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Ag-Cu-Pb-Bi mineralization from the Svishti Plaz gold deposit, Central Balkan Mountain, Bulgaria

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Abstract: A complex bismuthiferous association is found in the Svishti Plaz gold deposit situated in Central Balkan Mountain. The vein type mineralization is hosted in Paleozoic dioritic, granodioritic and quartz-dioritic plutonic bodies and related hornfelses. The ore consists of arsenopyrite, pyrite, native gold, galena, sphalerite, tennantite, pyrrhotite, magnetite. Gangue minerals are quartz and calcite. Four stages of mineralization have been outlined. Bismuth mineralization belongs to the third one.

The bismuthiferous association is complex and polyphase. According to microprobe data several groups of bismuth minerals are distinguished: native Bi, bismuthiferous galena, Pb-Bi, Cu-Pb-Bi, Ag(Cu)-Pb-Bi and Ag-Cu-Pb-Bi sulfosalts. According to structural relations a exsolution genesis from ISS or primary bismuth sulphosalt is suggested for native Bi, Ag(Cu)-Pb-Bi sulfosalts, Pb-Bi sulfosalts, bismuthinite-pekoite and chalcopyrite. Aikinite-friedrichite belongs to the same association but is obviously later than the previous minerals. Later Ag-Cu-Pb-Bi sulfosalts are found as longprismatic needlelike orientated crystals in bismuthiferous galena. They are both considered later than the other Bi-minerals. According to the microprobe analyses two different phases are distinguished: berryite and benjaminite. Galena contains 1.23 to 4.72 wt.% Bi and 1.06 to 1.86 wt.% Ag.

Inclusions of unidentified Ag-Cu-Pb-Bi-sulfosalts are observed in a cobalt-pyrite, morphologically very different from the other pyrites in the deposit. Multiple stages of mineralization involving possible reheating, late, high-temperature inflow of Cu, Ag, and Bi, and remobilization of elements (Pb) already presented in the earlier minerals are responsible for the formation of the complex Cu-Pb-Ag-Bi assemblage.

Key words: Bi minerals, Svishti Plaz, gold deposit, Bulgaria

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Резюме. В златорудното находище Свищи плаз, разположено в Централна Стара планина, е установена комплексна бисмутова минерализация. Жилният тип минерализация е вместена в палеозойски диоритови, гранодиоритови и кварц-диоритови тела и свързаните с тях хорнфелзи. Рудата е изградена от арсенопирит, пирит, самородно злато, галенит, сфалерит, тенантит, пиротин, магнетит. Жилните минерали са кварц и калцит. Отделени са четири стадия на минерализация. Бисмутовите минерали са отнесени в третия стадий.

Бисмутовата асоциация е сложна и обикновено полифазна. Според микросондовите анализи са отделени няколко групи от бисмутови минерали: самороден бисмут, бисмутоносен галенит, Pb-Bi, Cu-Pb-Bi-, Ag(Cu)-Pb-Bi- и Ag-Cu-Pb-Bi-сулфосоли. Въз основа на структурните взаимоотношения за самородния бисмут, Ag(Cu)-Pb-Bi-сулфосоли (матилдит?), Pb-Bi-сулфосоли, бисмутинит-пекоита и халкопирита се предполага , че са образувани в резултат на разпадане на твърд разтвор и на първична бисмутова сулфосол (?). Айкинит-фридрихитът е отложен в същата асоциация, но е очевидно по-късен. По-късните Ag-Cu-Pb-Bi-сулфосоли са установени като дългопризматични иглести ориентирани кристали в бисмутоносния галенит и са по-късни от другите Bi-минерали. Според микросондовите анализи са отделени два различни минерала: бериит и бенжаминит (?). Галенитът съдържа от 1,23 до 4,72 тегл.% Bi и от 1,06 до 1,86 тегл.% Ag. В кобалтсъдържащ пирит, който морфоложки се различава от другите пирити в находището, са наблюдавани неопределени Ag-Cu-Pb-Bi-сулфосоли. Образуването на комплексната Cu-Pb-Ag-Bi асоциация се дължи на многостадийната минерализация, вероятно подгряване, привнос на по-късни високотемпературни разтвори, носещи Cu, Ag и Bi и ремобилизация на елементи (Pb) от вече отложените минерали.

Ключови думи: Bi-минерали, Свищи плаз, златно находище, България

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Introduction

The Svishti Plaz gold deposit is situated in the Central Balkan Mountain at an altitude of about 1500 m. The ancient mine workings and large vast dumps are the evidence for mining activity in far and recent past. The deposit has been explored during 1969-1979 years and has never been operating because of the high As content. In the shear related zone, dozens of base metal-gold-quartz ore veins with average Au of 6.6 g/t, Ag of 16.6 g/t, Pb of 0.62% are established (Parvanov, Mateev, 1980). The presence of bismuth in Svishti Plaz ore is briefly mentioned by Kuikin et al. (1972), but without any mineralogical description. The first report concerning the bismuth mineralization was presented on GEODE workshop (Mladenova et al., 2000).

Geological setting

The area is build up of two complexes determining the geology and metallogenic features in the region (Kujkin, Milanov, 1970; Kuikin et al., 1972). The rocks of Paleozoic low-crystalline diabase-phyllitoid metamorphic complex are the most widespread in the region (Fig. 1). It comprises mainly quartz-sericite-chlorite schists and small diabasic bodies and diabasic tuffs. The Ordovician magmatic rocks of the Vezhen complex, comprising diorite, granodiorite and granit-porphyrite and numerous dikes of the same composition, intrude diabase-phyllitoid metamorphic complex. In the contact zones the rocks of diabase-phyllitoid metamorphic complex are transformed in hornfelses, porphyroblastic schists and amphibolites.

The rocks of Upper Paleozoic (Upper Carboniferous-Lower Permian) dike complex include quartz-syenodioritic and granodioritic porphyrites and granite-porphyry are widespread as a belt around the Kashana thrust. Triassic calcareous sediments are widespread on the northeastern, northern and southeastern slopes of Svishti Plaz peak.

Spessartites, gabbro-diorites, diorites, quartz-diorites and granodiorites and granite-porphyries from Late Alpine dike complex (Upper Cretaceous-Upper Eocene(?)) are widespread in Kashana thrust zone and southern. The most important structure in the region is the Kashana fault (Kujkin et al., 1970).

The vein type mineralization is hosted by Paleozoic low-crystalline schists, dioritic, granodioritic and quartz-dioritic plutonic bodies and related hornfelses. The ore-hosted structures are vein filled fissures related to tension and shear faults. Some ore veins are situated in the contact zone of the quartz-syenodioritic and granodioritic porphyrite dikes. More than 30 ore veins striking 150-160° and 175-180° SE, 0-10° NNE and 65-70° ENE were explored. They are dipping 60-90° SW. Most of the ore veins can be followed horizontally for around 100-350 m and some of them to 1 km. Their thickness varies from 0.20 to 2.5 m, usually 0.8-1 m (Kuikin et al., 1972).

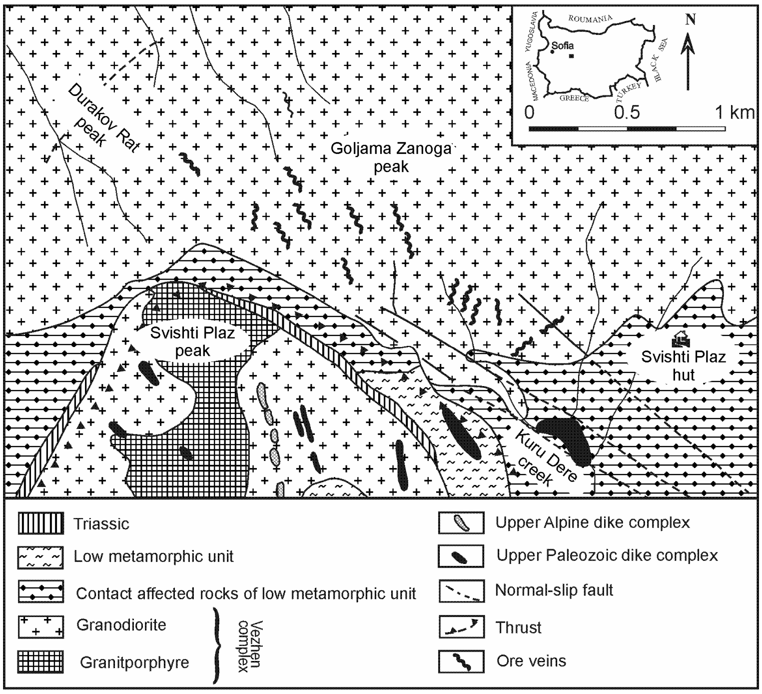

Fig. 1. Simplified geological map of Svishti Plaz deposit (after Kuikin et al., 1972)
Фиг. 1. Опростена геоложка карта на находище Свищи плаз (по Kuikin et al., 1972)

Thickness of vein-related wall-rock alteration is proportional to vein thickness and bleaches the rocks up to few meters from the veins. Alteration is characterized by silicificatios, sericitizations of plagioclase, kaolinitization of kalifeldspar, chloritization of biotite (Kuikin et al., 1972).

Methods of analysis

Specimens were collected from dumps in front of numerous minings along veins in Svishti Plaz deposit.

The discussed minerals have been recognized in polished sections by their anisotropism, white to yellow color and hardness similar to that of galena.

The chemical composition of Bi-minerals was determined using JEOL JSM 35 CF with Tracor Northern TN-2000 analyzing system, accelerating voltage of 25 kV and sample current of 1.10^{-9} A. The standards and lines used for analysis were: PbS - PbL_{α}, $CuFeS_2$ - CuK_{α} and SK_{α}; PbTe – TeL_{α}; pure Ag and Co - AgL_{α}, CoK_{α}; Bi_2S_3 - BiL_{α}; Sb_2S_3 – SbL_{α}. Acquisition times for all elements were 100 s.

Samples of the investigated material are available in the collections of the Geological Institute under N M.1.2001.2.1-3.

Mineral assemblages

The ore in Svishti Plaz deposit consists of arsenopyrite, pyrite, galena, sphalerite, tennantite, pyrrhotite, magnetite, and the phases, which are described here. Gangue minerals are quartz, calcite and barite. The hydrothermal mineralization in Svishti Plaz deposit can be divided into four paragenetic stages based on crosscutting relations and electron-microprobe analyses.

Stage 1. (Fe-As) consists mainly of pyrite, arsenopyrite and gray quartz. Rare pyrrhotite occurs within pyrite.

Stage 2. (Au-Ag-Pb-Zn-Cu) is the main stage. It is characterized by sphalerite, galena, chalcopyrite, electrum, native gold, tennantite with gray quartz. Minor, fine- to medium-grained pyrite, arsenopyrite and magnetite are intergrown with sphalerite. Chalcopyrite is frequently included within early sphalerite as blebs or subparallel layers. Small breccias of earlier vein materials are often enclosed by base metal sulfides, indicating that intense fracturing took place during their deposition.

Stage 3. (Ag-Pb-Cu-Bi) occurs in discordant veinlets and more complex relations. The bismuth minerals with chalcopyrite are neither cut nor replaced by later minerals.

Stage 4. (Fe-Ca-Ba) has a simple mineral composition. The only ore mineral is hematite and as gangue gray quartz, white calcite and milky barite are presented. They fill vugs and fractures in earlier minerals. Small breccias of earlier vein materials are often enclosed by carbonates, indicating that fracturing took place prior to the late carbonate phase. The main minerals in Svishti Plaz deposit are arsenopyrite and pyrite. The economically important minerals are the native gold and electrum. They were observed in all polished sections. The visible gold is precipitated later than the pyrite and arsenopyrite, but it is in close association with them. It fills cracks, microfissures or is precipitated in the quartz after the Fe-sulfides. Gold is in parageneses with galena, pale ores, sphalerite, chalcopyrite and quartz in variable relations. The visible gold has a variable size - from microscopic to almost visible with naked eye. We suppose that the arsenopyrite I contains invisible gold because of TEM and SEM evidences, but we don't have any quantitative data yet.

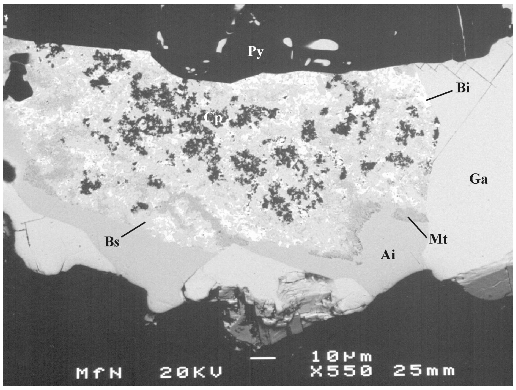

Fig. 2. Myrmekitic intergrowths of complex bismuth minerals and galena after pyrite. SEM, back-scattered electrons. Sample 7G/1; Ai - aikinite-friedrichite, Bi- native bismuth, Bs- bismuthinite-pekoite, Cp - chalcopyrite, Ga-galena, Mt - Ag(Pb)-Bi sulfosalts (matildite?), Py - pyrite

Фиг. 2. Мирмекитово прорастване на сложни бисмутови минерали и галенит, отложени след пирит. СЕМ, обратноотразени електрони. Образец 7G/1; Ai - айкинит-фридрихит, Bi - самороден бисмут, Bs – бисмутинит-пекоит, Cp – халкопирит, Ga - галенит, Mt - Ag(Pb)-Bi сулфосоли (матилдит?), Py – пирит

Bismuth mineralization

Bismuthiferous galena and Bi-bearing mineral phases were found only in specimens from one vein system. They are undoubtedly later than the pyrite-arsenopyrite and base metal assemblages. The only later mineral in this association is the Bi-containing galena. The bismuthiferous association is complex and commonly polyphase. The phase intergrowths are revealed only in back-scattered electron image (Figs. 2, 3, 4). The identification of all the minerals have been made using SEM and electron microprobe.

Several families of bismuth minerals are presented: native Bi, bismuthiferous galena, Pb-Bi, Cu-Pb-Bi, Ag(Pb)-Bi and Ag-Cu-Pb-Bi sulfosalts. According to textural relationships, relative succession among the Bi-minerals is established. Three sub-associations can be divided.

The earliest sub-association comprises native Bi, chalcopyrite, Cu-Pb-Bi sulfosalts and bismuthinite-pekoite. All they form

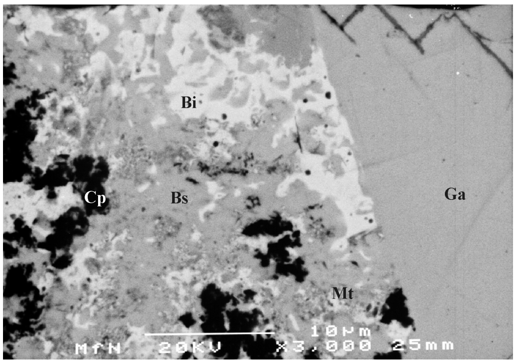

Fig. 3. Enlarged part of the right section of Fig. 2 better showing the mineral interrelations. SEM, back-scattered electrons. Sample 7G/1; Abbreviations as on Fig. 2

Фиг. 3. Увеличена дясна част на фиг. 2, показваща по-добре взаимоотношенията между минералите. СЕМ, обратноотразени електрони. Образец 7G/1; Съкращенията са същите като на фиг. 2

myrmekitic intergrowths with size of the different minerals less than 10 µm (Figs. 2, 3).

The second sub-association includes minerals with composition aikinite-friedrichite. They are deposited as 10 to 30 µm wide rims on the myrmekitic intergrowth (Fig. 2). In BSE they seem homogeneous.

The bismuthiferous galena with exsolved elongated grains of berryite and benjaminite is deposited last in the succession. It embraces the earlier bismuth minerals (Figs. 2, 3, 4).

Inclusions of unidentified Ag-Cu-Pb-Bi sulfosalts are observed in cobalt-pyrite, morphologically very different from the other pyrites in the deposit (Fig. 5). It is difficult to attribute categorically this pyrite to any of the mineral stages.

The identification of the bismuth minerals is complicated because of their small size and complex relations due to their typical occurrence as exsolved phases or to their genesis as a result of a breakdown of an ISS.

Native Bi

Native Bi is presented only in the myrmekitic intergrowths. It is easily distinguished because

Table 1. *Microprobe analyses of native Bi and galena from Svishti Plaz deposit, wt.%*

Таблица 1. *Микросондови анализи на самороден Bi и галенит от находище Свищи плаз, тегл.%*

No	Sample	Association	Pb	Cu	Ag	Bi	Te	Sb	S	Total
1.	7G/1	Native Bi in the intergrowth	5.69	1.78	1.79	90.59				94.16
2.	7G/1		3.63	0.75	0.50	94.66		0.38		96.29
3.	7G/1		5.76	0.45	0.00	93.47		0.40		94.32
4.	7G/1		11.50	0.30	1.03	87.58				88.91
5.	7G/1	Galena II with Bi- minerals	80.12	0.68	1.11	4.72			13.13	99.76
6.	7G/1		80.72	0.81	1.23	4.30			12.77	99.83
7.	7G/1		78.80	1.25	1.86	2.88			14.71	99.50
8.	7G/1		81.84	0.78	1.42	1.23	0.28		13.60	99.15
9.	7G/1x		81.76	0.34	1.06	3.21	0.32	0.19	12.84	99.72
10.	7G/1		84.17	1.02	0.84	1.38	0	0	12.23	99.64
11.	7G/1		81.30	0.26	0.97	4.08			13.29	99.90
12.	7G/1		80.08	1.09	1.57	2.39	0.27	0.34	13.63	99.37
13.	7G/1		79.79	0.28	1.64	3.54	0.26		13.55	99.06
14.	X2/10	Galena I with sphalerite	83.61	0.40	1.22		0.45		13.92	99.60
15.	X2/10		87.18	0.18			0.18		13.36	100.90
16.	X2/10		85.48	0.38			0.20		12.90	98.96

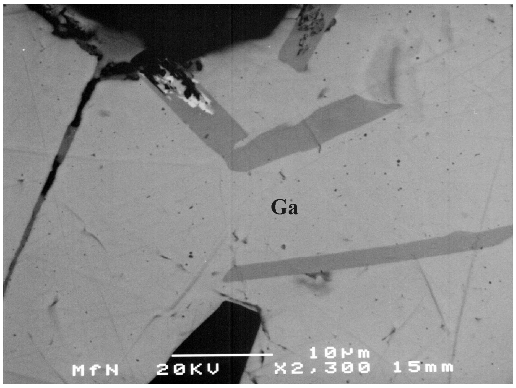

Fig. 4. Bismuthiferous galena containing longprismatic inclusions of berryite or benjaminite. SEM, backscattered electrons. Sample 7G/1

Фиг. 4. Бисмутоносен галенит с дългопризматични включения от бериит и бенжаминит(?). СЕМ, обратноотразени електрони. Образец 7G/1

of its white color and strong anisotropy (Figs. 2, 3). Despite the small sizes, the sufficiently coarse character of the intergrowths has permitted spot microprobe analyses. Despite the presence of other elements established in associated sulfosalts and not typical for native bismuth the absence of sulfur suggests correct analyses (Table 1).

Galena

The Svishti Plaz galena can be divided into two groups on the basis of electron microprobe analyses (Table 1) and optical study. The two kinds of galena are attributed to two different stages.

Widely presented is only galena I, deposited in stage 2 (Au-Ag-Pb-Zn-Cu). It is almost pure galena containing no exsolved phases and no Bi, rarely Ag and small quantities of Te (Table 1, analyses 14, 15, 16).

Galena II from the third stage (Ag-Pb-Cu-Bi) comprises needle-like, oval or round inclusions from Ag-Cu-Pb-Bi sulfosalts (Fig. 4). This galena contain silver from 0.84 to 1.86 wt.%, bismuth from 1.23 to 4.72 wt.% and copper from 0.26 to 1.25 wt.% (Table 1, an. 5 to 13). The complex variations in composition and physical properties of galena as well as associated complex sulfosalts are recorded in many base and precious metal deposits (Karup-Møller, 1977; Czamanske, Hall, 1975; Pattrick, 1984; Moëlo et al., 1987; Foord, Shawe, 1989; Efimov et al., 1990; Marcoux et al., 1996; Ciobanu, Cook, 2000).

The compositions of the two kinds of galena in Svishti Plaz deposit reflect the geochemical characteristic of the hydrothermal fluids in the different stages.

Pb-Bi sulfosalts

In the myrmekitic intergrowths Pb-rich phases with intensity in BSE intermediate between bismuthinite-pekoite and matildite were anlyzed. It is difficult to attribute with convition their composition to some of the known compounds (Table 2). They always contain small quantities of Cu and Ag. The Pb

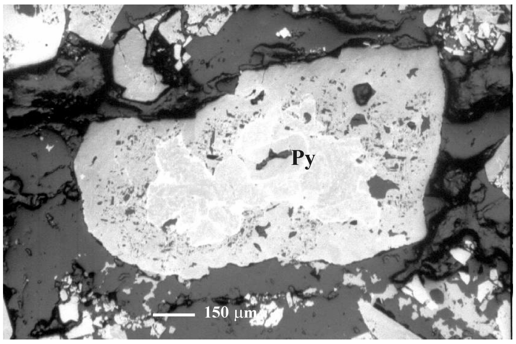

Fig. 5. Tarnishing of the cobalt-pyrite surface, containing inclusions of unidentified Ag-Cu-Pb-Bi-sulfosalts, few months after the polishing. The central parts of the crystals are solid and the porous periphery is probably a result of skeletal growth or replacement. The white parts are rich of cobalt. Parallel polars. Sample 5G/5

Фиг. 5. Окисление на повърхността на кобалтов пирит, включващ неопределени Ag-Cu-Pb-Bi-сулфосоли, няколко месеца след полирането. Централните части на кристалите са плътни, а порьозната периферия вероятно е резултат от скелетен растеж или заместване. Светлите части са богати на кобалт. Успоредни николи, Образец 5G/5

Table 2. *Microprobe analyses of Pb-Bi phases, wt.%*
Таблица 2. *Микросондови анализи на Pb-Bi-фази, тегл.%*

No	Sample	Cu	Pb	Ag	Bi	S	Te	Total
1.	7G/1x	0.81	64.34	1.34	18.57	16.26		101.32
2.	7G/1x	0.61	54.47	1.43	28.58	15.18		100.27
3.	7G/1x	1.98	47.92	1.56	36.44	13.10		101.00
4.	7G/1	0.35	52.37	0.94	32.36	14.11		100.13
5.	7G/1x	0.63	51.92	1.13	32.71	13.06	0.43	99.88
6.	7G/1	0.80	36.82	6.87	42.52	12.93		99.94
7.	7G/1x	0.87	38.57	0.63	43.90	15.06		99.03

varies from 28.07 to 64.34 wt.% and Bi from 18.57 to 43.90 wt.%. The very complex relation in the intergrowth hamper correct analyses and any other investigations and hence a correct diagnostic.

We suppose very cautiously that some of them could be related to lillianite homologues (heyrovskyite - an. 2; lillianite - analyses 3, 4, 5), cosalite (analyses 6, 7) and aschamalmite (beegerite) (an. 1) (Fig. 6).

Cu-Pb-Bi sulfosalts

The analyzed phases from this group were attributed to bismuthinite-aikinite series.

The *bismuthinite-aikinite series* forms a continuous solid solution at high temperature, which at low temperature becomes differentiated into a series of homeotypes with compositions close to the stoichiometric formulae (Harris, Chen, 1976; Mumme et al., 1976; Makovicky, Makovicky, 1978).

According to the chemical composition in Svishti Plaz deposit the members from the two edges of the series have been distinguished (Table 3, Fig. 7). The presence of compositions intermediate between bismuthinite-pekoite and aikinite-friedrichite is probably a result of rapid crystallization. Their deposition is separated in time.

Bismuthinite-pekoite. The light gray phases in myrmekitic intergrowths have composition intermediate between bismuthinite and pekoite. Silver is systematically present from 0.33 to 0.72 wt.% (Table 3).

Aikinite-friedrichite minerals show sharp contact with the minerals in myrmekitic intergrowth from the first bismuthiferous subassociation. They are deposited obviously later than them and form homogeneous rim 10 to 30 µm wide (Figs. 2, 3). They contain silver from 0.50 to 0.63 wt.% (Table 3).

Ag(Cu)-Pb- Bi sulfosalts

The Ag(Cu)-Pb-Bi phases are the darkest phases in the myrmekitic intergrowth (Figs. 2,

Table 3. *Microprobe analyses of phases from aikinite-bismuthinite series, sample 7G/, wt.%*
Таблица 3. *Микросондови анализи на фази от айкинит-бисмутинитовата серия, образец 7G/1, тегл.%*

N	Mineral	Cu	Pb	Ag	Bi	S	Total
1	bismuthinite-pekoite intergrowth	1.52	3.67	0.72	80.64	12.66	99.21
2		1.54	2.88	0.33	76.73	17.61	99.09
3	aikinite-friedrichite intergrowth	10.90	30.73	0.50	40.53	18.30	100.96
4		10.93	29.42	0.63	40.43	17.88	99.29
5		11.76	31.91	0.00	38.26	17.86	99.79
6		11.68	34.29	0.35	35.73	17.65	99.70
7		10.92	32.56	0.54	39.38	16.95	100.35
8		11.46	31.20	0.00	40.08	16.89	99.63
9		10.58	30.26	0.51	42.36	16.25	99.96
10		11.37	29.77	0.51	40.24	17.02	98.91

Table 4. *Microprobe analyses of Ag(Pb)-Bi phases, sample 7G/1, wt.%*
Таблица 4. *Микросондови анализи на Ag(Pb)-Bi фази, образец 7G/1, тегл.%*

No	Cu	Pb	Ag	Bi	S	Te	Sb	Total
1.1.	1.18	5.76	27.24	54.04	11.82			100.04
2.2.	1.04	5.18	23.32	58.79	11.43			99.76
3.3.	0.89	12.37	22.34	52.38	12.20			100.18
4.4.	0.37	5.59	26.17	57.29	10.63			100.05
5.5.	0.39	10.25	22.72	54.23	11.69		0.27	99.55
6.6.	0.52	16.47	19.38	51.56	12.30	0.30	0.44	100.97
7.7.	0.38	8.04	24.51	55.84	10.96	0.34	0.53	100.60

3). They show very variable composition (Table 4). Three of the analyses are plotted in the Pb_2S_2-Bi_2S_3-$Ag(Cu)_2S$ system near the matildite theoretical composition (Fig. 6). Pb is systematicaly presented in significant amounts. This fact is attributed to the close intergrowths of the minerals. Most of the other analyses fell near the galena-matildite solid solution (Fig. 6), but further detailisation of their diagnostics is hampered by their small size.

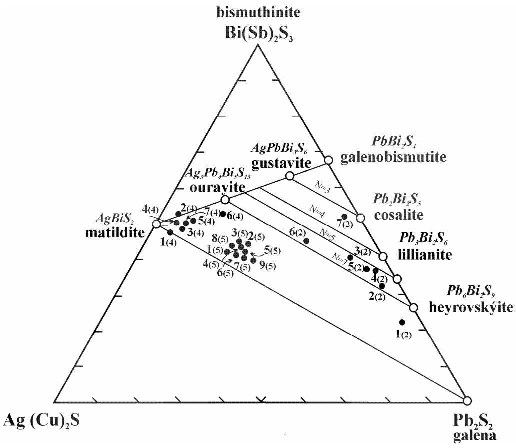

Fig. 6. Compositional plot in the Pb_2S_2-Bi_2S_3-$Ag(Cu)_2S$ system of the analysed minerals from the Svishti Plaz deposit. The numbers correspond to the respective analyses in the respective tables numbered in brackets. Open circles – theoretical compositions of minerals
Фиг. 6. Проекция на съставите в системата Pb_2S_2-Bi_2S_3-$Ag(Cu)_2S$. Номерата отговарят на номерата на анализите, а номерата в скобите са номерата на таблиците. Празни кръгчета – теоретичните състави на минералите

Ag-Cu-Pb-Bi sulfosalts

In the galena deposited after the polyphase bismuth association, needlelike (up to 60 µm in length and no more than 8 µm in width) or oval grains are observed (Fig. 4). No preferential orientation of these crystals is established.

According to the microprobe analyses two different phases are distinguished: berryite andbenjaminite (Table 5). The analyses are plotted on Fig. 6.

Berryite. Microprobe analyses calculated on the bases of 31 formula units show accordance with the generalized formula $Pb_3(Cu,Ag)_5Bi_7S_{16}$ (Nuffield, Harris, 1966). The analyses of Svishti Plaz material display a slight excess of (Ag+Cu) beyond 5 atoms per formula unit due to the Cu concentration. It is possible that it could be compensated by a small deficiency in Bi below 7 atoms p.f.u. Such assumption is made for the berryite from Baut occurrence, Romania by Cook (1998). In most analyses Pb shows slight excess too.

Benjaminite. The calculation of the analyses 7, 8 and 9 from table 5 fits well with the idealized formulae of benjaminite $Pb_2(Ag,Cu)_2Bi_4S_9$ (Nuffield, 1953) and $(Ag,Cu)_3(Bi,Pb)_7S_{12}$ (Gaines et al., 1997) where Ag/Cu ratio is 3. Benjaminite from Svishti Plaz has Ag/Cu ratio 0.70, 0.75 and 3.79. According to Karup-Møller and Makovicky (1979) in this part of the system Ag_2S-Cu_2S-Bi_2S_3-PbS both Bi and Cu could substitute Ag. The total of Bi and Pb in the formulae is nearly 7.

Inclusions of unidentified Ag-Cu-Pb-Bi sulfosalts are observed in a cobalt-pyrite, morphologically very different from the other

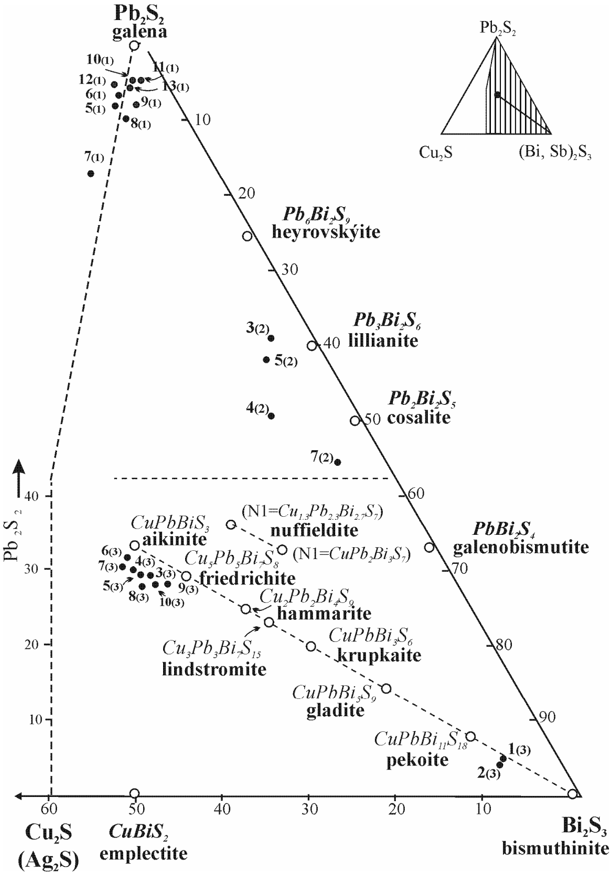

Fig. 7. The compositional plot in the Pb_2S_2-Bi_2S_3-$Cu(Ag)_2S$ system of the analysed minerals from Svishti Plaz deposits. The numbers correspond to the respective analyses in the respective tables numbered in brackets. Open circles – theoretical compositions of minerals

Фиг. 7. Проекция на съставите в системата Pb_2S_2-Bi_2S_3-$Cu(Ag)_2S$. Номерата отговарят на номерата на анализите, а номерата в скобите са номерата на таблиците. Празни кръгчета – теоретичните състави на минералите

pyrites in the deposit (Fig. 5). The central parts of the pyrite crystals are solid and the porous periphery is probably a result of skeletal growth or replacement. The white parts contain cobalt up to 4.52 wt.%.

Discussion

According to structural relations differences in the deposition of the three bismuthiferous sub-associations could be marked. A breakdown of an ISS or primary complex bismuth sulphosalt(?) for the first bismuth sub-association is suggested. As a result native Bi, matildite, Pb-Bi and Ag-Bi sulphosalts, bismuthinite-pekoite and chalcopyrite were formed. The presence of native Bi is evidence for low fS_2 in the hydrothermal solutions. The reason could be a rapid temperature decrease during the deposition. The second and third sub-associations were deposited obviously later by lower temperatures.

The lack of fluid inclusion and isotopic data of bismuth mineralization constrains some of the conclusions to be made by interpretation and involving of some experimental data and

Table 5. *Microprobe analyses of berryite and benjaminite(?), sample 7G/1, wt.%*
Таблица 5. *Микросондови анализи на бериит и бенжаминит(?), образец 7G/, тегл.%*

No	Mineral	Cu	Pb	Ag	Bi	S	Te	Sb	Total
1.	berryite	7.49	20.89	8.23	46.72	16.90			100.23
2.		6.23	24.19	7.01	44.94	16.58	0.24	0.19	99.38
3.		6.67	22.00	7.66	47.04	16.53			99.90
4.		6.57	22.98	7.68	45.75	15.63		0.49	99.10
5.		6.51	22.25	8.71	45.15	17.42			100.04
6.		6.88	23.37	7.89	46.99	15.78			100.91
7.	benjaminite (?)	6.04	26.82	7.69	42.17	16.73			99.45
8.		6.39	27.22	7.55	41.20	17.15			99.51
9.		2.18	28.07	13.88	39.90	15.63			99.56

1. $(Cu,Ag)_{5.73}Pb_{2.99}Bi_{6.63}S_{15.65}$
2. $(Cu,Ag)_{4.95}Pb_{3.57}Bi_{6.56}S_{15.83}$
3. $(Cu,Ag)_{5.31}Pb_{3.22}Bi_{6.82}S_{15.65}$
4. $(Cu,Ag)_{5.40}Pb_{3.45}Bi_{6.81}S_{15.20}$
5. $(Cu,Ag)_{5.38}Pb_{3.17}Bi_{6.89}S_{11.07}$
6. $(Cu,Ag)_{5.54}Pb_{3.46}Bi_{6.89}S_{15.11}$
7. $(Ag_{1.54}Cu_{2.04})_{3.58}Pb_{2.80}Bi_{4.35}S_{11.28}$
8. $(Ag_{1.49}Cu_{2.13})_{3.62}Pb_{2.80}Bi_{4.19}S_{11.40}$
9. $(Ag_{2.89}Cu_{0.77})_{3.66}Pb_{3.05}Bi_{4.38}S_{11.00}$

information on similar types of deposits. Abundant data, such as those from phase equilibrium, fluid inclusions and stable isotopes, indicate that most of the mineral assemblages belonging to the system Ag-(Cu)-Pb-Bi-S have crystallized at temperatures between 200 and 400˚C. At Ivigtut, Greenland, galena + Pb-Bi-Ag(Cu) sulfosalt assemblages are interpreted to have crystallized at 300 to 550˚C (Karup-Møller, 1977; Karup-Møller, Pauli, 1977). In the Darwin district, California temperature greater than 350˚C for galena and associated sulfosalts is assumed (Czamanske, Hall, 1975). Fluid inclusion study and sulfur isotope thermometry on the main pyrite-arsenopyrite and base metal stages in Svishti Plaz indicate a wide range of deposition between 320 and 230˚C (Bogdanov, Zairi, 1989). The complex bismuth mineralization established only in samples from one exploration mine working differs in mineralogical and chemical composition from that of the main vein assemblages in Svishti Plaz deposit. The absence of this mineralization in the other mine workings suggests its connection to a source different from the source creating the hydrothermal solutions of the main mineralisazion.

Svishti Plaz deposit is situated in Stara planina metallogenic zone but is in close space proximity with the Upper Cretaceous copper deposits of the Sredna Gora metallogenic zone. Bismuth mineralization and Bi as trace element in the common sulfides are typical for all types of copper deposits in this zone and cobalt mineralization is registered in some of them too (Bogdanov, 1987; Tokmakchieva, 1994; Popov et al., 2000, Tsonev et al., 2000). In porphyry-copper Medet deposit cobaltian pyrite and carrollite is found (Strashimirov, 1982). In the massive copper deposits Elshitsa and Radka from Panagyurishte district in Central Sredna Gora zone a complex Cu-Bi-Pb-Te mineralization is described (Kouzmanov et al., 2000).

The Sredna Gora copper deposits are hosted in Upper Cretaceous volcanites and are consequently much younger than Svishti Plaz deposit (270-285 Ma based on Pb isotopes in galena, Amov et al., 1981). A later treatment connects the mineralization of Svishti Plaz deposit with Upper Cretaceous dike magmatism without any supporting data (Cheshitev et al., 1995). The copper mineralization in Svishti

Plaz with Bi as trace element is considered to be generated from the Vezhen pluton but very cautiously is assumed a much younger age (Kuikin et al., 1972). Probably some of the faults hosting Bi-mineralization in Svishti Plaz deposit were open during Upper Cretaceous, what enabled the Sredna Gora ore-forming solutions to reach far from the place of their origin. The superposition of this mineralization on the earlier Svishti Plaz one, involving possible reheating and remobilization of elements (Pb) already present in the earlier minerals has resulted in the formation of the complex Cu-Pb-Ag-Bi assemblage.

Still being just a hypothesis, this assumption needs more structural support, fluid inclusion and detailed isotopic study of the host rocks, alteration and mineral assemblages to be finally confirmed.

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