.11	100.42
51	Ro-10A	3	emp	0.00	19.04	0.00	0.00	61.98	0.13	19.07	100.22
52	Ro-10A	6	emp	0.00	18.97	0.00	0.00	62.19	0.19	19.18	100.53
53	Ro-10A	7	emp	0.00	19.05	0.00	0.00	61.93	0.28	19.00	100.26
54	Ro-10	5-2a	emp	0.00	19.13	0.00	0.00	60.79	0.52	19.27	99.71
55	Ro-10A	12	hod	1.00	12.58	0.33	0.52	66.78	0.21	18.87	100.29
56	Ro-8	4b	hod	1.01	14.21	0.00	1.18	64.79	0.00	19.80	100.99
57	Ro-10A	12a	hod	0.55	12.18	0.39	1.10	67.15	0.69	18.68	100.74
58	Ro-10	4	hod	0.66	13.40	0.00	0.00	65.80	0.20	18.50	98.56
59	Ro-10	5-1a	hod	0.78	13.65	0.00	0.00	66.10	0.00	18.75	99.28
60	Ro-10	7	wit	0.25	39.16	0.00	0.00	40.32	0.18	19.64	99.55
61	Ro-10	3-2	wit	0.51	38.38	0.00	0.00	41.20	0.40	19.54	100.03
62	Ro-10	3-1	wit	0.60	38.65	0.00	0.00	40.93	0.31	19.85	100.34
63	Ro-10	8	wit	1.01	38.31	0.00	0.00	42.10	0.10	19.40	98.56
64	Ro-10	1-1	wit	1.06	38.86	0.00	0.00	40.20	0.13	19.89	100.14
65	Ro-8	2-1	wit	2.64	36.23	0.00	0.29	41.76	0.00	19.20	100.12
66	Ro-8	4c	wit	2.89	35.54	0.00	1.01	41.98	0.00	19.33	100.74
67	Ro-8	2-2	wit	3.96	35.20	0.00	0.30	41.82	0.00	18.54	99.82
68	Bi-55/88	1b-3	wit	3.09	35.82	0.66	0.00	39.96	0.00	19.15	98.61
69	Bi-55/88	3	wit	3.55	35.38	0.55	0.00	40.77	0.53	17.81	98.59
70	Bi-55/88	4	wit	3.56	34.79	0.25	0.00	42.11	0.00	17.67	98.38
71	Bi-55/88	2	wit	4.72	33.50	1.20	0.00	39.84	0.00	17.61	97.27
72	Bi-55/88	2a-4	wit	4.93	34.57	0.68	0.00	39.43	0.99	18.89	99.45
73	Bi-55/88	2b-4	wit	5.26	33.81	0.57	0.00	40.22	1.03	18.61	99.50
74	Bi-55/88	1d-2	wit	5.95	33.72	0.18	0.00	39.87	0.66	18.42	98.79
75	Bi-55/88	1b-4	wit	12.13	29.07	0.49	0.00	39.26	0.99	17.90	99.84

Analyses 50 - 54 emplectite (emp); 55 - 59 - hodrushite (hod); 60 - 75 - wittichenite (wit) and wittichenite solid solution.

Minerals of the system Cu(±Ag) - Bi(±Pb) - S

In contrast to the above described sulfosalts of the Ag-Cu-Pb-Bi-S system, minerals of the Cu-Bi-S system are common in the Rozália Vein although wittichenite associates often with the former group and matildite and PbS_{ss} with the latter.

Emplectite, $CuBiS_2$(Tab. 4, analyses 50 - 54) is a typical mineral of copper ores in the upper parts of the Rozália Vein (VIth deep horizon) where it associates with hodrushite, aikinite, wittichenite, paděraite, the $(Cu, Ag)_4PbBi_6S_{12}$ sulfosalt and gold. Analysed grains of the mineral differ in stoichiometric ratios and among impurities in Rozália Vein emplectite were detected only low selenium concentrations (to 0.52 wt.%).

Unlike emplectite, the *hodrushite* studied exhibits considerable variations of chemical composition (Tab. 4, analyses 55 - 59). This is related to its structure which consists of two layer types parallel to (100): the first type layers are identical with those of cuprobismutite, the second type layers are different (Makovický 1981, 1989). Besides main elements of the mineral, copper (12.18 - 14.21 wt.%), bismuth (64.79 - 67.15 wt. %) and sulphur (18.50 - 19.80 wt.%) are constantly present low concentrations of silver (0.55 - 1.01 wt.%), or iron (to 1.18 wt.%), lead (to 0.39 wt.%), and selenium (to 0.69 wt.%). The obtained hodrushite analyses may be, with the allowance to permitted variability in the structure, well recalculated to the general formula:

$Cu_{7.12-8.03}Ag_{0.19-0.35}Pb_{0-0.07}Fe_{0-0.75}Bi_{11.02-11.93}S_{21.61-21.95}Se_{0-0.32}$

Among the minerals of the studied group only *wittichenite* was found both in the Bieber and Rozália Veins in the association with matildite and hodrushite (Fig. 7) in deeper parts of this vein (XIIIth deep horizon). Optical properties of the mineral are standard, the grain size varies considerably attaining in some cases 150 - 200 μm. It is remarkable that in the intergrowths with PbS_{ss} and matildite is wittichenite relatively latest mineral occurring either in peripheral parts of the aggregates or intersecting them (Figs. 1, 3-5, 7). However, the analogical intergrowths it forms with the copper-enriched minerals of the Ag-Cu-Pb-Bi-S system, appear to be in equilibrium relations.

A noteworthy feature of the Štiavnica wittichenite chemical composition is the presence of relatively high silver concentrations (Tab. 4). Particularly typical is it for the wittichenite of the Bieber Vein and deep horizons of the Rozália Vein. The silver content of this wittichenite is 2.5 - 6 times (in a single case even

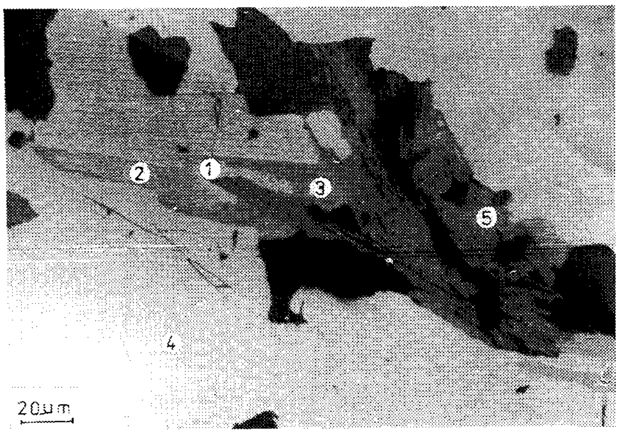

Fig. 7. The aggregate of matildite - 1, hodrushite - 2, wittichenite - 3, rimming both minerals in the centre of chalcopyrite - 4, and hematite - 5. Black - quartz. Sample Ro- 8.

12 times) higher than Ag content of wittichenite from the shallower parts of veins (Tab. 4, analyses 60 - 75). Such high silver concentrations are not typical for natural wittichenite although experimental investigation of the Ag_2S - Cu_2S - PbS - Bi_2S_3 system (Chang et al. 1988) showed that, in the Cu and Ag portion of the system, at 500 °C the wittichenite solid solution reaches the composition $Cu_{2.5}Ag_{0.5}BiS_3$. Just this composition has one of the studied wittichenites (Tab. 4, analyses 75). It should be noted that wittichenite from the deeper parts of ore bodies contains increased concentrations of iron (Rozália Vein Tab. 4, analyses 65 - 67), lead (Bieber Vein, analyses 68 - 75) and selenium (up to 1.03 wt.%) compared to the wittichenite of shallower parts of veins (to 0.4 wt.% Se) being, moreover, free of Fe and Pb.

Discussion

The bismuth mineralization found at the Banská Štiavnica deposit is, similarly as in other gold-silver-polymetallic deposits (Kanimansur, Adrasman, Madzharovo, Idarado Mine, Round Mountain and others), closely space-related to quartz-hematite-chalcopyrite ores, enriched relatively in gold and silver, and occurring usually in deep horizons of the deposits. The similarity of occurrence, mineral assemblages of bismuth sulfosalts, their chemical compositions and geochemical profile as well as a considerable (usually about 1 km and more) vertical reach of the ore veins in similar world deposits (Bortnikov et al. 1985, 1986; Breskovska et al. 1976; Foord & Shawe 1988, and others) suggest an analogical general cause for the origin of this mineralization. One such cause, according to the ideas of the authors, might have been a relatively high temperature, probably thermostatic, regime of the ore formation in deep zones, the neccessary heat bein supplied by near intrusive and subvolcanic bodies of porphyritic granitoids.

Indeed, the fluid inclusion data (Kovalenker et al. 1991) show that the formation of the bismuth sulfosalts containing mineral assemblage, at deep horizons of the Banská Štiavnica deposit, began in the temperature interval 330 - 300 °C and continued in slowly cooling fluid. The relatively high temperature character of mainly chalcopyrite mineralization of deeper zones of the deposit is supported also by very low Sb/Bi values in galena (<0.00n), which usually indicate relatively high temperature and considerable depths of mineralization origin. High starting temperatures of the studied mineralization origin along with the multi-component composition of ore-forming fluid (Kovalenker et al. l.c.) caused the formation of high-temperature galena solid solution which was able to bind isomorphously all the mineral-forming elements (Pb, Cu, Ag, Bi, Se, S and others) present in the fluid. Such conditions were favourable for the formation of highly silver-rich wittichenite solid solution as well.

Upon cooling below 215 °C the high-temperature PbS_{ss} decomposes into galena solid solution (with variable Ag and Bi contents) and matildite (ß-matildite). According to Foord & Shawe (1988), in the case of bismuth excess in the system, may co-precipitate various Ag-Pb-Bi sulfosalts of the galena - matildite and lillianite homologous series, and in the presence of copper, also various Ag-Cu-Pb-Bi sulfosalts. In this view is easy to account for the observed wealth of bismuth sulfosalts in copper ores in deep horizons of ore veins.

At lower temperature conditions, in shalower horizons of the Rozália Vein, a copper - bismuth mineralization originated practically lacking PbS_{ss} and matildite, indicators of high-temperature solid solutions. Here, of course, did not originated any Ag-Cu-Pb-Bi sulfosalts enriched in silver.

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