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Metallic minerals of productive assemblages of the Zlatá Baňa deposit (Eastern Slovakia); specialities of chemical composition

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Рудные минералы продуктивных ассоциаций месторождения Злата Баня (Восточная Словакия); особенности химизма

В работе впервые охарактеризован химизм рудных минералов содержащих золото и серебро на месторождении Злата Баня. Между изучаемыми минералами встречаются самородное золото, минералы группы тетраэдрита сульфаантимониды свинца, меди-свинца, серебра-меди, серебра-олова и др., которые раньше на месторождении Злата Баня и также во всей Словакии не были известны (миаргирит, андорит, рамдогрит, физелиит, овигеэлит, фрайслебенит, робинсонит и др.). Определены были также минералы $AgCuSb_2S_4$, $Pb_7Sb_6S_{167}Pb_{13}Sb_{12}$ S_{31}, Pb_8Sb_{10} S_{23} и Fe_5SbS_{11}, которые до сих пор в природных условиях не были исвестны.

Metallic minerals of productive assemblages of the Zlatá Baňa deposit (Eastern Slovakia); specialities of chemical composition

For the first time the chemical composition of metallic minerals, bearers of Au and Ag on the Zlatá Baňa deposit, has been detaily characterized in the submitted article. Native gold, minerals of tetrahedrite group, sulphoantimonides of Pb, Cu — Pb, Ag — Cu, Ag — Pb and other minerals, which were not known, neither on the Zlatá Baňa deposit nor in Slovakia (miargyrite, andorite, ramdohrite, fizelyite, owyheeite, freieslebenite, robinsonite etc.) are present among investigated mineral assemblages. Mineral phases of $AgCuSb_2S_4$, $Pb_7Sb_6S_{16}$, $Pb_{13}Sb_{12}S_{31}$, $Pb_8Sb_{10}S_{23}$ and Fe_5SbS_{11}, which were not known under natural conditions, have been ascertained, too.

For the first time the chemical composition of basic metallic minerals forming productive gold and silver assemblages on the Zlatá Baňa deposit, has been detaily characterized. Native gold, minerals of tetrahedrite group, sulphoantimonides of Pb, Cu — Pb, Ag — Cu, Ag — Pb (many of them were not known on the deposits of Slovakia: andorite, ramdohrite, fizelyite, owyheeite, freieslebenite, robinsonite, plumosite and others) are present among investigated minerals. The chemical composition of $AgCuSb_2S_4$, $Pb_7Sb_6S_{16}$, $Pb_{13}Sb_{12}S_{31}$, $Pb_8Sb_{10}S_{23}$, Fe_5SbS_{11} compounds, which were not known under natural conditions before, has been preliminary investigated, too. The character of mineral composition of ores from the Zlatá Baňa deposit tends more towards the gold- polymetallic deposits of the East Carpathians (volcanic areas of Romania) than towards the deposits of the West Carpathians (the deposits of Middle Slovakian neovolcanites).

The Zlatá Baňa deposit is situated in the northern part of the Slanské vrchy Mts., 13 km east by south of Prešov, in the central volcanic zone of the Zlatá Baňa complex stratovolcano, acting during Lower Sarmatian — Lower Pannonian.

This andesite stratovolcano, which is built by various types of andesites and their pyroclastics, lies directly on the older rhyolite volcano, acting during Eggenburgian — Badenian.

The central volcanic zone, which is built by the andesite complex, is areally hydrothermally altered and cross-cut by the complicated intrusive complex of dykes, necks and stocks of diorite porphyries.

Ore structures have mainly the north-south strike, dipping steeply (75°—90°) towards the east and west respectively.

Morphostructural type of ore mineralization gradually changes in the horizontal and vertical course of the ore structures in dependence on the rheologic properties of rocks. It varies from the vein-stockwork type, which is developed mainly in the andesite complex, through the brecciated type, which is developed mainly on the contacts of the andesite complex with bodies of diorite porphyries, to the stockwork-disseminated type, which is characteristic for the rhyolite complex.

Types of ore mineralization on the deposit are the following: copper-molybdenum, gold-polymetallic, copper-lead-zinc, antimony, mercury and precious opal.

The Zlatá Baňa polymetallic deposit is of the greatest importance among the objects of the ore field. On the basis of series of features, its ore mineralization could be classified with gold-polymetallic formation, which is widespread in the Carpathians (Naumenko, Gontcharuk, Koptyukh, 1986).

Ores of the Zlatá Baňa deposit are characterized by very complicated composition. More than 30 minerals have been identified by Ďuďa and others here. These minerals belong to native elements, simple and complex sulphides, sulphosalts and tellurides (Ďuďa et al., 1981).

Investigated samples of ores, mainly of vein-stockwork type, have been taken from the upper parts of the deposit, from the Gemerka and Mária adits respectively. Samples No. 1, 2, 3, 4, 5, 6, 11 were taken on the Gemerka adit horizon (the P-6 crosscut, mine face, 105 m); sample No. 9 was taken from the SM-1 gate, 29 m; sample No. 10 from the store-room of explosives, the Gemerka adit, 35 m; sample No. 12 from the Sl-3 heading, mine face, 8 m, the Gemerka adit; sample No. 13 from the Sl-2 heading, mine face, 60 m, the Gemerka adit; samples No. 7 and 8 were taken from the Mária adit, 35 and 80 m from the adit collar respectively.

Mineral composition of ores from the zones with rich ore mineralization ("columns of ores"), uncovered 35 m from the Mária adit collar and 105 m from the P-6 cross-cut collar of the Gemerka adit, has appeared very variable.

Minerals of tetrahedrite group and various sulphoantimonides of Cu, Cu — Pb, Pb — Ag — Cu and Ag — Pb, play an important role in the above zones, along with widespread pyrite, sphalerite, chalcopyrite, arsenopyrite and marcasite. These minerals are of less importance in ores from other parts of the deposit. Native gold and silver occur only in the zones with rich mineralization.

Minerographic investigations and observations of mutual relations of metallic minerals witness for the origin of native gold and silver, minerals of tetrahedrite group and sulphoantimonides in the final stage of the formation of ore mineralization, after deposition of main mass of pyrite, sphalerite, galena and chalcopyrite, which are the principal minerals of polymetallic ore mineralization. Because minerals of gold and silver play an important role in the composition of relative late assemblages, these are defined, in agreement with ideas of Petrovskaya (1973), as productive ones.

Investigations, made by wide utilization of X-ray spectroscopy, enabled to identify boulangerite, miargyrite, Cu miargyrite, plumosite, robinsonite, andorite, ramdohrite, diaphorite, freieslebenite, owyheeite, berthierite, and a number of others, maybe new mineral phases, for the present without the name: ($AgCuSb_2S_4$, $Pb_7Sb_6S_{16}$, $Pb_{13}Sb_{12}S_{31}$, $Pb_8Sb_{10}S_{23}$, Fe_5SbS_{11}), and investigate the chemical composition of native gold, minerals of tetrahedrite group, bournonite, luzonite, sphalerite and arsenopyrite.

Basic productive assemblages will be discussed in the submitted article and specialities of chemical composition of minerals, which form them, will be characterized.

Native gold

The increased content of gold in ores of the Zlatá Baňa deposit was known long ago, but its mineral forms have not been investigated. Native gold has been ascertained in ore bodies uncovered in both adits.

Very small inclusions of native gold are rarely present in sphalerite (Fig. 1a) in samples of polymetallic ores taken on the Gemerka adit horizon, in the area of the P-6 cross-cut (105 m). Ore mineralization is represented by minerals of early assemblages — by sphalerite, pyrite, galena and chalcopyrite. Bournonite, low and high Ag tetrahedrite, freibergite, boulangerite, plumosite and mineral $Pb_7Sb_6S_{16}$ are present in smaller quantities.

Native gold is more abundant in ores from the part of the ore body enriched by utility components, which is uncovered on the horizon of the Mária adit, 35 m from the adit collar. Accumulations of native gold occur here along with thin, ramifying veinlets of dolomite, which cut aggregates of older sphalerite, galena and pyrite. Elongated, xenomorphic inclusions of gold are present either in galena, sphalerite, chalcopyrite, pyrite or on boundaries of these minerals (Fig. 1b, c, d). High Ag tetrahedrite, bournonite, boulangerite and other sulphoantimonides often occur along with native gold (Fig. 1d).

The analysis of 5 grains of native gold from the Mária adit has shown a remarkable constancy of their composition: Au — 81.50—82.64 wght. %; Ag — 17.37—18.86 wgt. %; Small quantities of Cu (0.04—0.08 wgt. %) and Hg (0.05—0.1 wgt. %) have been determined, too.

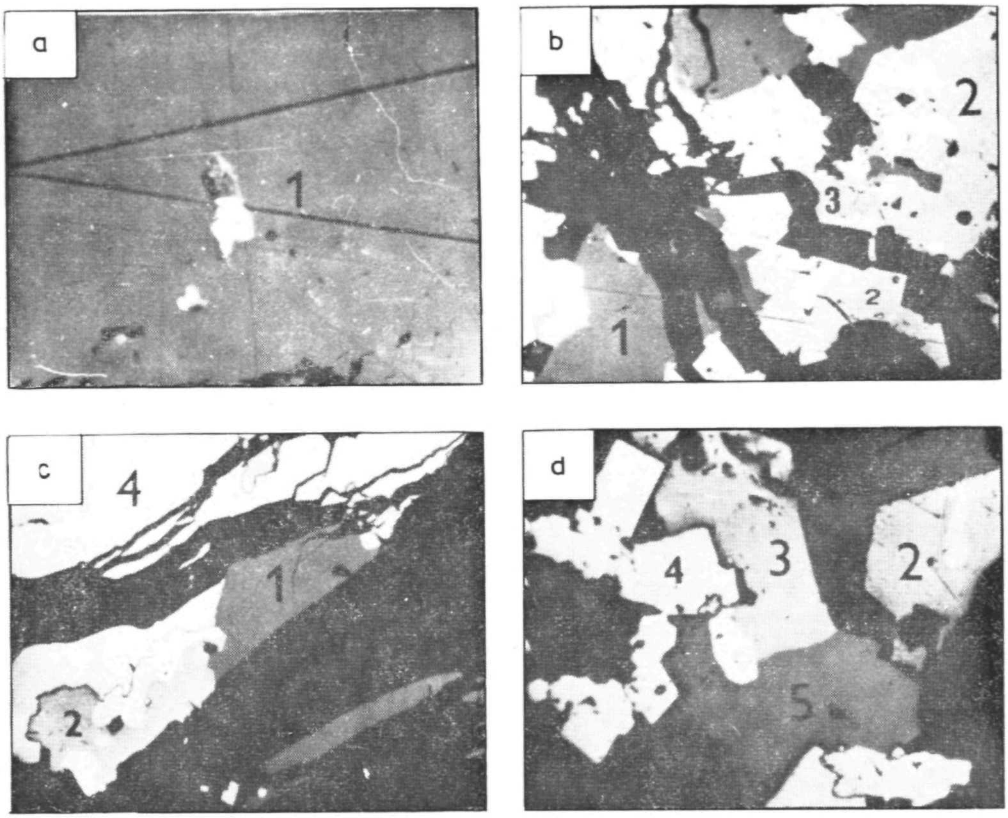

Fig. 1. Morphology of native gold segregations (white). a — in sphalerite (1), magn. x500; b — between sphalerite (1), galena (2) and chalcopyrite (3) near dolomite veinlet (black), magn. x200; c — on boundary of galena (2) and pyrite (4), black — dolomite, dark grey (1) — sphalerite, magn. x200; d — between sphalerite (1), galena (2), chalcopyrite (3), pyrite (4) and high Ag tetrahedrite (5), magn. x320.

Minerals of tetrahedrite group

Tennantite, low and high Ag tetrahedrite and freibergite have been determined among minerals of tetrahedrite group on the basis of their chemical composition.

Tennantite, usually closely associating with luzonite, has been ascertained in 29 m of the SM-1 gate, and in the store-room of explosives and in 80 m of the Mária adit. Most often it forms thin veinlets in older chalcopyrite (Fig. 2a) or it grows, along with luzonite, on chalcopyrite.

Low Ag tetrahedrite occurs almost everywhere, most often in association with chalcopyrite, they both fill either spaces between grains of pyrite or they form filling of cracks and irregular segregations in sphalerite (Fig. 1b).

High Ag tetrahedrite and freibergite occur mainly in richer parts of ore bodies. They form, along with native silver, thin veinlets in chalcopyrite (Fig. 2c), rounded segregations, or along with chalcopyrite they form veinlets in bournonite (Fig. 2d, e), they grows on tennantite and chalcopyrite (Fig. 2f).

Observed relations of minerals of the

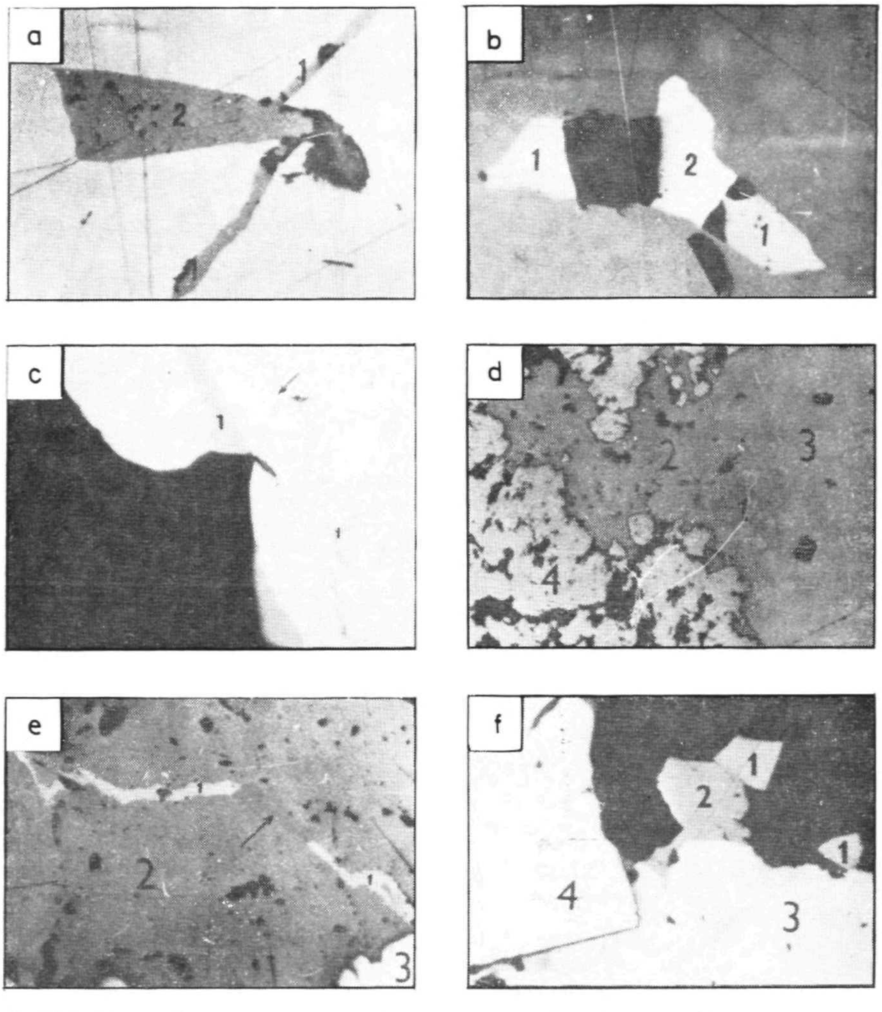

Fig. 2. Relations of minerals of tetrahedrite group with sulphides. a — veinlet of tennantite (1) and luzonite (2) in early chalcopyrite, magn. x500; b — intergrowth of low Ag and high Zn tetrahedrite (1) with chalcopyrite (2) in sphalerite, magn. x200; c — veinlets of high Ag tetrahedrite (1) with native silver (white, with arrow) in chalcopyrite, magn. 500; d — inclusion of freibergite (1) in bournonite (2) on boundary of galena (3) and pyrite (4), magn. x200; e — veinlet of high Ag tetrahedrite (shown with arrow) and chalcopyrite (1) in bournonite (2), pyrite (3), magn. x320; f — crystals of high Ag tetrahedrite (1) growth on tennantite (2) and chalcopyrite (3), pyrite — 4, magn. x200.

tetrahedrite group with sulphides enable to suppose that tennantite is the earliest mineral of this group and high Ag tetrahedrite and freibergite are the latest ones.

Chemical composition of minerals of the tetrahedrite group has been studied on 27 separated samples, which represent ore mineralization (including rich parts) on both horizons. It follows, from the results of analyses summarized in Tab. 1 that

TAB. 1

Chemical composition (wgt. $^0/_0$) of tennantite and minerals of tetrahedrite-freibergite series from the Zlatá Baňa deposit

No. of analyse	No. of sample	Cu	Ag	Fe	Zn	Sb	As	S	Sum
1	9— 2a	44.53	0.93	6.99	0.20	0.00	19.28	28.79	100.72
2	9— 4	43.61	0.71	4.77	2.88	0.00	20.01	28.81	100.79
3	2— 2	37.67	0.43	0.38	7.78	28.84	0.49	25.43	101.05
4	2— 1b	37.27	0.81	0.29	7.57	27.94	2.10	25.17	101.15
5	6— 2	37.14	1.46	0.50	7.42	28.77	0.41	25.15	100.85
6	2— 1a	37.20	2.09	0.31	7.89	26.14	1.57	25.29	100.59
7	6— 3a	36.37	2.71	0.90	7.10	29.18	0.00	25.16	101.42
8	2— 3	36.46	3.18	0.37	7.53	28.86	0.00	25.05	101.45
9	10— 7	34.36	7.39	3.30	4.45	27.12	0.72	23.96	101.30
10	10— 6	34.40	8.21	2.63	4.73	26.65	0.00	24.08	101.70
11	6— 3	26.25	17.44	3.24	3.65	27.16	0.39	23.76	101.89
12	9— 5	25.93	17.98	6.22	0.17	27.88	0.00	23.37	101.55
13	8—24b	22.55	19.36	4.43	2.86	26.22	0.32	22.92	98.70
14	9— 3	23.79	19.57	5.29	1.76	27.61	0.00	23.78	101.80
15	8—28	23.00	19.64	4.20	2.59	25.58	0.40	22.70	98.11
16	8—27	22.70	19.74	4.43	2.53	26.80	0.26	23.00	99.46
17	8— 7	23.77	19.92	4.40	2.35	27.85	0.57	23.40	102.26
18	8—26	22.57	20.37	4.24	2.38	25.09	0.92	22.63	98.20
19	8—16	23.00	20.83	3.67	3.26	26.00	0.55	23.00	100.31
20	8—19b	21.58	20.85	4.12	2.26	26.43	0.20	22.64	98.08
21	8—33	21.76	21.48	4.00	2.28	26.88	0.12	22.68	99.21
22	8—18	21.75	21.48	3.97	2.88	26.55	0.12	22.80	99.55
23	8—17	21.84	21.61	4.35	2.37	26.00	0.28	22.72	99.17
24	10—11	22.92	21.70	4.26	2.52	27.46	0.21	22.50	101.87
25	8—19a	21.87	22.25	4.70	1.61	21.06	3.36	23.00	97.85
26	10—10	22.61	22.56	4.91	2.43	27.17	0.60	22.45	102.70
27	2—10	21.68	22.67	4.11	2.26	26.83	0.00	22.85	100.40

1—2 — tennantite, 3—27 — minerals of tetrahedrite-freibergite series, 13, 15, 16, 18—23 and 25 — analyses performed by Sandomirskaya, the others by Malov.

contents of all elements, which entered into the composition of minerals of the tetrahedrite group, undergo variations.

Tennantite (analyse No. 1 and 2) is characterized by the low content of silver (below 1 wgt. $^0/_0$), by prevailing content of iron over that of zinc and by the lack of antimony, i. e. it corresponds, according to its composition, to rare variety of tennantite — lauranite — $Cu_{10}Fe_2As_4S_{13}$.

Two groups have been defined among minerals of tetrahedrite-freibergite series according to their chemical composition in ores of the Zlatá Baňa deposit. Tetrahedrite with low Ag content (0.43—3.19 wgt. $^0/_0$, analyses No. 3—8), in which iron strongly prevails over antimony and arsenic, belongs to the first group. This mineral can be considered as a variety of tetrahedrite containing silver — siegerlandite $Cu_{10}Zn_2Sb_4S_{13}$. Tetrahedrites characterized by the average (7—8 wgt. $^0/_0$) and high (17—22 wgt. $^0/_0$) content of silver (analyses No. 9—27) and freibergites (over 22 wgt. $^0/_0$ of Ag) belong to the second group. Iron prevails over zinc in all these minerals and the content of antimony is the same, on the whole, as in low Ag tetrahedrites.

Variations of Ag relations (Ag/Ag + Cu),

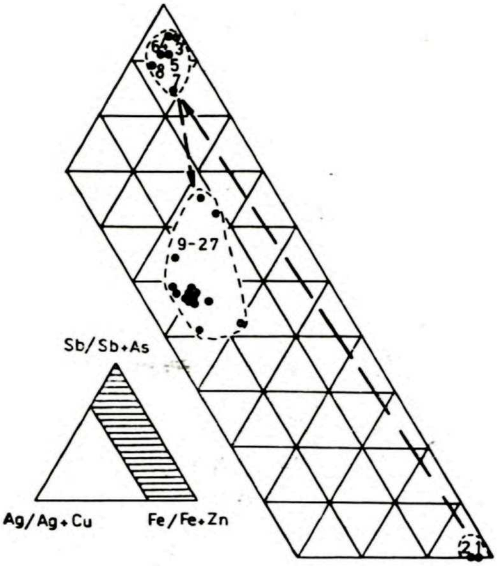

Fig. 3. Diagram of variations of Ag/Ag + Cu, Fe/Fe + Zn and Sb/Sb + As ratios in minerals of tetrahedrite group of the upper parts of the Zlatá Baňa deposit. The arrow shows supposed succession of crystallization of minerals. Numerals — numbers of analyses from Tab. 1.

Fe relations (Fe/Fe + Zn) and Sb relations (Sb/Sb + As) in minerals of the tetrahedrite group can be seen in diagram (Fig. 3). The arrow in this diagram shows supposed evolution of the chemical composition of minerals of the above group: the content of antimony increases, while the content of iron decreases from the earliest to the latest generations respectively, the content of silver increases paralelly with it. Described law is, on the whole, a typomorphic one for minerals of the tetrahedrite group of gold — silver — polymetallic ores of volcanic arcs (Kovalenker, Bortnikov, 1985).

Minerals of miargyrite — $AgCuSb_2S_4$ series

Miargyrite, which is a common mineral for some types of gold and silver ore mineralization in volcanic arcs, is very rare on the deposits of Slovakia. Miargyrite and mineral $AgCuSb_2S_4$, similar in composition to miargyrite, have been discovered in parts of ore bodies enriched by chalcopyrite, in store room for explosives on the Gemerka adit horizon and 35 m from the Mária adit collar.

Segregation of miargyrite and mineral $AgCuSb_2S_4$ are present, as a rule, in chalcopyrite, or they are present in pyrite — chalcopyrite aggregates (Fig. 4). Crystal intergrowths of miargyrite containing Cu (up tu 3 wgt. %) with $AgCuSb_2S_4$ mineral have been observed in a great number of cases (Fig. 4c—e), however, they more often occur in form of single grains of these minerals. Segregations of high Ag tetrahedrite, owyheeite, and other minerals are often present near accumulations of miargyrite and $AgCuSb_2S_4$ mineral phase (Fig. 4a), while crystal intergrowths have been observed only between $AgCuSb_2S_4$ mineral phase and high Ag tetrahedrite. The high content of copper, which is complementary to silver (Tab. 2, Fig. 5), is a specific characteristic of the composition of miargyrite from the Zlatá Baňa deposit. According to the latest handbooks (Minerals of precious metals: Handbook, 1986), the concentration of copper in miargyrite does not reach 1 wgt. %. Practically continual changes of Ag/Cu ratio up to Ag:Cu = 1 : 1.36 have been observed in this mineral from the Zlatá Baňa deposit (Fig. 5).

A remarkable part of analyses is concentrated around the point, in which the Ag/Cu ratio is 1 : 1 (analyses No. 14—24), i. e. it corresponds to the composition of $AgCuSb_2S_4$ mineral phase. The probability of discovery of continuous succession between miargyrite and chalcostibite is small, because the above minerals are not isostructural (Cc, a = 12.86; b = 4.41; c = 13.22; β = 98°38′; Z = 8 for miargyrite; Pnma, a = 6.14; b = 3.91;

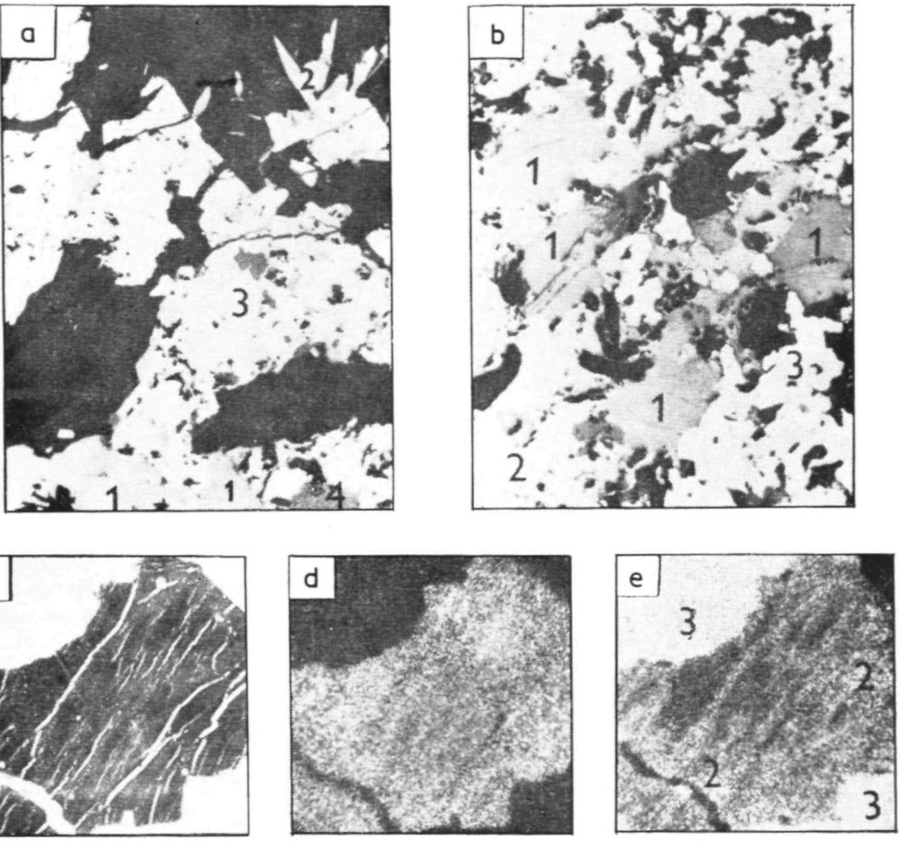

Fig. 4. Miargyrite and $AgCuSb_2S_4$ mineral phase. a — relations of miargyrite (1) and owyheeite (2) with chalcopyrite (3) with inclusions of sphalerite (4), magn. x200; a group of grains of $AgCuSb_2S_4$ mineral phase (1) in chalcopyrite (2) and pyrite (3), magn. x200; c—e — relicts of miargyrite (1) in $AgCuSb_2S_4$ mineral phase (2) in chalcopyrite (3), magn. x800; c — picture in absorbed electrons; d — Ag; e — Cu.

$c = 14.53$; $Z = 4$ for chalcostibite). Preliminary data has shown that X-ray diffraction patterns of miargyrite and $AgCuSb_2S_4$ mineral phase are close. It enables to look at these minerals as terminal members of isomorphous series. Miscibility between $AgCuSb_2S_4$ mineral phase and chalcostibite is probably limited.

Sulphoantimonides

Manifestations of antimony mineralization were known in the Zlatá Baňa ore field a long ago. Bournonite, boulangerite and berthierite have been described from the Zlatá Baňa polymetallic deposit. Antimonite, boulangerite and jamesonite have been described from the Zlatá Baňa antimony deposit. The presence of Ag sulphoantimonides was supposed here (Ďuďa et al., 1981).

We have identified sulphoantimonides in samples from the Gemerka adit (samples No. 1, 3, 6, 10, 11) and from the Mária adit (sample No. 8). Thanks to detailed

TAB. 2

Chemical composition (wgt. %) of minerals of miargyrite $AgCuSb_2S_4$ mineral phase series

No. of analyse	No. of sample	Ag	Cu	Sb	As	S	Sum
1	8—31a	35.92	0.50	40.20	0.63	21.86	99.11
2	10—21	34.32	1.39	40.32	1.16	21.60	98.79
3	8—90a	32.04	2.80	42.27	0.00	22.42	99.53
4	8—82a	32.09	3.02	41.89	0.00	22.04	99.04
5	8—85a	31.74	3.52	42.17	0.00	22.08	99.51
6	10—22	31.18	3.57	41.61	0.49	22.14	98.99
7	8—90c	30.76	3.61	41.08	1.18	22.59	99.22
8	8—93a	30.00	4.68	41.75	0.49	22.12	99.04
9	8—80	27.68	6.15	42.45	0.44	22.53	99.25
10	10—24a	26.80	6.18	43.36	0.20	22.27	98.81
11	8—89	26.75	6.83	42.90	0.71	22.91	100.10
12	10—23	23.71	8.47	43.26	0.76	23.71	99.29
13	8—88	22.42	9.58	43.54	0.22	23.00	98.76
14	8—90b	21.38	10.80	43.55	0.82	23.60	100.15
15	8—85b	21.20	10.87	43.61	0.71	23.60	99.99
16	8—81	20.17	11.10	44.63	0.58	23.21	99.69
17	8—82b	20.39	11.35	43.43	1.00	23.71	99.88
18	8—15	20.44	11.40	44.00	0.54	23.60	99.98
19	8—78	20.23	11.62	44.07	0.59	23.12	99.63
20	8—77	19.84	11.72	43.95	0.51	23.59	99.61
21	8—31b	18.87	11.90	43.31	0.48	23.22	97.78
22	8—29	18.12	12.20	42.93	0.70	23.18	97.13
23	8—79	19.61	12.36	43.05	0.67	23.59	99.28
24	8—93b	19.21	12.67	43.76	1.21	23.48	100.34
25	8—84	17.68	12.94	44.51	0.61	24.29	100.03
26	8—30	16.44	13.45	44.07	0.14	23.40	97.50
27	8—87	17.35	13.94	43.67	0.62	23.69	99.27

Analyses performed by Sandomirskaya.

study of chemical composition of sulphoantimonides by electron microprobe analyzer, we have identified bournonite, boulangerite, minerals close related to semseyite, plumosite, robinsonite, mineral phases of transitive composition ($Pb_{13}Sb_{12}S_{31}$, $Pb_8Sb_{10}S_{23}$) and also owyheeite, diaforite, freieslebenite, andorite, fizelyite. Besides, chemical composition of antimonite, berthierite, mineral phase similar to pyrite, which composition is close to Fe_5SbS_{11}, has been studied. These minerals have been discovered in single sample (No. 12) from the Sl-3 heading of the Gemerka adit.

Sulphoantimonides, as a rule, are closely intergrown (Fig. 6). They are usually present in carbonate veinlets on boundaries of grains of older galena, chalcopyrite and pyrite, they grow, corrode and replace them. Most often the accumulations of sulphoantimonides occur along with galena. According to the observed relations, bournonite is the oldest mineral among sulphoantimonides.

Results of study of chemical composition of Pb sulphoantimonides are given in Tab. 3 and they are also depicted on diagram (Fig. 7). These data have shown that the composition of studied minerals coincides with the area between falkmanite $Pb_3Sb_2S_6$ and tintinaite $Pb_5Sb_8S_{17}$.

Boulangerite and other needle sulpho-

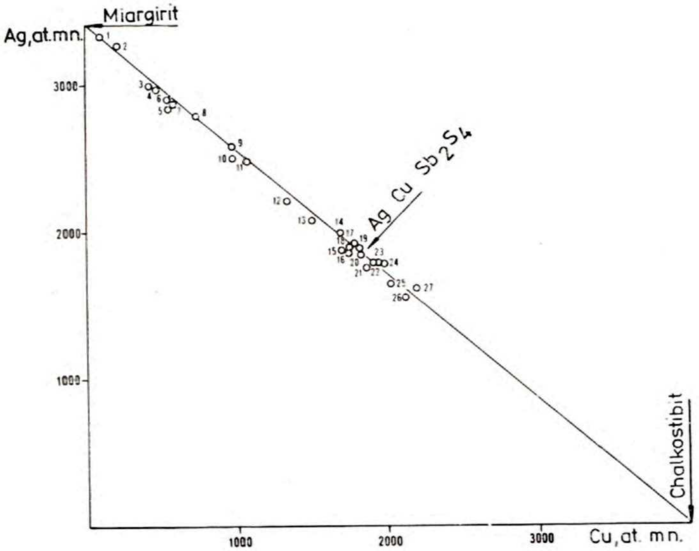

Fig. 5. Diagram of dependence between the contents of Ag and Cu (in at. wgt.) in minerals of miargyrite — $AgCuSb_2S_4$ mineral phase series. Numerals — numbers of analyses from Tab. 2.

antimonides of Pb are minerals with variable composition. A large number of minerals belongs to this group, among them such relatively abundant as boulangerite, zinckenite, jamesonite, but, on the other hand, such rare as plumosite, robinsonite, falkmanite and even those, which are known from rare occurences, discovered only in the last years: launayite, dadsonite, playfairite and other minerals (Mozgova, 1985).

Minerals belonging to the solid solution of boulangerite (Fig. 7) have been distinctly defined among studied sulphoantimonides of Pb on the basis of their chemical composition. The composition of studied grains of boulangerite coincides with the area of natural boulangerite (Mozgova, 1985). Pb:Sb ratio ranges in them from 1.24—1.26 (analyses No. 1, 2) to 1.20 (analyse No. 6), i. e. towards decreasing PbS content.

A group of analyses (No. 9—19) is situated between the area of boulangerites and semseyite, which forms a quasi-continuous series. Only some of them (No. 11, 19) draw near composition of semseyite, while most of them can be expressed by formula of $Pb_7Sb_6S_{16}$ (Tab. 3, Fig. 7). The above minerals, as a rule, occur in close intergrowths with boulangerite and other sulphoantimonides, which does not enable to gain their reliable X-ray characteristics. The lack of these data complicates the identification of mineral phase with composition $Pb_7Sb_6S_{16}$. It can be classified conditionally with the group of semseyite. Its formula can be expressed, according to the idea of Mozgova (1985) as $Pb_{3+2n}Sb_8S_{15+2n}$ (n above 2.75).

Two groups of analyses are situated between composition of semseyite and plumosite (Fig. 7). The first of them (No. 20—25)draws near the formula of $Pb_{13}Sb_{12}S_{31}$, the second draws near composition of plumosite $Pb_2Sb_2S_5$.

Sulphoantimonides of Pb, in which PbS:Sb_2S_3 ratio is shifted towards antimony, are present in ores of the Zlatá Baňa deposit in form of compounds, which composition draws near the formula $Pb_8Sb_{10}S_{23}$ (analyses No. 29—30) and robinsonite (analyses No. 31—32). Robinsonite usually forms tiny (10—15 μm) vermi-

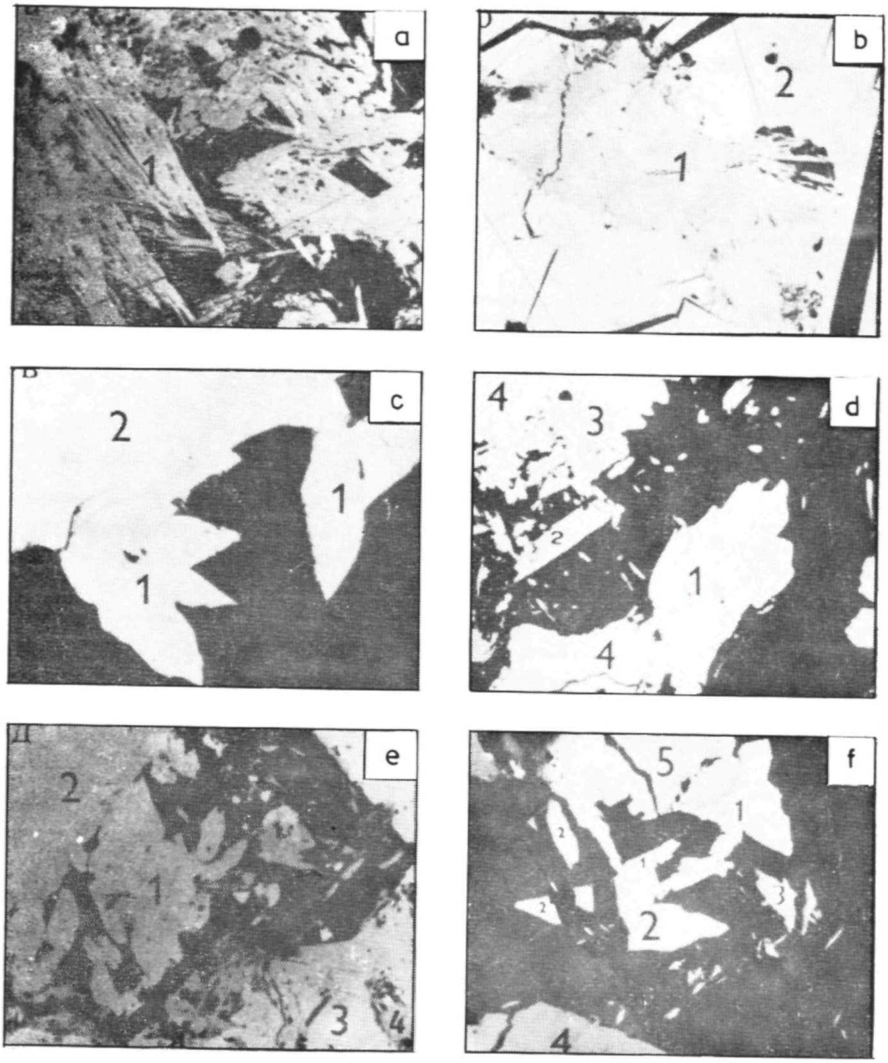

Fig. 6. Sulphoantimonides of Pb, Cu — Pb, Ag — Pb. a — boulangerite (1) in carbonate (black), magn. x200; b — boulangerite (1) in galena (2), cut by veinlets of dolomite (black), magn. x200; c — plumosite (1) growths on bournonite (2), magn. x200; d — $Pb_{13}Sb_{12}S_{31}$ mineral phase (1), $Pb_7Sb_6S_{16}$ mineral phase (2), bournonite (3), and galena (4) in dolomite (black), magn. x200; e — fine mixture of freieslebenite, diaphorite and mineral similar to semseyite — $Pb_7Sb_6S_{16}$ (1) in galena (2) and chalcopyrite (3) with inclusions of miargyrite (4), magn. x200; f — plumosite (1), diaphorite (2) and ramdohrite (3) in carbonate (dark grey), sphalerite (4) and bournonite (5), magn. x200.

cular inclusions in some grains of mineral, which is similar to plumosite (analyses No. 26—28). These intergrowths remind textures of disintegration of solid solution.

Textural investigation of most studied sulphoantimonides of Pb did not manage because of very small sizes of their segregations and close intergrowths. So it is

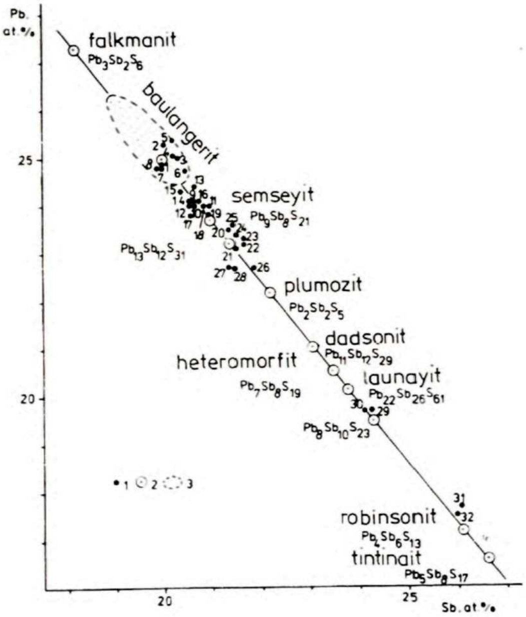

Fig. 7. Diagram of dependence of the contents of Pb and Sb (in at. %) in sulphoantimonides of lead from the Zlatá Baňa deposit. 1 — numbers of analyses from Tab. 3, 2 — theoretical composition of minerals, 3 — the area of composition of natural boulangerite (according to Mozgova, 1985).

premature to make any conclusion on mineral individuality of mineral phases $Pb_7Sb_6S_{16}$, $Pb_{13}Sb_{12}S_{31}$, $Pb_8Sb_{10}S_{23}$ only on the basis of their chemical composition.

Another group of antimony compounds, represented by sulphoantimonides of Pb and Cu, Pb and Ag, forming usually close intergrowths with sulphoantimonides of Pb (Fig. 6e, f) is present in ores of the Zlatá Baňa deposit.

Arsenic has not been determined in bournonite from the Zlatá Baňa deposit (Tab. 4) contrary to some gold-polymetallic deposites of the Romanian Carpathians, where members of seligmanite-bournonite series are predominantly developed. Formula of this basic mineral of sulphoantimonide mineralization of the Zlatá Baňa deposit is close to formula of $CuPbSbS_3$.

A number of mineral phases can be defined among sulphoantimonides of lead and silver on the basis of their chemical composition (Tab. 4), their composition corresponds to the composition of well-known minerals (Fig. 8). Analyses No. 16—17 recalculate very well to formula $AgPb_2Sb_3S_7$, which corresponds to ramdohrite, described by Bondarev et al. (1971), but they differ from formulae of this mineral, which were suggested by Ahlfeld (1930) and by Hellner (1958). The composition of one grain of mineral similar to ramdohrite (analyse No. 18) is closer to the composition of fizeleyite (Fig. 8). The question is open, because X-ray spectroscopy has not managed up to now.

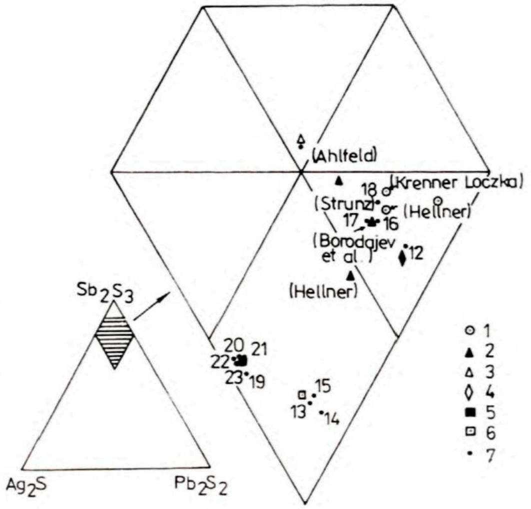

Fig. 8. Part of Ag_2S-Pb_2S_2-Sb_2S_3 diagram. The relation of real compositions of sulphoantimonides of Ag from the Zlatá Baňa deposit and theoretical compositions (according to literature) of some minerals of Ag-Pb-Sb-S system. 1 — fizelyite, 2 — ramdohrite, 3 — andorite, 4 — owyheeite, 5 — ramdohrite, 6 — freieslebenite, 7 — X-ray spectroscopic analyses of Ag sulphoantimonides from the Zlatá Baňa deposit. Numerals — numbers of analyses from Tab. 4.

TAB. 3

Chemical composition (wgt. %) of Pb sulphoantimonides

No. of analyse	No. of sample	Pb	Sb	S	Sum	Formula
1	1—1—1	54.90	25.94	18.79	99.13	$Pb_{4.98}Sb_{4.00}S_{11.02}$
2	8—27b—1	54.94	25.58	18.35	98.87	$Pb_{5.06}Sb_{4.01}S_{10.93}$
3	8—27b—2	54.74	26.19	18.51	99.44	$Pb_{5.00}Sb_{4.07}S_{10.93}$
4	8—27c	54.50	25.87	18.39	18.76	$Pb_{5.01}Sb_{4.05}S_{10.94}$
5	8—31	54.59	25.54	18.07	98.20	$Pb_{5.08}Sb_{4.05}S_{10.87}$
6	8—28a	55.12	26.82	18.81	100.75	$Pb_{4.95}Sb_{4.10}S_{10.95}$
7	8—13—5	55.71	26.31	19.05	101.07	$Pb_{4.98}Sb_{4.00}S_{11.02}$
8	8—13—6	55.66	26.26	19.22	101.14	$Pb_{4.96}Sb_{3.98}S_{11.06}$
9	1—1—4	54.45	27.35	19.14	100.94	$Pb_{7.03}Sb_{6.00}S_{15.97}$
10	1—1—7	54.29	27.59	19.43	101.31	$Pb_{6.95}Sb_{6.00}S_{16.05}$
11	1—1—2	53.71	27.62	18.97	100.29	$Pb_{6.97}Sb_{6.10}S_{15.93}$
12	1—1—3	54.91	27.15	19.27	101.32	$Pb_{6.96}Sb_{5.96}S_{16.08}$
13	8—95a	53.77	26.83	18.76	99.36	$Pb_{7.07}Sb_{6.00}S_{15.93}$
14	8—97	53.70	26.99	19.07	99.76	$Pb_{6.99}Sb_{5.98}S_{16.03}$
15	10—49a	53.19	26.32	18.74	98.43	$Pb_{7.04}Sb_{5.93}S_{16.03}$
16	10—55b	53.56	27.12	18.90	99.78	$Pb_{7.00}Sb_{6.03}S_{15.97}$
17	10—52g	53.30	27.09	19.23	99.62	$Pb_{6.91}Sb_{5.98}S_{16.11}$
18	10—58a	52.63	21.83	18.80	98.26	$Pb_{6.95}Sb_{6.02}S_{16.03}$
19	8—101b	53.37	27.59	19.15	100.11	$Pb_{6.91}Sb_{6.08}S_{16.01}$
20	8—13—2	52.87	28.24	19.20	100.31	$Pb_{13.15}Sb_{11.96}S_{30.89}$
21	8—13—3	52.33	28.62	19.39	100.34	$Pb_{12.95}Sb_{12.05}S_{31.00}$
22	8—13—9	52.26	28.05	19.36	99.67	$Pb_{13.00}Sb_{11.88}S_{31.12}$
23	8—28b	52.13	27.88	19.18	99.19	$Pb_{13.06}Sb_{11.89}S_{31.05}$
24	8—26a	52.94	28.33	19.33	100.60	$Pb_{13.11}Sb_{11.94}S_{30.95}$
25	1—1—6	53.56	28.67	19.24	101.48	$Pb_{13.22}Sb_{12.05}S_{30.73}$
26	8—29	51.08	28.93	19.31	99.32	$Pb_{2.04}Sb_{1.97}S_{4.99}$
27	8—20	51.59	28.59	19.64	99.82	$Pb_{2.04}Sb_{1.93}S_{5.03}$
28	8—19a	51.43	28.67	19.56	99.66	$Pb_{2.04}Sb_{1.94}S_{5.02}$
29	8—13—4	46.56	33.68	20.48	100.72	$Pb_{8.08}Sb_{9.95}S_{22.97}$
30	8—13—11	46.60	33.62	20.56	100.78	$Pb_{8.07}Sb_{9.91}S_{23.02}$
31	8—13—7	41.65	37.39	21.08	100.12	$Pb_{3.97}Sb_{6.05}S_{12.97}$
32	8—13—8	42.93	37.05	20.90	100.98	$Pb_{4.10}Sb_{6.01}S_{12.89}$
33	8—13—10	41.98	36.74	20.98	99.70	$Pb_{4.02}Sb_{5.99}S_{12.99}$

Analyses 1—8 — boulangerite, 9—19 — $Pb_7Sb_6S_{16}$ mineral phase similar to semseyite, 20—25 — $Pb_{13}Sb_{12}S_{31}$ mineral phase, 26—28 — "plumosite", 29—30 $Pb_8Sb_{10}S_{23}$ mineral phase, 31—33 — robinsonite. Analyses 1, 9—12 and 25 performed by Malov, the others by Sandomirskaya.

Low content of copper in the above minerals from the Zlatá Baňa deposit is remarkable from specialities of their chemical composition (Tab. 4).

The composition of other sulphoantimonides recalculates well to formulae of owyheeite (analyse No. 12), freieslebenite (analyses No. 13—15), diaphorite (analyses No. 19—23) and andorite (analyse No. 24) (see Tab. 4, Fig. 8). The presence of the above minerals in ores of the Zlatá Baňa deposit is undoubted.

Sulphoantimonides entering into the composition of productive assemblages form several constant parageneses: freieslebenite + owyheeite; diaphorite + freieslebenite + $Pb_7Sb_6S_{16}$; diaphorite + ramdohrite + $Pb_7Sb_6S_{16}$; diaphorite + plumosite + ramdohrite; diaphorite + ramdohrite + andorite. The investigation

TAB. 4

Chemical composition (wgt. %) of Cu — Pb and Ag — Pb sulphoantimonides

No. of analyse	No. of sample	Ag	Cu	Pb	Sb	S	Sum	Formula
1	3—3—9	0.09	13.17	43.32	25.73	19.39	101.70	$Cu_{1.01}Pb_{1.02}Sb_{1.03}S_{2.94}$
2	3—3—8	0.16	12.88	42.40	24.71	20.79	100.74	$Cu_{0.97}Pb_{0.98}Sb_{0.96}S_{3.09}$
3	3—2—11	0.14	12.08	42.41	25.74	19.59	100.18	$Cu_{0.94}Pb_{1.01}Sb_{1.04}S_{3.01}$
4	8a—4	0.00	12.96	43.77	25.38	19.15	101.26	$Cu_{1.00}Pb_{1.04}Sb_{1.02}S_{2.93}$
5	6—1	0.00	13.07	42.80	25.39	19.34	100.60	$Cu_{1.01}Pb_{1.01}Sb_{1.02}S_{2.96}$
6	8—20b	0.11	13.00	41.64	25.15	19.87	99.77	$Cu_{1.00}Pb_{0.98}Sb_{1.00}S_{3.02}$
7	8—52c	0.00	12.61	41.89	24.44	20.02	98.96	$Cu_{0.97}Pb_{0.99}Sb_{0.98}S_{3.06}$
8	8—61	0.00	12.47	42.76	23.63	19.60	98.46	$Cu_{0.48}Pb_{1.02}Sb_{0.98}S_{3.00}$
9	8—60	0.00	12.85	42.45	23.95	19.38	98.63	$Cu_{1.00}Pb_{1.02}Sb_{0.98}S_{3.00}$
10	8—95b	0.00	12.64	42.74	24.70	19.51	99.59	$Cu_{0.98}Pb_{1.02}Sb_{1.00}S_{3.00}$
11	8—98b	0.00	12.62	45.10	22.50	19.16	99.38	$Cu_{0.99}Pb_{1.09}Sb_{0.93}S_{2.99}$
12	8—101c	6.42	1.10	41.80	30.00	19.61	98.93	$(Ag_{1.47}Cu_{0.43})_{1.90}Pb_{4.97}Sb_{6.07}S_{15.06}$
13	8—101a	19.30	0.00	40.80	22.64	18.14	100.88	$Ag_{0.99}Pb_{1.03}Sb_{1.00}S_{2.98}$
14	8—98c	18.81	0.19	41.19	21.42	17.49	99.10	$(Ag_{0.95}Cu_{0.02})_{0.97}Pb_{1.09}Sb_{0.96}S_{2.98}$
15	8—52a	18.79	0.17	39.74	22.43	17.87	99.00	$(Ag_{0.94}Cu_{0.02})_{0.96}Pb_{1.04}Sb_{0.99}S_{3.01}$
16	10—49b	8.10	0.87	37.40	32.90	20.15	99.42	$(Ag_{0.83}Cu_{0.15})_{0.98}Pb_{2.01}Sb_{3.01}S_{7.00}$
17	8—55a	7.25	1.36	37.62	33.25	20.70	100.68	$(Ag_{0.78}Cu_{0.23})_{1.01}Pb_{1.98}Sb_{2.98}S_{7.03}$
18	9—19c	8.26	0.15	38.05	33.30	20.02	99.78	$(Ag_{0.86}Cu_{0.03})_{0.89}Pb_{2.05}Sb_{3.06}S_{7.00}$
19	8—98a	23.01	0.32	30.84	26.17	18.22	98.63	$(Ag_{2.06}Cu_{0.07})_{3.03}Pb_{2.05}Sb_{2.99}S_{7.92}$
20	8—52b	23.00	0.35	30.25	26.66	18.72	98.98	$(Ag_{2.92}Cu_{0.08})_{3.00}Pb_{2.00}Sb_{3.00}S_{8.00}$
21	8—58b	23.56	0.00	30.41	26.18	18.92	99.07	$Ag_{2.99}Pb_{2.01}Sb_{2.94}S_{8.06}$
22	8—49c	23.10	0.26	29.85	26.68	18.50	98.39	$(Ag_{2.96}Cu_{0.05})_{3.01}Pb_{1.99}Sb_{3.03}S_{7.97}$
23	8—19b	24.04	0.16	30.51	27.14	18.72	100.57	$(Ag_{3.02}Cu_{0.04})_{3.06}Pb_{2.00}Sb_{3.02}S_{7.92}$
24	10—48	10.26	1.26	24.00	41.50	22.20	99.22	$(Ag_{0.83}Cu_{0.17})_{1.00}Pb_{1.00}Sb_{2.97}S_{6.03}$

Analyses 1—11 — bournonite, 12 — owyheeite, 13—15 — freieslebenite, 16—18 — ramdohrite, 19—23 — diaphorite, 24 — andorite. Analyses 1—5 — performed by Malov, the others by Sandomirskaya.

TAB. 5

Chemical composition (wgt. %) of berthierite and Fe_5SbS_{11} mineral phase

No. of anal.	No. of sample	Fe	Co	Sb	As	S	Sum	Formula
1	12—5	12.80	0.00	55.86	0.11	29,05	97.82	$Fe_{1.00}(Sb_{2.01}As_{0.01})_{2.02}S_{3.98}$
2	12—5a	12.98	0.04	55.53	0.32	29.15	98.02	$Fe_{1.02}(Sb_{1.99}As_{0.02})_{2.01}S_{3.97}$
3	12—5b	12.68	0.04	55.46	0.33	29.11	97.62	$Fe_{1.00}(Sb_{2.00}As_{0.02})_{2.02}S_{3.98}$
4	12—4	12.69	0.45	56.07	0.38	29.80	99.39	$(Fe_{0.99}Co_{0.03})_{1.02}(Sb_{1.99}As_{0.02})_{2.01}S_{3.97}$
5	12—7	12.53	0.07	55.60	0.32	29.60	98.12	$Fe_{0.98}(Sb_{1.99}As_{0.002})_{2.01}S_{4.01}$
6	12—7a	12.51	0.06	56.26	0.29	29.72	98.84	$Fe_{0.97}(Sb_{2.00}As_{0.02})_{2.02}S_{4.01}$
7	12—1a	37.34	0.06	11.76	0.56	48.31	98.03	$(Fe_{4.98}Co_{0.01})_{4.99}(S_{11.23}Sb_{0.72}As_{0.05})_{12.01}$
8	12—1b	37.15	0.03	12.54	0.69	48.29	98.70	$Fe_{4.95}(S_{11.21}Sb_{0.77}As_{0.07})_{12.05}$
9	12—1c	37.84	0.07	12.64	0.49	48.48	99.52	$(Fe_{5.00}Co_{0.01})_{5.01}(S_{11.17}Sb_{0.77}As_{0.05})_{11.99}$

Analyses 1—6 — berthierite, 7—9 — $Fe_5(S, Sb)_{12}$ mineral phase. Analyses performed by Sandomirskaya.

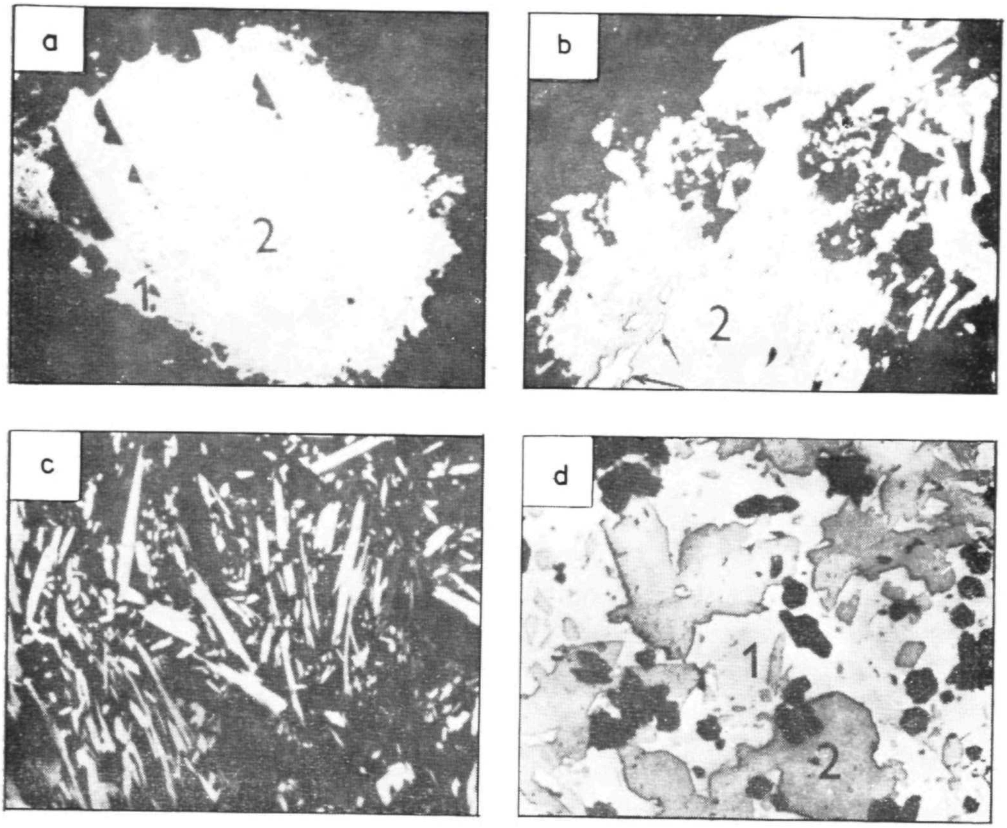

Fig. 9. Minerals of antimonite-berthierite assemblage. a — growth of antimonite (1) on galena (2), magn. x200; b — lamellar segregations of berthierite (1), skirt aggregates of antimonite grains (2), in which small segregations of Fe_5SbS_{11} mineral phase are present (shown by arrows), magn. x200; c — accumulations of lamellar grains of berthierite in carbonate, magn. x200; d — intergrowths of Fe_5SbS_{11} mineral phase (1) with antimonite (2), magn. x200.

of mutual relations of the above minerals has shown that these parageneses are very close to each other, both by the time of their origin and by the general composition of minerals, which form them. Their origin was controlled, above all, by local changes of activities of silver, lead and antimony, which were responsible for crystallization of individual sulphoantimonides.

The assemblage of antimony minerals will be concisely studied, in which antimonite, berthierite and mineral phase Fe_5SbS_{11} were identified (Fig. 9). Direct relations between the above minerals and minerals of productive assemblages have not been observed. At the same time the cases of growth of antimonite on galena do not contradict the ideas about relatively late origin of mineralization with antimonite. This origin was not earlier, in the limited case, than that of productive assemblages.

The composition of berthierite and mineral phase Fe_5SbS_{11}, which is similar to pyrite, and which often occurs intergrown with antimonite (Fig. 9), is given in Tab. 5. Analyses of berthierite recalculate well to crystallochemical formula of this mineral. The presence of small quantities of arsenic and traces of cobalt in its composition deserves attention.

The high content of antimony is characteristic for mineral, which is concurrent, according its reflectance and hardness, with pyrite, but it manifests a weak anisotropy at crossed nicols. Its composition is well recalculated to formula $Fe_5(S, Sb, As)_{12}$ or $Fe_5(Sb, As)_{11}$. X-ray diffraction patterns of the above mineral include several supplementary lines in comparison with powder X-ray diffraction patterns of pyrite.

Conclusion

Performed research has enabled to gain new data about the composition of productive assemblages of the Zlatá Baňa deposit, about specialities of the chemical composition of minerals forming these assemblages. For the first time such minerals as native gold, miargyrite, plumosite, robinsonite, owyheeite, freieslebenite, andorite, ramdohrite, diaphorite have been determined and studied in ores of this deposit. First data about the existence of compounds $Pb_7Sb_6S_{16}$, $Pb_{13}Sb_{12}S_{31}$, $Pb_8Sb_{10}S_{23}$, Fe_5SbS_{11} under natural conditions have been gained.

The above data has shown that the Zlatá Baňa deposit differs by the composition of productive mineral assemblages of its upper parts from the silver-polymetallic Banská Štiavnica deposit represented by acanthite, polybasite, pearceite, pyrargyrite, stephanite, freibergite and electrum.

At the same time productive mineralization of the Zlatá Baňa deposit has got a great number of common features with gold-silver mineralization of the Baia Mare district deposits in Romania. Miargyrite, andorite, ramdohrite, boulangerite, plumosite, bournonite and other sulphosalts of antimony are characteristic for productive assemblages of these deposits, as well as for the Zlatá Baňa deposit.

Basic correspondence has been observed in the composition of pre-productive assemblages, too. Pyrite, sphalerite and galena are their principal minerals. This all has enabled to look at mineralization of the Zlatá Baňa deposit as belonging to gold-polymetallic formation. Further investigations of metallic minerals of productive assemblages in the whole interval of ore mineralization will enable to throw light upon basic features of zoning of this deposit and to determine its prospects.

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Rudné minerály produktívnych asociácií ložiska Zlatá Baňa, zvláštnosti chemizmu

Z praktického hľadiska je v zlatobanskom rudnom poli najvýznamnejšia polymetalická mineralizácia, ktorú možno radiť k zlato-polymetalickej formácii. Rudné telesá sa priestorovo viažu na dajky dioritových porfyritov strmého sklonu (75—90 °) v smere SSZ—JJV. Zrudnenie tvorí široká asociácia rudných minerálov (Ďuďa et al., 1981). Podrobne sa študovali rudné vzorky žilníkovo-žilného typu zo štôlní Gemerka a Mária. Zrudnenie tu tvorí predovšetkým pyrit, sfalerit, galenit, chalkopyrit, arzenopyrit a markazit. Miestami majú významnú úlohu minerály skupiny tetraedritu, rôzne sulfoantimonidy a zlato. Podľa mineralogického štúdia zlato, striebro, tetraedrity a sulfoantimonidy vznikli v záverečných fázach rudnej mineralizácie, po vzniku hlavnej masy pyritu, sfaleritu, galenitu a chalkopyritu.

Rýdze zlato

Zvýšený obsah zlata v rudách bol známy dávnejšie. Ojedinelé inklúzie zlata sa zistili vo sfalerite (obr. 1a) z polymetalickej rudy v štôlni Gemerka (P-6/105 m) v asociácii s pyritom, galenitom, chalkopyritom, bournonitom, nízko- a vysokostriebronosným tetraedritom, freibergitom, boulangeritom, plumozitom a minerálom $Pb_7Sb_6S_{16}$. Zlato sa oveľa častejšie vyskytuje v štôlni Mária (35 m), viazané na jemné žilky dolomitu, pretínajúce starší sfalerit, galenit a pyrit. Xenomorfné zrnká zlata sú na okrajoch týchto rudných minerálov (obr. 1b, c, d). Zlato často sprevádza vysokostriebronosný tetraedrit (obr. 1d), bournonit, boulangerit a iné sulfoantimonidy. Analyzovalo sa 5 zŕn zlata zo štôlne Mária s obsahmi Au 81,50—82,64 hmot. %, Ag 17,37—18,86 hmot. % a s prímesami Cu (0,04—0,08 hmot. %) a Hg (0,05—0,10 hmot. %).

Tetraedrity

Na základe chemického zloženia sa na ložisku Zlatá Baňa vyskytuje tennantit, nízko- a vysokostriebronosný tetraedrit a freibergit. Tennantit je v asociácii s luzonitom (štôlňa Gemerka, Sm-1/29 m, štôlňa Mária — 80 m). Časté sú jeho jemné žilky v chalkopyrite (obr. 2a) alebo spolu s luzonitom narastá na chalkopyrit. Nízkostriebronosný tetraedrit je najčastejšie v asociácii s chalkopyritom, s ktorým tmelí agregáty pyritových zŕn alebo pretína zrná sfaleritu (obr. 1b).

Vysokostriebronosný tetraedrit a freibergit sa nachádza v nadurených častiach rudných telies. Spolu s rýdzim Ag tvorí drobné žilky v chalkopyrite (obr. 2c) alebo s chalkopyritom žilky v bournonite (obr. 2d, e). Zo zistenej asociácie a mikroskopického charakteru je zrejmé, že z minerálov tetraedritovej skupiny je najstarší tennantit a najmladší vysokostriebronosný tetraedrit a freibergit. Chemické zloženie minerálov tetraedritovej skupiny je v tab. 1.

Tennantity (analýza 1 a 2) majú nízky obsah Ag (pod 1 hmot. %), viac Fe ako Zn a neobsahujú Sb. Zložením zodpovedajú zriedkavej variete tennantitu — lauranitu $Cu_{10}Fe_2As_4S_{13}$. Veľmi rozšírené sú minerály tetraedritovo-freibergitového radu. V prvej skupine (analýza 3—8) sú nízkostriebronosné tetraedrity (obsah Ag od 0,43 do 3,18 hmot. %) s prevahou Zn nad Fe a Sb nad As. Zložením zodpovedajú variete tetraedritu — siegerlanditu $Cu_{10}Zn_2Sb_4S_{13}$. V druhej skupine (analýza 9—27) sú tetraedrity s mierne zvýšeným obsahom Ag (7—8 hmot. %) a vysokým obsahom Ag (17—22 hmot. %) a freibergity (nad 22 hmot. % Ag). Vo všetkých týchto minerálоch prevláda Fe nad Zn a Sb nad As. Variáciu striebritosti (Ag/Ag + Cu), železitosti (Fe/Fe + Zn) a antimonnosti (Sb/Sb + As) v minerálоch tetraedritovej skupiny zo Zlatej Bane uvádzame v diagrame na obr. 3. Zistené výsledky sú typické pre tetraedrity zlatých a strieborných polymetalických ložísk vulkanických zón (Kovalenker, Bortnikov, 1985).

Minerály radu miargyrit — mineral $AgCuSb_2S_4$

Minerály tohto radu boli zistené v štôlňach Gemerka aj Mária v asociácii s chalkopyritom a pyritom (obr. 4). V okolí vysokostriebronosného tetraedritu a owyheeitu (obr. 4a) je Cu-miargyrit (do 3 hmot. % Cu) často prerastený minerálom $AgCuSb_2S_4$ (obr. 4c—e). Pre miargyrit zo Zlatej Bane je charakteristický vysoký obsah Cu, komplementárny s Ag (tab. 2, obr. 5). Pomer Ag : Cu = 1 : 1,36 (obr. 5) je vyšší, než je doposiaľ v miargyritoch známe (obsah Cu do 1 hmot. %). Oba minerály (miargyrit aj minerál $AgCuSb_2S_4$) boli študované aj rtg analýzami. Vzhľadom na to, že sú si röntgenogramami veľmi blízke, možno ich považovať za krajné členy izomorfného radu, pretože medzi miargyritom a chalkostibitom pravdepodobne nejestvuje nepretržitý rad, lebo oba minerály nie sú izoštruktúrne.

Sulfoantimonidy

Boli na ložisku Zlatá Baňa známe už dávnejšie (bournonit, boulangerit, berthierit a jamesonit; Ďuďa et al., 1981). Hlbším štúdiom sulfoantimonidov zo štôlne Gemerka a Mária boli zistené ďalšie minerály, blízke semseyitu, plumozitu, robinsonitu, fázam $Pb_{13}Sb_{12}S_{31}$ a $Pb_8Sb_{10}S_{23}$, ale tiež owyheeitu, diaforitu, freieslebenitu, andoritu a fizélyitu. Zistený bol minerál zloženia Fe_5SbS_{11}, podobný pyritu. Sulfoantimonidy sa spravidla vyskytujú v tesnej asociácii, tesne poprerastané (obr. 6), viazané na karbonátové žilky, miestami aj s galenitom. Chemické zloženie sulfoantimonidov je v tab. 3 a výsledky sú vynesené v diagrame (obr. 7). Chemické zloženie boulangeritu je blízke variáciám prírodného boulangeritu (obr. 7; Mozgova, 1985). Pomer iónov Pb : Sb je od 1,24 do 1,26 (analýza 1 a 2) a do 1,20 (analýza 6), teda do oblasti znižovania obsahu molekuly PbS. Medzi oblasťou boulangeritov a semseyitov je skupina analýz (analýza 9—19) akoby neprerušeného radu. Vzhľadom na to, že minerály sú vzájomne tesne poprerastané, nemožno z nich vyhotoviť rtg analýzy, čo sťažuje bližšiu identifikáciu fázy $Pb_7Sb_6S_{16}$, blízkej skupine semseyitu. Medzi zložením semseyitu a plumozitu sú dve skupiny analýz (obr. 7). Prvá z nich (analýza 20—25) zodpovedá kryštalochemickému vzorcu $Pb_{13}Sb_{12}S_{31}$, druhá (analýza 26—28) je blízka zloženiu plumozitu $Pb_2Sb_2S_5$.Sulfoantimonidy Pb, v ktorých pomer $PbS : Sb_2S_3$ je v prospech Sb, predstavujú v zlatobanských rudách zlúčeniny, zloženie ktorých je blízke $Pb_8Sb_{10}S_{23}$ (analýza 29—30) a robinsonitu (analýza 31—32). Robinsonit tvorí drobné (10—15 m) červíkovité vrastlice v mineráli blízkom plumozitu, veľmi pripomínajúce štruktúry rozpadu pevných roztokov. Túto identifikáciu sulfoantimonidov Pb zo Zlatej Bane považujeme iba za orientačnú.

Ďalšou skupinou sulfoantimonidov v Zlatej Bani sú sulfoantimonidy Pb — Cu a Pb — Ag, tvoriace obyčajne zrasty so sulfoantimonidmi Pb (obr. 6c, f). V ložisku Zlatá Baňa, na rozdiel od rumunských Karpát, je zo sulfoantimonidov Pb — Cu zistený iba bournonit (tab. 4). Nezistil sa seligmanit a ďalšie prechodné As členy.

Zo sulfoantimonidov Pb — Ag (tab. 4) možno vyčleniť niekoľko fáz, zodpovedajúcich známym minerálom (obr. 8). Analýzy 16—17 zodpovedajú kryštalochemickým vzorcom $AgPb_2Sb_3S_7$ ramdohritu opísanému Borodajevom et al. (1971), ale líšia sa od vzorca ramdohritu opísaného Ahlfeldom (1930) a Hellnerom (1958). Jedna analýza (č. 18) vykázala zloženie blízke fizélyitu (obr. 8). Bez rtg analýz zostáva ich identita nedoriešená. Zloženie iných sulfoantimonidov Pb — Ag je dobre prepočítateľné na kryštalochemický vzorec owyheeitu (analýza 12), freieslebenitu (13—15), diaforitu (19—23) a andoritu (24; tab. 4, obr. 8). Prítomnosť týchto minerálov na ložisku Zlatá Baňa je nepochybná.

Sulfoantimonidy tvoria na ložisku niekoľko stálych paragenetických radov: freieslebenit — owyheeit, diaforit — freieslebenit — $Pb_7Sb_6S_{16}$, diaforit — ramdohrit — minerál $Pb_7Sb_6S_{16}$, diaforit — plumozit — ramdohrit, diaforit — ramdohrit — andorit. Dané paragenetické rady poukazujú na časovú blízkosť ich vzniku.

Pri štúdiu chemického zloženia antimonitu, berthieritu a minerálu Fe_5SbS_{11} (obr. 9) sa nezistil priamy vzťah týchto minerálov k predchádzajúcim asociáciám. Zloženie berthieritu a minerálu Fe_5SbS_{11} je v tab. 5. Minerál Fe_5SbS_{11} je odraznosťou a tvrdosťou zhodný s pyritom, ale je slabo anizotropný a má vysoký obsah Sb.

Záver

V ložisku Zlatá Baňa sme objavili celý rad nových minerálov, ktoré sa doteraz na Slovensku nenašli. Zistili sa nové prírodné zlúčeniny, doteraz inde neznáme — $Pb_7Sb_6S_{16}$, $Pb_{13}Sb_{12}S_{31}$, $Pb_8Sb_{10}S_{23}$, Fe_5SbS_{11}.

Ložisko Zlatá Baňa sa od Ag-polymetalického ložiska Banská Štiavnica výrazne líši asociáciou Ag minerálov, pretože hlavnými nositeľmi Ag v Zlatej Bani sú sulfoantimonidy Pb — Ag (andorit, ramdohrit, diaforit, fizélyit, owyheeit a freieslebenit), kým v Banskej Štiavnici je to stephanit, pyragyrit, polybázit, pearceit, akantit atď. Zlatá Baňa má mnoho spoločných čŕt s Au — Ag mineralizáciou ložísk baia-marského rudného rajónu v Rumunsku.