Bismuth minerals of the Beregovo ore field: mineral assemblages and spatial zonation (Transcarpathian, Ukraine)

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New compositional data on Bi-mineralization from ores of epithermal gold-(± copper)-silver-base metal deposits of the Beregovo ore field in the Ukraine are presented. The Bi-minerals are developed at deep levels of these deposits and occupy narrow zones at the limits of the ore bodies. Bi-sulphosalts form a temporal range (from early to late) of: Ag-Pb-Bi and Ag-Cu-Pb-Bi (± Pb-Cu-Bi) and Bi_2S_3. Bi-minerals escaped from destruction during successive processes owing to their occurrence in a dense quartz matrix. Spatially Bi-mineralization is developed as a frontal zone of massive chalcopyrite aggregates.

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INTRODUCTION

Minerals of the Pb-Cu-Bi-Ag-S-system are typical of epithermal gold deposits, but their complexity and wide variation in chemical composition have prevented accurate determination of their correlation with Au and base metal ores. The variable mineral composition of such associations has usually been explained in terms of multistage oreforming processes.

The Beregovo ore field is situated in the Carpathian province of Neogene Au-Ag deposits, which extend from the Stiavnica stratovolcano (Slovakia) to south of the Apuseny Mountains deposits (Romania). These deposits are connected with the Intracarpathian volcanic belt. Most of the deposits of the northern segment are of epithermal, gold-base metal, adular-sericitic type (Koptuh, 1992). Ores of these deposits are characterized by the antagonism of Zn and Pb sulphides on the one hand and Cu on the other, caused by a gradual transition from an epithermal to a copper-porphyry type of oreformation.

In a number of ore bodies in the Stiavnica ore district, particularly in ores with poor but systematic content of chalcopyrite, bismuthinite and various Bi-sulphosalts have been observed. Bi-minerals are found in a similar situation in many epithermal deposits in Nevada and California (Foord *et al.*, 1988; Foord and Shawe, 1989). Literature review of deposits of such type (Foord *et al.*, 1988; Kovalenker *et al.*, 1993) indicates a decrease in the variety of bismuthinite and Bi-sulphosalts with an increase in the chalcopyrite content of the ores.

The ores of Beregovo ore field provide good material for research on this problem, as their composition gradually changes from pure Pb-Zn-Ag ores to Cu-Au ores. Our goal was to study changes in the composition of paragenesis of Bi-minerals during such a transition.

GEOLOGICAL SETTING OF BEREGOVO ORE FIELD

The Beregovo ore field includes two gold-silver-base metal deposits — Beregovo and Muzievo (Skakun *et al.*, 1992) (Fig. 1). These are situated in an explosion caldera of Sarmatian age, which is filled with fused tuffs and ignimbrites. The caldera walls are composed of alternating layers of Neogene rhyolite tuffs and sedimentary rocks, lying on a Triassic-Cretaceous basement (sandstones, limestones, phyllites, spilites). The ignimbrites are covered by maar sediments (clays, argillites, tuffites). The overlying rhyolite agglomerate tuffs frame the rhyolitic domes which are intruded along the western and southern steep rims of the caldera.

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The chemical composition of Bi-sulphosalts and bismuthinite from ores of Beregovo ore field
(X-ray microprobe analysis data)

No. analysis	Min-erals	Locality		Phase	Ag	Cu	Pb	Bi	Se	S	Sb	Au	As	Zn	Fe	Total
		hole	depth (m)							weight %						
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Or	1345i	414.5	(3)–1	14.97	0.13	19.57	45.62	0.83	15.93	0.03	0.00	0.00	0.05	0.07	97.2
2	Or	1345i	414.5	(2)–4	17.98	0.39	10.52	53.09	0.57	15.92	0.00	0.02	0.00	0.03	0.10	98.6
3	Or	1345	334.1	1	16.89	0.17	15.76	50.21	0.00	16.15	0.00	0.03	0.00	0.00	0.08	99.3
4	Or	1345i	414.5	(3)–5	20.95	0.23	5.74	57.64	0.47	16.64	0.07	0.34	0.00	0.00	0.01	102.1
5	–	1347	521.1	1–2/1	15.62	2.67	23.01	40.51	0.66	16.26	0.00	0.36	0.53	0.06	0.12	99.8
6	Or	1345i	414.5	2–1/3	17.20	0.81	12.45	49.95	0.40	16.80	0.04	0.15	1.30	0.02	0.28	99.4
7	Or	1345i	334.5	1	14.75	0.11	21.46	45.52	0.06	16.48	0.00	0.10	0.00	0.11	0.12	98.7
8	Or	1345i	414.5	3–2	10.51	0.03	35.92	38.44	0.10	12.20	0.08	0.02	1.12	0.00	0.00	98.4
9	Or	1345i	334.5	2	14.42	0.66	23.94	43.29	0.08	16.02	0.00	0.00	0.43	0.08	0.40	99.3
10	Trs	1345i	414.5	2–1/1	8.58	0.51	22.75	50.66	0.26	16.02	0.00	0.37	1.07	0.19	0.09	100.5
11	Trs	1345i	414.5	2–1/2	9.80	0.33	20.11	50.74	0.29	15.99	0.03	0.26	2.26	0.00	0.10	99.9
12	Trs	1345i	414.5	2–3	10.74	0.32	20.92	49.21	0.35	16.08	0.00	0.00	0.00	0.08	0.00	97.7
13	Gu	1347	561	–	5.72	0.32	29.20	48.62	0.68	16.33	0.00	0.28	0.00	0.02	0.03	101.2
14	S	1312	655	–	9.68	2.30	36.93	34.86	4.41	11.14	0.00	0.00	0.00	0.00	0.87	100.2
15	S	1312	655	–	9.98	1.77	38.54	29.31	3.92	12.52	0.00	0.00	0.00	027	1.29	97.6
16	Bnj	1345i	414.5	3–10/3	9.23	3.01	8.46	60.22	0.50	16.50	0.04	0.20	0.03	0.00	0.32	98.5
17	Bnj	1345i	414.5	3–10/4	11.93	2.46	8.34	59.33	0.57	16.39	0.09	0.00	0.00	0.04	0.05	99.2
18	Ber	1345i	414.5	2–2	5.56	4.82	22.28	51.68	0.36	15.03	0.07	0.00	0.06	0.02	0.02	99.9
19	Ber	1345i	414.5	2–1/4	5.05	4.98	22.10	50.05	0.67	14.60	0.03	0.18	0.23	0.00	0.00	97.9
20	–	1347	520.5	1	26.64	3.70	4.79	45.17	0.92	16.20	0.00	0.35	0.76	0.00	0.17	98.7
21	–	1347	520.5	2	26.86	8.26	9.36	37.80	0.98	16.61	0.07	0.00	0.00	0.04	0.18	100.1
22	–	1347	520.5	3	25.57	1.63	3.52	51.26	0.88	16.26	0.00	0.01	0.00	0.02	0.05	99.2
23	Gl	1347	521.1	1–2/2	0.12	5.19	14.94	60.24	0.61	16.85	0.02	0.10	0.84	0.08	0.34	99.3
24	Gl	1347	556.2	1	0.00	4.53	13.68	61.98	0.38	18.11	0.08	0.11	0.45	0.02	0.11	99.4
25	Bis	1345i	414.5	3–10/2	0.06	0.48	0.00	78.43	0.03	18.43	0.00	0.00	0.72	0.06	1.38	99.6
26	Bis	1345i	414.5	3–10/1	0.00	0.84	1.05	75.22	0.29	18.11	0.03	0.00	1.47	0.06	1.83	98.9
27	Bis	1347	556.2	2	0.16	2.26	1.81	73.67	0.46	18.02	0.04	0.00	0.67	0.02	0.69	97.8
28	Ga	1345i	414.5	3–3	0.87	0.14	82.25	1.81	0.20	14.02	0.05	0.27	0.15	0.00	0.05	99.8
29	Ga	1345	334.1	2	4.34	0.50	71.33	8.66	0.00	14.22	0.02	0.06	0.00	0.00	0.38	99.5
1r	Gu	–	–	–	3.00	0.57	39.10	40.90	n.d.	16.50	0.00	n.d.	0.44	n.d.	n.d.	100.6
2r	Gu	–	–	–	3.20	1.10	39.60	40.60	n.d.	16.00	0.15	n.d.	0.36	n.d.	n.d.	101.0
3r	Gu	–	–	–	4.40	0.20	31.80	47.80	n.d.	13.80	0.00	n.d.	0.00	n.d.	n.d.	98.0

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
4r	Gu	–	–	–	5.50	0.40	31.70	48.40	n.d.	15.70	0.00	n.d.	0.00	n.d.	n.d.	101.7
5r	Ber	–	–	–	9.90	4.40	17.50	50.80	n.d.	15.30	n.d.	n.d.	n.d.	n.d.	n.d.	97.9
6r	Ber	–	–	–	10.40	4.20	22.10	47.8	n.d.	16.50	n.d.	n.d.	n.d.	n.d.	n.d.	100.6
7r	Mt	–	–	–	20.80	0.70	22.20	40.50	n.d.	16.70	n.d.	n.d.	n.d.	n.d.	n.d.	100.9
8r	Bis	–	–	–	0.10	0.40	3.70	79.0	n.d.	16.50	n.d.	n.d.	n.d.	n.d.	n.d.	99.7

n.d. — not determined; 1r–8r — from the paper by Matkovsky *et al.* (1987) and Remeshilo *et al.* (1989); minerals: Bis — bismuthinite, Ga — galena, Or — ourayite, Gu — gustavite, Ber — berryite, Trs — treasurite, S — schirmerite, Gl — gladite, Bnj — benjaminite, Mt — matildite

MINERALIZATION AND ALTERATION

Due to intensive metasomatic transformation no unaltered volcanic rocks are found in the region. They are altered to quartz-adularia, quartz-sericites and argillic metasomatites. They contain sulphides, quartz-sulphide, quartz-barite and carbonate veins and veinless zones. We divide the hydrothermal processes that caused ore formation into four stages. They differ in mineral parageneses of veinless and metasomatic alterations.

During the first stage (sulphide) the following sequence of parageneses occurred: siderite+ankerite+pyrrhotite – pyrite+marcasite – pyrite+sphalerite – sphalerite+galena+ boulangerite – bournonite+pyrargyrite+polybasite-I; in host rocks adularia is intensively replaced by sericite. In this stage commercial deposits of Pb-Zn-Ag ores were formed.

The second stage (quartz-barite) is characterized by sequential formation of the following mineral parageneses: ilvaite+garnet (andradite)+carbonate+fluorite – chalcopyrite+fahlerz+ Bi-sulphosalts+electrum+quartz-I – barite-I. This stage is accompanied by dissolution of sulphide Pb-Zn-Ag minerals and mass deposition of the fine-grained quartz-I, that forms quartz (+barite ± sulphide) veins with patchy kaolinite alteration in the host rocks. In this stage commercial deposits of Au-ores were formed (Au-sulphide ore type).

The third stage (carbonate-quartz) is characterized by formation of: calcite – quartz-II – barite-II+(native Ag+acanthite+polybasite-II). This stage was accompanied by quartz-kaolinite and quartz-smectite alteration.

During the fourth stage (carbonate-goethite) carbonates (calcite, dolomite, siderite), chalcedony+quartz-IV, jarosite, goethite, native Au, barite-III, cinnabar were formed

sequentially. Formation of veins was accompanied by quartz-alunite, quartz-kaolinite-dickite and quartz-illite metasomatites.

BISMUTH MINERALIZATION IN THE BEREGOVO ORE FIELD

Bi-mineralizations in the Beregovo ore field appeared was first described by Matkovsky *et al.* (1987) and Remeshilo *et al.* (1989). In two samples they described bismuthinite and Bi-sulphosalts, whose chemical composition corresponded with berryite, gustavite-lillianite series minerals, schirmerite and cosalite.

Our investigations show that bismuthinite and Bi-sulphosalts are widespread in the central part of the ore field. In the western part they are rare and in the eastern part they are lacking completely. The depth interval of Bi-minerals distribution is more than 500 m and they are not found at higher levels.

Bi-sulphosalts are generally associated with fine-grained quartz-I (Skakun, 1994). Aggregates with Bi-minerals always contain chalcopyrite, which, together with pyrite, is the main sulphide mineral. Bi-sulphosalts are not found in areas with significant concentrations of galena and (or) chalcopyrite.

The quartz-chalcopyrite-bismuthinite-Bi-sulphosalts association marks the beginning of quartz vein formation. This association replaced earlier pyrite-sphalerite-galena aggregates. Dissolution of sulphides occurred in the sequence: sphalerite-galena-pyrite (Skakun, 1994). In completely developed aggregates of this association sphalerite is practically absent; disseminated mineralization of fine xenomorphic grains of galena is relict. Pyrite is observed both in the form of relict aggregates, banded by druses, and in the form of idiomorphic grains of a new generation which occur in quartz and chalcopyrite.
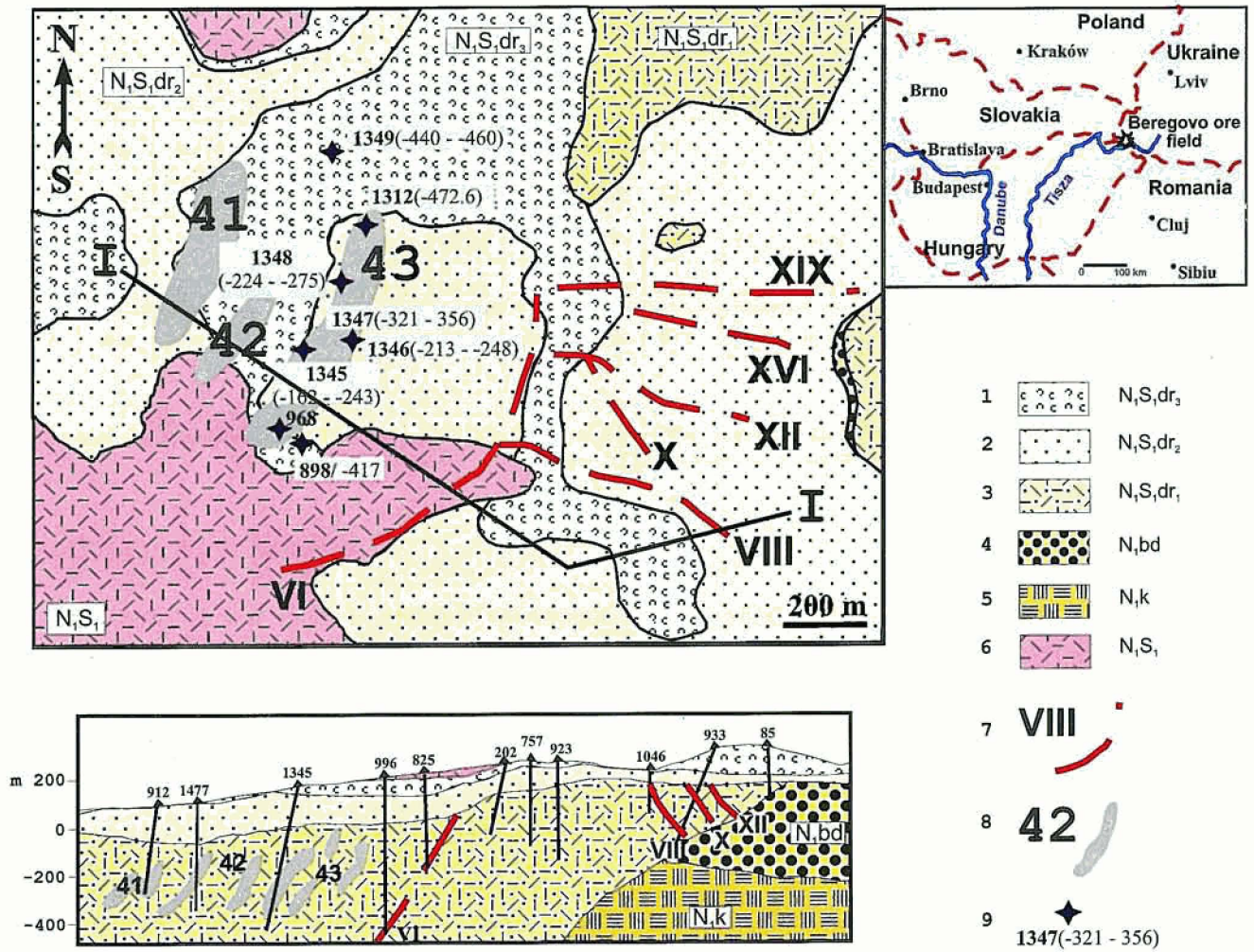
Fig. 1. Schematic geologic map and cross-section of the Beregovo ore field showing the spatial distribution of bismuth mineralization

1 — upper tuff unit (rhyolite tuffs, lava breccia, seams of tuffite) ($N_1S_1dr_3$ — Miocene, Sarmatian stage, Upper Dorobratov Series); 2 — upper sedimentary unit (argillites, tuffs) ($N_1S_1dr_2$ — Middle Dorobratov Series); 3 — middle tuff unit (rhyolite tuffs, ignimbrites) ($N_1S_1dr_1$ — Lower Dorobratov Series); 4 — lower sedimentary unit (argillites, sandstones) (N_1bd — Miocene, Badenian stage); 5 — lower tuff unit (rhyolite tuffs) (N_1k — Miocene, Karpatian stage); 6 — domes and flows of rhyolite, perlite and perlitic lava breccia (N_1S_1 — Sarmatian Subvolcanic Formation); 7 — Au-quartz-base metal ore veins of the Muzievo deposits and their number; 8 — zones of shot-veinless mineralization (Beregovo deposit), with their number; 9 — boreholes with number, in brackets — the interval with Bi-sulphosalts (m)

CHEMICAL COMPOSITION OF Bi-MINERALS

Bismuth sulphosalts occur as fine (0.001–0.35 mm) grains in fine-grained quartz, frequently as intergrowths with chalcopyrite and galena, rarely with pyrite and bismuthinite.

Bismuth sulphosalts are very difficult to identify optically. Their identification and study was done using X-ray microprobe CAMEBAX under the following conditions: accelerating voltage 20 kV, current 10 nA, analytical lines L_α for Ag, Pb, Sb, Bi, S, Au, Se, Zn, Cu, Fe and K_β — for As. The following standards were used: PbS (Pb), FeS$_2$ (S), AsSe (As, Se) and pure metals. The tiny size of many grains prevented their X-ray identification.

Basing on their chemical composition these sulphosalts (Tab. 1) can be subdivided into three systems: Ag-Pb-Bi-S, Ag-Cu-Pb-Bi-S and Pb-Cu-Bi-S, each characterized by variations in contents of the major and minor components. Se is always present, at up to 1 wt.%. In a large number of samples admixtures of Sb, As, Zn, Fe, Au occur. Contents of As, Au, Fe vary widely.

The commonest minerals belong to the **Ag-Pb-Bi-S system**. Ag and Bi contents display a wide variation (5.6–20.5 and 34.8–56.5 wt.%, respectively) whereas the content of Cu is insignificant (0.1–0.8 wt.%). These sulphosalts are observed only in galena grains, forming myrmekites and lamella grains (Figs. 2a, b). They were formed as a result of exchange of Pb to Bi and Ag in galena. On the diagram of Ag(Cu)-Pb-Bi (Fig. 3) the
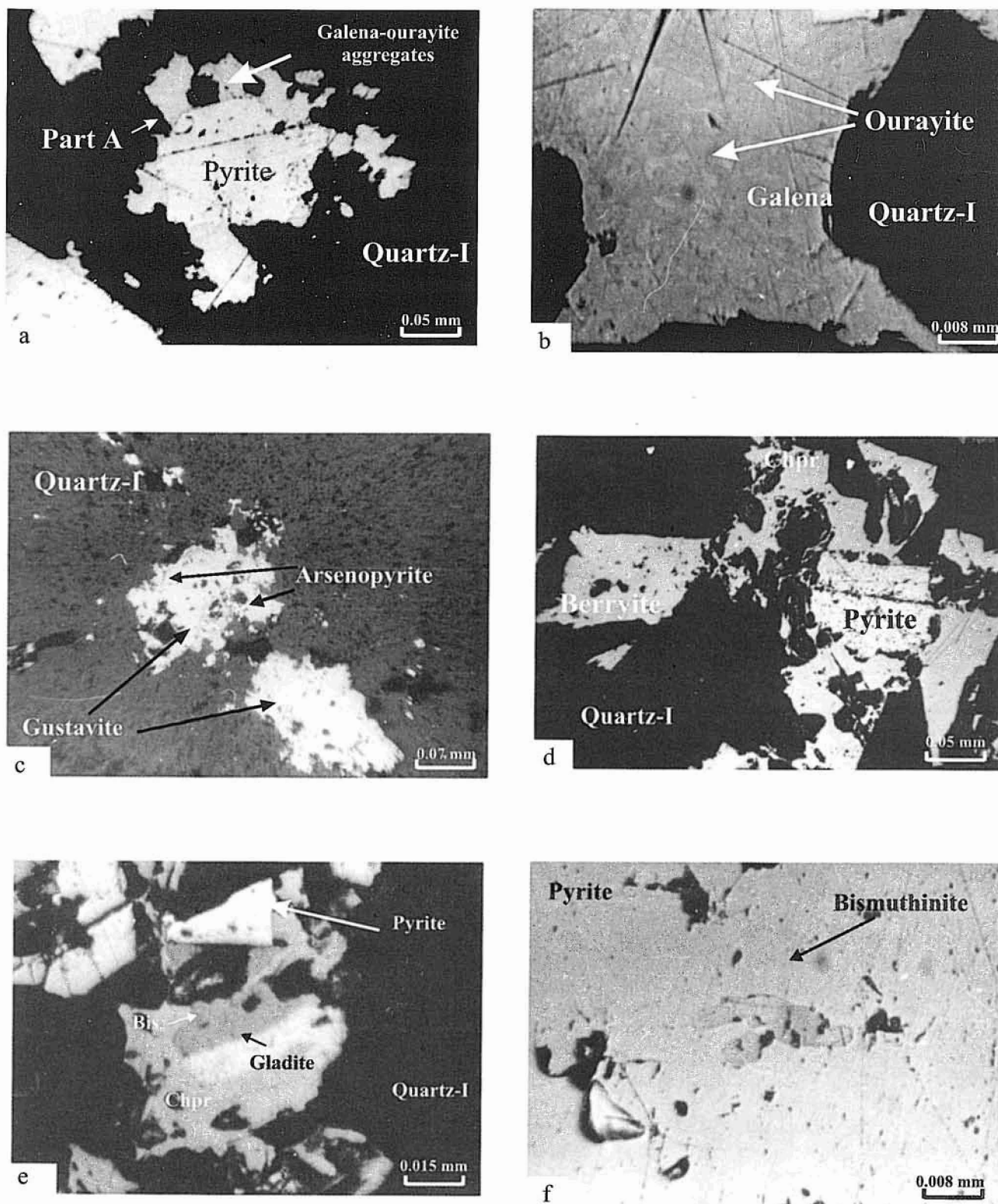
Fig. 2. The forms and assemblages of sulphide and Bi-sulphosalts from the Beregovo ore field

a — overgrowth of metacrystal pyrite by galena-ourayite aggregates in a matrix of fine-grained quartz, reflected light, oil immersion; b — lamellae of ourayite in galena, part A on the Fig. a; c — interstitial grains of gustavite in fine-grained quartz, light phases are relicts of arsenopyrite; d — intergrowth of chalcopyrite and berryite (analysis 19); e — intergrowth of gladite and bismuthinite in chalcopyrite (analyses 24 and 27); f—twins of bismuthinite in pyrite (analysis 25)
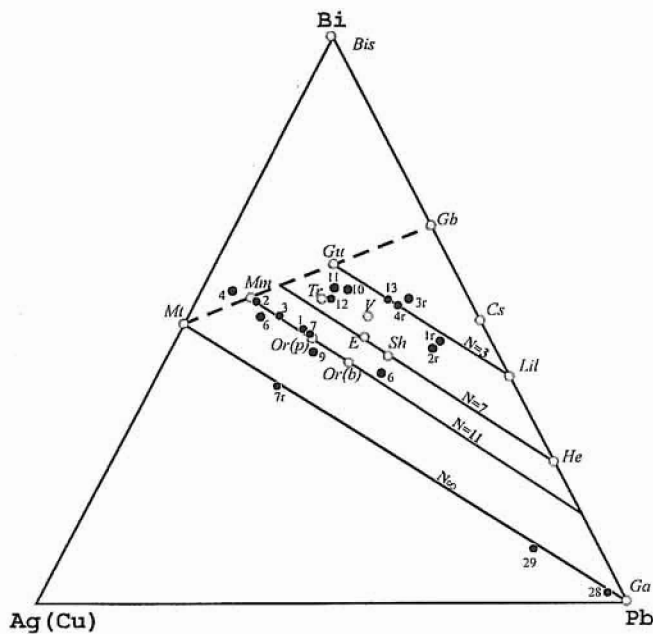
Fig. 3. Triangular plot (atomic) showing compositions of galena and sulphosalts of Ag-Bi-Pb-S analysed in this study in terms of the system Ag-Bi-Pb

Grey circles — theoretical compositions of some minerals and synthetic phases: Ga — galena, Bis — bismuthinite, Mt — matildite, Gb — galenobismutite, Cs — cosalite, Lil — lillianite, Or — ourayite, He — heyrovskyite, Mm — mummite, Gu — gustavite, Tr — treasurite, V — vikingite, Sh — schirmerite, E — eskimoite; black circles minerals analysed in this study. The numbers correspond to those of analyses in Table 1. N = N_{chem} — number of octahedrons in galena-similar domains of the unit cell in the plane roughly parallel to (001) and ab projection. Analysis 2r, 3r, 4r, 7r from the paper by Matkovsky *et al.* (1987) and Remeshilo *et al.* (1989)

chemical composition of these sulphosalts lies in the field constrained by lines of galena-matildite, gustavite-lillianite, matildite-galenobismutite and argentite-cosalite.

Our sulphosalts represent several groups, identification of which is uncertain due to the lack of X-ray data.

Minerals of the galena-matildite group are represented by two grains of galena solid solution (Pb$_{ss}$) (Foord *et al.*, 1989) of composition Gal$_{94}$Mat$_6$ (analyses 28 and 29) and intermediate phase Gal$_{21}$Mat$_{79}$ (Matkovsky *et al.*, 1987). Generally, minerals of the Ag-Pb-Bi-S system are less common in the Beregovo ore field than in other deposits of the Carpathian Neogene volcanic zone (Mato, 1992; Kovalenker *et al.*, 1993).

Deviation of sulphosalts analyses points from the matildite-galena line is a result of increasing content of Bi in Ag-Pb-Bi sulphosalts (Fig. 3). This is caused by a change of galena type superstructure into a domain structure which is typical for lillianite homologues (Makovicky and Kapur-Moller, 1977a). In this structure layers of galena type interchange with galenobismutite type layers. N — number of octahedrons in galena type layers is a determinant characteristic of such a structure. N is calculated by the formula N_{chem} = 1 + [1/(Bi + Pb/2 − 0.5)] (Makovicky and Kapur-Moller, 1977a, b) and it is the only criterion for identification of the mineral-homologues of lillianite based on chemical composition. Therefore, most of the phases

investigated in the galena can be referred to minerals of the ourayite-mummite series (analyses 1–4 and 6–9).

Sulphosalts of this group are characterized by stable values, of N_{chem} = 11–13 with significant fluctuations of Pb and Ag contents and, to a smaller degree, Bi. Their composition can be approximated by the series Ag$_4$Pb$_7$Bi$_3$S$_{14}$–Ag$_5$Pb$_3$Bi$_6$S$_{14}$–Ag$_6$PbBi$_6$S$_{13}$. Admixture of Se (up to 1 wt.%) and Cu (up to 0.8 wt.%) was systematically detected. Admixture of As (up to 1.5 wt.%), Au (0.0–0.34 wt.%), Fe and Zn were found in single phases. These admixtures are not consistent. The content of Sb is with in the limits of system analysis error. Ourayites with similar composition were described in Stiavnica-Hodrusa ore field (Slovakia) (Kovalenker *et al.*, 1993) and in some epithermal deposits of Nevada (Foord *et al.*, 1988)

The phase with N_{chem} between 10 and 6 was not determined. Three phases in a single sample (analyses 10–12) have a similar value of N_{chem} and their Pb/Ag ratio corresponds to treasurite. A phase that corresponds to analysis 12 with a composition Ag$_{6.3}$Cu$_{0.3}$Pb$_{6.4}$Bi$_{15}$S$_{32}$ closely resembles treasurite.

Another two phases (analyses 10 and 11) are characterized by significant levels of As (1–2 formula units — f.u.), a low content of Ag and S and high levels of Pb. Cu is always present in amounts of 0.3–0.5 f.u. The phase corresponding to analysis 10 may be considered as intermediate between treasurite and the gustavite-lillianite mineral series (N_{chem} = 4.1).

Minerals of gustavite-lillianite series were described earlier (Matkovsky *et al.*, 1987; Remeshilo *et al.*, 1989) (analyses 3r
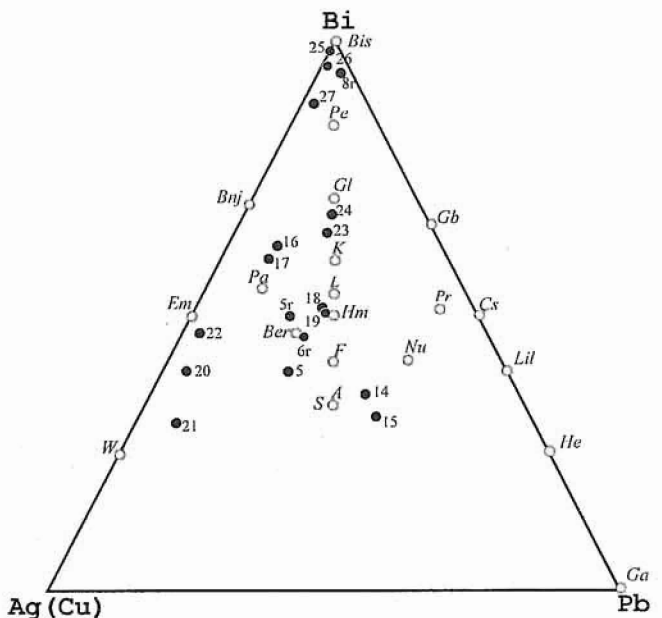

Fig. 4. Triangular plot (atomic) showing compositions of galena and sulphosalts of Ag-Cu-Bi-Pb-S and Cu-Bi-Pb-S analysed in this study in terms of the system Ag(Cu)-Bi-Pb

Grey circles: Bnj — benjaminite, Pe — pekoite, Pa — paderaite, Gl — gladite, K — krupkaite, Em — emplectite, L — lindströmite, Hm — hammarite, Pr — proudite, Ber — berryite, W — wittichenite, F — friedrichite, S — soucekite, A — aikinite, Nu — nuffildite; analysis 5r and 6r from paper by Remeshilo *et al.* (1989); for other explanations see Fig. 3
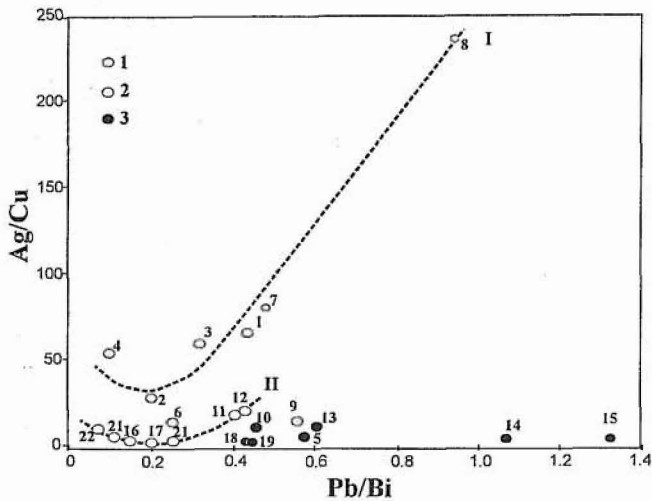
Fig. 5. Dependence of a parity (ratio) Ag/Cu to Pb/Bi for Ag-bearing sulphosalts of a Beregovo ore field

1 — sulphosalts of the ourayite series; 2 — Ag-Cu-Bi-Pb-sulphosalts; 3 — sulphosalts of the gustavite-lillianite series; I and II — trends of change in sulphosalt composition; numbers of the points correspond to those of the analyses in Tab. 1

and 4r in Tab. 1). Analyses 1r and 2r with $N_{chem} = 3.5–3.9$, that were described as cosalite, can be also referred to these series. Our recent investigations revealed one more phase (Fig. 2c, analysis 13), which lies on the gustavite-lillianite line and which corresponds to $Gus_{61}L_{39}$. In most of the grains high concentrations of Cu (0.2–1.1 wt.%) and Au (0.28 wt.%, analysis 13) are noted.

Sulphosalts of **Ag-Cu-Pb-Bi-S system** are represented as single grains or as intergrowths with galena, chalcopyrite and Ag-Pb-Bi-sulphosalts in quartz (Fig. 2d). The size of grains is 0.002–0.3 mm. Their chemical composition is determined by variations of Pb/Bi (0.04–0.42) and Ag/Cu = 0.7–9.3 ratios. As shown on the diagram Ag (Cu)-Bi-Pb (Fig. 4) the analyses of these minerals form two series.

The first series is parallel to the Bi-Pb axis. It is formed by three separate groups of analyses with a nearly constant sum of Ag+Cu. These can be tentatively referred to Ag-bearing soucekite (analyses 14 and 15), berryite (analyses 18, 19, 5r, 6r) and Pb-bearing benjaminite (analyses 16 and 17). The similarity of the compositions of phases 14 and 15 to soucekite is confirmed by high Se concentrations (3.9–4.4 wt.%).

The second series of analyses extends from the benjaminite field in the direction of increasing Ag(Cu) content almost parallel to the Ag-Bi axis. Analyses 20 and 21 are with in the Ag-Cu-Pb-Bi-S system. Any natural minerals or synthetic analogs of this system are unknown. An empirical formula, calculated using the results of chemical analyses with independent positions for Ag and Cu and approximate for sulphur and selenium, is close to $Ag_5CuBi_4Pb(S, Se)_{11}$. A number of similar phases was described in copper ores from the Stiavnica–Hodrusa ore field (Slovakia) (Kovalenker et al., 1993).

Pb-Cu-Bi-S sulphosalts have not been found earlier in the Beregovo ore field. We have found two phases with such a composition. These form an intergrowth with chalcopyrite and bismuthinite (Fig. 2e). They occupy an intermediate position between gladite and krupkaite. Their composition can be described by the empirical formula $CuPbBi_3S_6$ (analyses 23 and 24). These sulphosalts are characterized by admixtures of As (up to 0.8 wt.%) and Se (up to 0.6 wt.%). The Pb/Bi ratio is varies from 0.17 to 0.3.

Bismuthinite is found mostly as fine inclusions in sulphidic, essentially pyritic aggregates (Fig. 2f) in constant association with chalcopyrite. The same association is distinguished in case of observation of bismuthinite in fine-grained quartz aggregates. The chemical composition of bismuthinite phases is characterized by a wide variety of admixtures (Pb, Ag, Cu, Se, Fe, As) to significant levels (Tab. 1, analyses 25–27, 8g). The Pb content changes from 0.0 to 3.7 wt.%, Ag — from 0.0 to 0.16 wt.%, Se — from 0.0 to 3.7 wt.%, Fe — from 0.7 to 1.8 wt.% and As — from 0.7 to 1.5 wt.%. For three recently investigated phases of bismuthinite the direct dependence between Cu and Se contents was established. Basing on the content of Cu (2.3 wt.%) and Se (0.46 wt.%) analysis 27 (Tab. 1) approximates pekoite.

DISCUSSION AND CONCLUSIONS

In general, the association of Pb-Bi-Ag-Cu-sulphosalts in the Beregovo ore field is typical for gold-rich epithermal ores (Foord et al., 1988). In the Beregovo ore field the complex sulphosalts described above are found in the same samples, or with narrow intervals of ore bodies. In all cases the mineral associations are uniform with fine-grained quartz always present.

Quartz was the earliest phase. It replaced various unstable aggregates of carbonates and sulphides. Chalcopyrite was formed a little later, replacing remaining sulphide aggregates. The recrystallization of quartz occurred simultaneously and was accompanied by formation of fine-grained aggregates and extrusion of chalcopyrite to the periphery of the recrystallization zone. Intensive development of such processes caused formation of continuous chalcopyrite aggregates in the periphery of fine-grained quartz areas. Crystallization of Bi-minerals occurred prior to the crystallization of chalcopyrite and took place peripheral to quartz aggregate formation. Bi-sulphosalts gradually disappear with the approaching chalcopyrite crystallization wave. In areas with a maximum development of chalcopyrite Bi-minerals are absent.

Fine-grained aggregates of quartz are very sensitive to late-stage hydrothermal processes, expressed as recrystallization zones and changes in sulphide and quartz grain morphology. Absence of recrystallization effects caused by sulphosalt formation shows that the association of fine-grained quartz+chalcopyrite+bismuthinite+Bi-sulphosalts is the result of a single process superposed on the sulphide aggregates.

We noted the relationship of sulphosalt composition to the associated minerals. In quartz with widespread relict galena minerals of the ourayite groups are dominant. Where such galena relicts are absent from quartz, mineral grains with a composition close to treasurite and gustavite-lillianite are observed.

The appearance of chalcopyrite is accompanied by the development of Ag-Cu-sulphosalts. Complete disappearance of galena from the quartz-chalcopyrite-bismuthinite association is accompanied by the formation of gladite-krupkaite minerals. In massive chalcopyrite and chalcopyrite-pyrite aggregates where the replacement processes are clear, Bi-sulphosalts are not found. Bismuthinite is detected in pyrite-chalcopyrite aggregates. These observations prove that Bi-minerals accompany the formation of chalcopyrite aggregates with their maximum development at the chalcopyrite crystallization front. Bi-sulphosalts can also be considered as metastable phases, forming in the early stages of replacement of galena by chalcopyrite under the influence of solutions with a high activity of Bi and Ag. Distribution of Bi-sulphosalts in the Beregovo ore field was controlled by the kinetics of several interconnected processes (Fig. 5) that finally led to the formation of copper ores and quartz veins.

At an early stage the replacement of carbonate-sulphide aggregates by cryptocrystallic quartz causes the isolation of single galena grains in a quartz matrix. A diffusion wave of Bi outpaced copper at the incipient stage of the chalcopyrite crystallization. Bismuth is localized in the most favourable geochemical traps — in galena grains. Its gradual accumulation in the galena structure caused changes in the phase composition of the galena-matildite-ourayite path. The increase of Cu activity which followed led to the expulsion of Pb from the sulphosalts and changed their composition towards Ag-Cu-Bi and Cu-Bi phases. More detailed analyses of the causes of such variations in the composition of this association are not yet possible due to the insufficient study of phase equilibrations in Ag-Cu-Pb-S system. The final chalcopyrite crystallization was developed in conditions of instability for most of the Bi-minerals. This caused the disappearance of Bi-sulphosalts and bismuthinite from pure chalcopyrite aggregates.

Our observations indicate that we are dealing with metastable phases — intermediate links in the chain of galena-chalcopyrite replacements that were preserved owing to their isolation in a tight quartz matrix. Their appearance, evolution and preservation was determined by kinetic factors and circulation of hydrothermal solutions through the heterogenous and constantly changing substrate of evolving mineral aggregates.

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