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A review of Pb-Sb(As)-S, Cu(Ag)-Fe(Zn)-Sb(As)-S, Ag(Pb)-Bi(Sb)-S and Pb-Bi-S(Te) sulfosalt systems from the Boranja orefield, West Serbia

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Abstract. Recent mineralogical, chemical, physical, and crystallographic investigations of the Boranja orefield showed very complex mineral associations and assemblages where sulfosalts have significant role. The sulfosalts of the Boranja orefield can be divided in four main groups: (i) Pb-Sb(As)-S system with ±Fe and ±Cu; (ii) Cu(Ag)-Fe(Zn)-Sb(As)-S system; (iii) Ag(Pb)-Bi(Sb)-S; (iv) and Pb-Bi-S(Te) system. Spatially, these sulfosalts are widely spread, however, they are the most abundant in the following polymetallic deposits and ore zones: Cu(Bi)-FeS Kram-Mlakva; Pb(Ag)-Zn-FeS_2 Veliki Majdan (Kolarica–Centralni revir–Kojići); Sb-Zn-Pb-As Rujevac; and Pb-Zn-FeS_2-$BaSO_4$ Bobija. The multi stage formation of minerals, from skarn-hydrothermal to complex hydrothermal with various stages and sub-stages has been determined. All hydrothermal stages and sub-stages of various polymetallic deposits and ore zones within the Boranja orefield are followed by a variety of sulfosalts.

Key words: Sulfosalts, Boranja orefield, West Serbia.

Апстракт. Досадашња минералошка, хемијска, геохемијска и кристалографска проучавања показала су да се у рудном пољу Борање јављају веома сложене минералне асоцијације и парагенезе, где у њеним полиметаличним минерализацијама доминирају минерали из групе сулфосоли. Сулфосоли из рудног поља Борање могу се поделити у четири веће групе: (i) систем Pb-Sb(As)-S, са ±Fe и ±Cu; (ii) систем Cu(Ag)-Fe(Zn)-Sb(As)-S; (iii) систем Ag(Pb)-Bi(Sb)-S; (iv) систем Pb-Bi-S(Te). Ове сулфосоли су просторно веома распрострањене, међутим, оне су најзаступљеније у следећим полиметаличним лежиштима и рудним зонама: Cu(Bi)-FeS Крам–Млаква; Pb(Ag)-Zn-FeS_2 Велики Мајдан (Коларица–Централни ревир–Којићи); Sb-Zn-Pb-As Рујевац; Pb-Zn-FeS_2-$BaSO_4$ Бобија. Утврђено је вишеетапно стварање минерала, где прва одговара скарн-хидротермалном а друга сложеном хидротермалном, са већим бројем стадијума и подстадијума. Сви стадијуми и подстадијуми хидротермалне етапе у минералним асоцијацијама различитих полиметаличних лежишта и рудних зона, праћени су појавом широке лепезе сулфосолних минерала.

Introduction

Sulfosalts are complex sulfide minerals with the general formula: $A_mB_nS_p$; where A represents a metal such as Cu, Pb, Ag, Fe and rarely Hg, Zn, V; B usually represents semi-metal such as As, Sb, Bi and rarely Ge, or metals like Sn and rarely In; and S is S or rarely Se or/and Te (Anthony *et al.* 1990; Moëlo *et al.* 2008). Formerly, it was believed that the sulfosalts were salts of complex hypothetical thioantimonic or

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thioarsenic acids (e.g., $HSbS_2$, $H_{18}As_4S_{15}$, H_3AsS_3). X-ray diffraction (XRD) analyses indicate that the crystal structures of Pb-Sb-As-S sulfosalts are based on structural fragments of simpler compounds such as galena (lead sulfide; PbS) blocks and stibnite (antimony trisulfide; Sb_2S_3) sheets (Wernick 1960). No encompassing theory has been evolved to rationalize many of these curious compounds. The complexity of many of the structures evidently results from them having crystallized at low temperatures and the consequent high degree of ordering of the metal atoms. Syntheses of such compositions at higher temperature usually result in structures simpler than the complicated low-temperature forms. There are about 200 known sulfosalts (Moëlo *et al.* 2008).

These minerals were formed under the mutual influence of different sulfantimonide, sulfarsenide, sulfstanate, sulfbismuthinide, etc. anions (e.g. SbS_2^{1-}, $As_4S_{15}^{18-}$, AsS_3^{3-}, $Bi_2S_6^{6-}$), with metal ions (e.g., $Cu^{1+;2+}$, Ag^{1+}, Fe^{2+}, Pb^{2+}). These reactions occur only in mineralized solutions with increased alkalinity and high concentration of H_2S. Deposition of miargirite $AgSbS_2$, pyrargyrite Ag_3SbS_3 and stephanite Ag_5SbS_3 occur during mutual influence of sulfantimonide anions with Ag^{1+}. Interactions between already deposited sulfides (galena, chalcopyrite, etc.) and mineralized solutions (ascendant and/or descendent) may result in the formation of younger sulfosalts. The typical example of the reaction crystallization is contact between galena-chalcopyrite with sulfantimonide solutions when bournonite $PbCuSbS_3$ was deposited. The corrosive reaction is characteristic for influence of sulfantimonide solutions along galena surfaces thus creating wool-like variety boulangerite $Pb_4Sb_3S_{11}$ and/or semseyite $Pb_9Sb_8S_{21}$ (Ramdohr 1980; Anthony *et al.* 1990). Moreover, decrease of temperature and pressure led to decomposition of high-temperature solid solutions when two or more stable sulfosalts phases were formed. This is particularly visible in Pb-Ag-bearing sulfbismuthinide when complex exsolutions with lamellae structures were deposited (i.e., phases along the lillianite-gustavite solid solution $Pb_3Bi_2S_6$-$AgPbBi_3S_6$) (Cook 1997).

Although under exceptional circumstances some sulfosalts may constitute Ag ores (i.e., proustite, pyrargyrite, and stephanite), and other species have constituted Ag ores (in minor amounts), Hg, Tl, As, and Sb (i.e., boulangerite, livingstonite, enargite, and tennantite-tetrahedrite groups), their economic importance is sometimes significant (Ag in the Pb-concentrate) and sometimes trivial. Aside from mineralogical curiosities, the sulfosalts are of interest because their electronic properties are related to those of semiconductors (Chvilyova *et al.* 1988).

The Boranja orefield (BOF) is well-known since the Roman Empire and Medieval times and is still important factor of modern mining in this part of Serbia. Significant research began during the second half of the 20th century. Comprehensive mineralogical, crystallographic, geochemical and petrological studies yielded important results in defining mineral compositions of the mineralizations and surrounding rocks (e.g. Karamata 1955; Radukić 1960; Tomić 1962; Borodaev 1978; Janković 1978; Radosavljević *et al.* 1982). This study shows a synthesis of previous research of sulfosalts with revisited and new data.

Materials and methods of study

Polished sections were prepared for reflected-light microscopy and Electron Probe Micro–analyses (EPMA), following standard preparation and polishing steps (Picot & Johan 1982). The Carl-Zeiss polarizing microscope, model JENAPOL-U equipped with 10×, 20×, 50×, 100× (oil immersion) objectives and a system for a photomicrography (“Axiocam 105 color” camera and “Carl Zeiss AxioVision SE64 Rel. 4.9.1.” software package with „Multiphase” module).

EPMA were performed on a JEOL JSM-6610LV scanning electron microscope (SEM) connected with an INCA energy-dispersion X-ray analysis unit; EDX analytical system. An acceleration voltage of 20 kV was used. The samples were coated with gold. The following standards and analytical lines were used: FeS_2 (FeKα, SKα), ZnS (ZnKα, SKα), Mn (MnKα), Ni (NiKα), Co (CoKα), Cu (CuKα), InAs (AsKα,), InSb (SbLα), SnO_2 (SnLα), Ag_2Te (AgLα), CdS (CdLα), HgS (HgMα), PbS (PbMα), and Bi (BiMα). EDX detection limits were $2\sigma \sim 0.3$ wt% (counting time 60 sec). General formulae were calculated according to Anthony *et al.* (1990).

Occurrence and geological settings

The Podrinje metallogenic district (PMD) belongs to the Serbo-Macedonian Metallogenic Province (SMMP) and includes several smaller orefields: Boranja (Serbia), Cer (Serbia), and Srebrenica (Bosnia and Herzegovina) (Vanđel 1978; Janković 1990). The Boranja orefield (BOF) covers an area of about 200 km^2. It is situated on the SE margin of the Oligocene granodiorite pluton of Boranja (Delaloye *et al.* 1989; Steiger *et al.* 1989), which belongs to the Dinaridic granitoid suite of the Late Paleogene – Early Neogene age (Cvetković *et al.* 2000), and is situated on a border of three terranes – the Jadar block terrane (Filipović 2005), the Vardar zone composite terrane and the Drina–Ivanjica terrane (Karamata & Krstić 1996; Karamata *et al.* 1997).

It consists of Paleozoic, Mesozoic, and Tertiary formations (Fig. 1). Paleozoic is represented by Carboniferous sediments, mostly slates and sandstones of low-grade metamorphism, and limestones (“the Drina series”). Mesozoic complex consists of Triassic, Jurassic and Cretaceous formations, mostly slates, limestones, volcanic sediments, basic and ultrabasic rocks (SIMIĆ 1957; ĐOKOVIĆ 1985; NEUBAUER 2002).

Mineralization of the BOF is concentrically distributed around the Tertiary granodiorite of Boranja (Fig. 1). Around the intrusion, in the skarn alteration halo, several small Fe deposits occur (magnetite and pyrrhotite), and less frequently Bi, W and Mo deposits (Velika Reka, Vranovac). The Cu(Bi)-FeS Kram-Mlakva ore zone belongs to small Cu polymetallic skarn deposits (Fig. 1). Outwards the granodiorite, the Pb(Ag)-Zn Veliki Majdan ore zone consists of ore bodies embedded in carbonates on the contact with quartz latite and Paleozoic slates (Fig. 1). The main mineral association includes pyrrhotite, pyrite, sphalerite, galena, chalcopyrite, and Pb(Ag)-Sb sulfosalts in lesser amounts (ČIKIN *et al.* 1983).

The outermost halo hosts several Sb deposits (Fig. 1). The most important are situated in the Brasina–Zajača–Stolice–Dobri potok intrusive-volcanic zone with the following leading ore elements Sb, Pb, Zn, Fe, Ba, and F; in the Rujevac–Crvene stene–Vujanoviča–Brezovica volcanogenic-sedimentary zone of Diabase-Chert Formation (DCF) with the following metals: Sb, Pb, Zn, Fe, As, Ba, and Hg. The ore bodies occur as irregular pipes and lenses in silicified Carboniferous limestones (BORODAEV 1978; JANKOVIĆ 1979; ĐURIČKOVIĆ 2005).

Minerals of the BOF were deposited in several successive stages, which together correspond to a single regional-scale mineralization event that is related to the subvolcanic-plutonic intrusions of the Boranja magmatic complex. This is well demonstrated by the

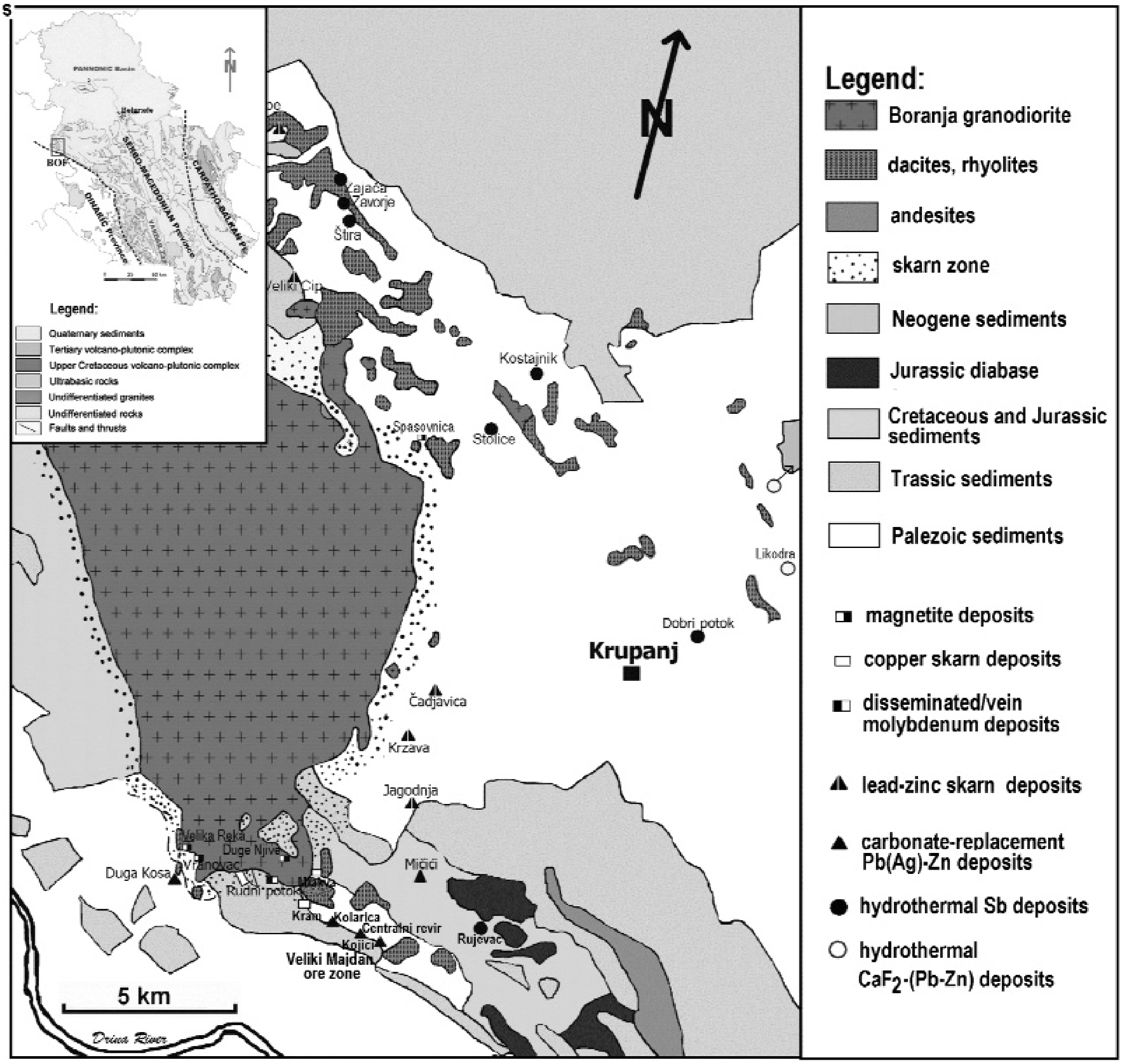

Fig. 1. Detailed geological and metallogenic map of the BOF (modified according to Basic Geological Map of Serbia, 1:100,000). Upper left corner shows exact location of BOF within Serbia (MONTHEL *et al.* 2002).

zonal arrangement of several metallic mineral associations (Fe-Cu(Bi)→ Pb(Ag)-Zn→ Sb(As)-Pb-Zn→ CaF_2(Pb-Zn), with increasing distance from the Boranja granodiorite (Radosavljević *et al.* 2013a).

The Bobija polymetallic barite-sulfide deposit is situated in East slopes of Sokolske Mnt., which is some 15 km to the NE away from Ljubovija. The deposit itself consists of complex geological composition mainly built of Paleozoic and Mesozoic sediments (Janković 1990). The Bobija deposit is composed of massive barite and sulfide FeS_2-Pb-Zn-Cu elongated lens-like ore bodies. Massive barite ore bodies are consisted of 50 to 90 wt% of $BaSO_4$ (Radosavljević *et al.* 2013b).

Mineralogy of sulfosalts

The sulfosalts of the BOF can be divided in the four main groups: (i) Pb-Sb(As)-S system, with ±Fe and ±Cu – *zinkenite, fülöppite, plagionite, robinsonite, boulangerite, jamesonite, bournonite, twinnite, geocronite* and *gratonite*; (ii) Cu(Ag)-Fe(Zn)-Sb(As)-S system – *tetrahedrite, tennantite,* and *Ag-bearing tetrahedrite*; (iii) Ag(Pb)-Bi(Sb)-S system – *pyrargyrite, diaphorite, freieslebenite, Sb-bearing schirmerite*, *Ag-bearing nuffieldite*, and *fizélyite*; (iv) Pb-Bi-S(Te) system – *bursaite, cannizzarite, cosalite, aikinite, ustarasite*, and *tetradymite*. Spatially, these sulfosalts are widely spread, but they are most abundant in the following polymetallic deposits and ore zone: Cu(Bi)-FeS Kram–Mlakva, Pb(Ag)-Zn-FeS_2 Veliki Majdan (Kolarica–Centralni revir–Kojići), Sb-Zn-Pb-As Rujevac, and Pb-Zn-FeS_2-$BaSO_4$ Bobija (Fig. 1). Most of them are lead gray with a metallic luster, brittle and difficult to distinguish without using XRD method and Electron Microprobe analyses (EPMA).

Their mutual structural and textural characteristics are complex, and characterized by small grain size (<5–100 µm), which beside intergrowths (effects of reaction and/or corrosive processes, high-temperature exsolution products, etc.) additionally makes it difficult to single it out for crystallographic (XRD) and chemical (spectrochemical and mass spectrometric) investigations. Chemical composition of the minerals was calculated according to Anthony *et al.* 1990. Besides so far determined sulfosalts, new minerals from the Pb-Ag-Bi-Sb-S system could be discovered (Radosavljević 1988).

Sulfosalts of the Pb-Sb(As)-S system, with ±Fe and ±Cu

This sulfosalt group is most abundant occurring in almost all deposits and mineralizations of the Boranja orefield. Sulfosalts of Pb-Sb(As) composition are the most common in the Rujevac polymetallic Sb-Zn-Pb-As deposit. In this deposit Pb was characteristically deposited after Sb (Borodaev 1978), which genetically deviates from other Sb deposits and occurrences within the SMMP. There are various of sulfosalts belonging to the sphalerite-Pb-Sb(As) sulfosalt-As mineral assemblage, which are very dominant. So far, the following sulfosalts have been determined: *zinkenite* – $Pb_{8.93}(Sb_{18.94},As_{3.08})_{\Sigma22.02}S_{42.02}$; *fülöppite* – $Pb_{2.86}(Sb_{7.01},As_{1.07})_{\Sigma8.08}S_{15.06}$; *plagionite* – $Pb_{4.97}(Sb_{7.29}, As_{0.76})_{\Sigma8.02}S_{17.00}$; *robinsonite* (?); *twinnite* – $Pb_{0.97}(Sb_{1.42},As_{0.60})_{\Sigma2.02}S_{4.00}$; and *gratonite* (determined only microscopically, Radosavljević 1988; 2012).

The most abundant sulfosalt of the sphalerite-Pb-Sb(As) sulfosalt-As mineral assemblage is zinkenite. It was first discovered by Janković *et al.* (1977) and Moëlo *et al.* (1983), and later supplemented by new data by Radosavljević (1988), Zarić *et al.* (1992), Radosavljević (2012), Radosavljević *et al.* (2012), and Radosavljević *et al.* (2014a). It occurs in the following mineral association: Pb-Sb(As) sulfosalts, sphalerite, arsenopyrite, realgar, duranusite, native As, stibarsen, dolomite, and quartz. It occurs as tabular, needle- and wool-like fibrous individuals (plumosite), forming larger individual aggregates mostly in the interstices of the quartz matrix. Its central zones are locally replaced by plagionite. Moreover, zinkenite intensively intersects, penetrates and overgrowths cataclased sphalerite aggregates (Fig. 2f). It also contains inclusions of quartz and duranusite. When replacing crystal aggregates of older stibnite, it is often penetrated and overgrown along its edges by dolomite metacrysts. Twinnite is characterized by polysynthetic twinning and commonly occurs as the youngest sulfosalt along the edges of stibnite, lesser plagionite. Although it is mentioned in the literature (Janković *et al.* 1977), robinsonite was not confirmed in our study. In addition, according to Pruseth *et al.* (1997), robinsonite is unstable at temperatures below 300 °C, confirming its absence in this deposit.

Besides major elements, EPMA of sulfosalts usually show presence of As (up to 8.00 wt%), Ag (up to 0.04 wt%), Cu (up to 0.03 wt%) and Fe (up to 0.01 wt%). Hg, Zn, Cd, Bi and Tl were not detected (Radosavljević 2012).

Pb-Sb(As) sulfosalts, associated to the Veliki Majdan ore zone, include: *jamesonite* – $Pb_{3.99}(Fe_{1.00},Cu_{0.01})_{\Sigma1.01}Sb_{6.00}S_{14.00}$; *boulangerite* – $Pb_{5.02}Sb_{4.15}S_{10.83}$; *geocronite* – $Pb_{14.21}(Sb_{3.05},As_{2.74})_{\Sigma5.79}S_{23.00}$ (Fig 2a); *bournonite* – $Pb_{1.00}Cu_{1.00}(Sb_{0.94},As_{0.06})_{\Sigma1.00}S_{3.00}$; *As-bournonite* – $Pb_{1.00}(Cu_{0.97},Fe_{0.02})_{\Sigma0.99}(Sb_{0.54},As_{0.48})_{\Sigma1.02}S_{2.99}$; and accompanying the pyrite-galena-sphalerite mineral assemblage (Dimitrijević & Rakić 1978; Rakić *et al.* 1984; Radosavljević *et al.* 1993; Radosavljević *et al.* 2013a).

The most abundant sulfosalt of the Veliki Majdan ore zone is jamesonite. It occurs as short-prismatic crystals, deposited in the interspaces of chalcopyrite and calcite aggregates. Bournonite most frequently occurs at the grain boundaries between galena and chalcopyrite replacing galena (Fig. 2b). It is Ag-free, and contains As from 0.5 to 7.7 wt%. As-bearing bournonite also occurs in the epithermal Au-Te vein system of the Sacarimb deposit in Romania (Ciobanu *et al.* 2005). EPMA data yielded stoichiometric composition, without presence of any other element except As.

Besides these Pb-Sb sulfosalts, new analyses confirmed presence of a Sb-member with the highest Sb content (46.4–46.7 wt%) in the Centralni revir locality within the Veliki Majdan ore zone. EPMA yielded following average crystallochemical formula of fülöppite $Pb_{3.02}Sb_{7.97}S_{15.01}$ (3 analyses). It is deposited in interspaces between pyrite grains in short prismatic forms (Fig. 2c). Unlike fülöppite from the Rujevac polymetallic deposit, this one is As-free.

Sulfosalts of the Cu(Ag)-Fe(Zn)-Sb(As)-S system

Tetrahedrite is a Cu-Sb sulfosalt mineral with following average crystallochemical formula: $(Cu,Ag)_{10}(Fe,Zn)_{12}Sb_4S_{13}$. It is the Sb end-member of the continuous solid solution series with As-bearing tennantite. Other elements also substitute in the structure, most notably Fe and Zn, along with less common Ag, Hg and Pb. Bismuth also substitutes Sb, and Bi-bearing tetrahedrite or annivite is a recognized variety.

Tetrahedrite-group minerals occur in coarse crystalline aggregates only within the Veliki Majdan ore zone. These minerals are closely related to chalcopyrite and bournonite, forming part of the galena-sphalerite mineral assemblage. Furthermore, they usually

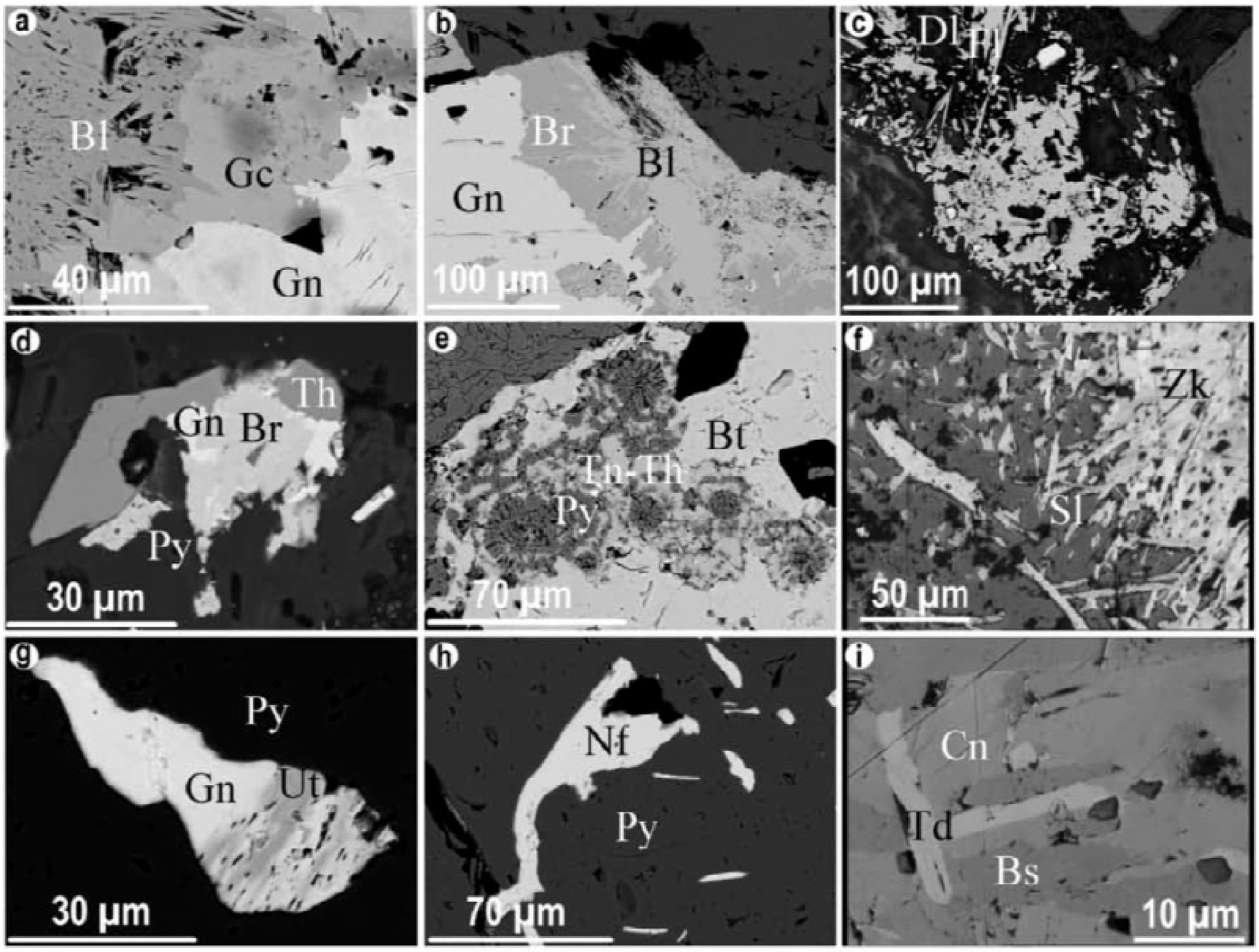

Fig. 2. Reflected light and SEM (BSE) photomicrographs of different sulfosalts within the BOF: **a.** Galena overgrown by geocronite and needle-like boulangerite – Kolarica (SEM); **b.** Galena overgrown by bournonite and wooly boulangerite – Centralni revir (SEM); **c.** Needle-like crystals of fülöppite embedded in dolomite matrix – Centralni revir (SEM); **d.** Intergrowth of tetrahedrite with galena which is almost completely replaced by bournonite in pyrite matrix – Kolarica (SEM); **e.** Colloform formations of tennantite-tetrahedrite with zoned pyrite embedded in barite matrix – Bobija (SEM); **f.** Sphalerite overgrown by needle-like zinkenite – Rujevac (reflected light, air, II N); **g.** Ustarasite inclusions in galena embedded in pyrite matrix – Kolarica (SEM); **h.** Elongated and curved lamellae of Ag-bearing nuffieldite embedded in pyrite – Kolarica (SEM); **i.** Intergrowth of bursaite with cannizzarite with needle-like inclusions of tetradymite – Kram (reflected light, oil immersion, II N). Mineral abbreviations: **Gn** – Galena, **Gc** – geocronite, **Bl** – boulangerite, **Br** – bournonite, **Fl** – fülöppite, **Dl** – dolomite, **Th** – tetrahedrite, **Py** – pyrite, **Tn-Th** – tennantite-tetrahedrite, **Bt** – barite, **Sl** – sphalerite, **Zk** – zinkenite, **Ut** – ustarasite, **Nf** – nuffieldite, **Bs** – bursaite, **Cn** – cannizzarite, **Td** – tetradymite.

cement older cataclastic pyrite aggregates. Tetrahedrite-group minerals rim galena aggregates and are also replaced by boulangerite. According to both, optical observations and measurements in polished sections (microhardness and reflectance spectra) and chemical analyses, two types of tetrahedrite-group minerals can be recognized (Radosavljević *et al.* 1986).

EPMA data showed that they belong to the Fe-bearing tetrahedrite – $(Cu_{9.17},Ag_{0.60})_{\Sigma 9.77}(Fe_{1.52},Zn_{0.60},Cd_{0.02})_{\Sigma 2.14}(Sb_{3.60},As_{0.27})_{\Sigma 3.87}S_{13.23}$ and Ag-bearing tetrahedrite – $(Cu_{7.42},Ag_{2.16})_{\Sigma 9.58}(Zn_{1.13},Fe_{1.09},Cd_{0.02})_{\Sigma 2.24}Sb_{4.16}S_{13.02}$ solid solution series. Microhardness of tetrahedrite-group minerals increases with increasing content of Fe and decreasing content of Ag. Tetrahedrite fills cracks and fissures within cataclastic pyrite. Tetrahedrites show variable contents of Zn and Fe (2.2–4.2 and 3.4–5.4 wt%, respectively), whereas some grains contain up to 13.1 wt% Ag. Ag-bearing tetrahedrite is characterized by a Ag/(Ag+Cu) atomic ratio between 0.33 and 0.34. The tetrahedrite-group minerals display Sb/(Sb+As) and Zn/(Zn+Fe) ratios between 0.89 and 1.00 and between 0.27 and 0.31, respectively.

Besides these tetrahedrite-group minerals, new analyses confirmed presence of a Sb-end-member with the lowest Ag content (0.8–1.1 wt%) in the Centralni revir locality (Veliki Majdan ore zone). EPMA analyses yielded following average crystallochemical formula: $(Cu_{9.85},Ag_{0.16})_{\Sigma 10.01}(Zn_{1.46},Fe_{0.53})_{\Sigma 1.99}Sb_{4.01}S_{13.00}$ (4 analyses). It usually crystallizes along galena grain boundaries in a form of elongated crystals, overgrown by bournonite (Fig. 2d). Tetrahedrite shows uniform content of Zn and Fe (5.1–6.0 and 1.5–2.2 wt%, respectively). Zn/(Fe+Zn) atomic ratio amounts between 0.73 and 0.76, which corresponds to the variety with a higher Zn content.

The mineralogical investigation confirmed that the Bobija deposit consists of a simple mineral association composed of sulfides, sulfosalts (tetrahedrite-tennantite group), native Ag, barite and gangue minerals. Tetrahedrites are significantly abundant in the ore. According to the optical features they generally correspond to tennantite, and partly to tetrahedrite. These minerals are often in association with pyrite, sphalerite, and galena but in a lesser extent. Colloform grains of tetrahedrite-tennantite composition are not rare, and are separated from pyrite and sphalerite in the assemblage (Fig. 2e). Occurrence of disperse pyrite in tetrahedrite surfaces when it completely changes its optical features is not rare. Central parts of these aggregates are sometimes seized by zoned pyrite.

EPMA confirmed that tetrahedrite from Bobija is of As-Sb composition with Ag, Hg, and Mn in small amounts (0.7–1.8 wt%, < 0.3–2.2 wt%, and < 0.3–0.5 wt%, respectively). The average EPMA yielded following crystallochemical formula: $(Cu_{9.82},Ag_{0.16})_{\Sigma 9.98}(Zn_{1.25},Fe_{0.64},Hg_{0.10},Mn_{0.02})_{\Sigma 2.01}(As_{2.60},Sb_{1.38})_{\Sigma 3.98}S_{13.02}$ (Radosavljević *et al.* 2013b). The Sb/(Sb+As) atomic ratio ranges from 0.21 to 0.43 corresponding to a variety with an increased content of tennantite component. These minerals show variable contents of Zn (4.3–6.0 wt%), and Fe (1.7-3.5 wt%). The Zn/(Fe+Zn+Mn+Hg) atomic ratio ranges between 0.5 and 0.7, which corresponds to a variety with an increased Zn content.

Sulfosalts of the Ag(Pb)-Bi(Sb)-S system

This group belongs to Ag-rich sulfosalts (pyrargyrite family) and ternary sulfosalts (freieslebenite family) (Moëlo *et al.* 2008). Within the Veliki Majdan ore zone, pyrargyrite was determined only microscopically, embedded in carbonate matrix accompanied with galena (Radosavljević 1988).

According to Radosavljević *et al.* (2013a), Ag content incorporated in the structure of galena amounts to approximately 15 wt%, while the rest is in a form of micron (“visible”) and/or submicron (“invisible”) particles of Ag minerals. The following Ag minerals diaphorite, fizélyite, freieslebenite, schirmerite, and Ag-bearing tetrahedrite were determined qualitatively into the insoluble residue using XRD method.

Ore microscopic and EPMA investigations confirmed presence of schirmerite in the Veliki Majdan ore zone (Kolarica locality). It is determined as Sb-bearing schirmerite with a following average crystallochemical formula: $(Ag_{1.96},Fe_{0.96})_{\Sigma 2.91}Pb_{6.11}(Bi_{5.98},Sb_{0.84})_{\Sigma 6.82}S_{18.16}$ (5 analyses).

Besides schirmerite, in the same locality a sulfosalt with a following chemical composition was determined (in wt%): S (16.99–17.05), Fe (0.45–2.38), Ag (5.52–6.27), Sb (2.83–6.80), Pb (33.42–36.84), Bi (33.56–36.57). Cu, As and Te are below a detection limit <0.3 wt%. It usually cements cracks and fissures of pyrite crystals and/or is deposited in them, mostly forming a very fine lamina or bent “comb-like” lamellae up to 100 μm in length (Fig. 2h). Luster is moderately high (~35–45 %), microhardness is higher than galena with noticeable pale gray to gray-violet bireflectance. According to optical and chemical characteristics this sulfosalt was defined as Ag-bearing nuffieldite with a following average crystallochemical formula: $Pb_2(Ag_{0.72},Fe_{0.30})_{\Sigma 1.02}(Sb_{0.54},Pb_{0.24},Bi_{0.21})_{\Sigma 1.00}Bi_{2.00}S_{6.98}$ (4 analyses). According to these analyses Cu has been completely substituted by Ag and Fe (Moëlo *et al.* 1997; Pršek *et al.* 2006).

Sulfosalts of the Pb-Bi-S(Te) system

This group belongs to lillianite homotypic series. The definition and crystal chemistry of this homologous series were presented by Makovicky (1977) and Makovicky & Karup-Møller (1977a, 1977b).

Sulfosalts occurring in the Kram-Mlakva ore zone are related to the pyrite-chalcopyrite mineral assemblage, and are represented by: *bursaite* - $(Pb_{4.81},Fe_{0.03},Cu_{0.08},Ag_{0.16})_{\Sigma 5.08}Bi_{3.87}(S_{10.99},Te_{0.06})_{\Sigma 11.05}$; *cannizzarite* - $(Pb_{3.05},Ag_{0.02})_{\Sigma 3.07}Bi_{4.00}S_{8.93}$; *cosalite* - $(Pb_{1.95},Cu_{0.08})_{\Sigma 2.03}(Bi_{1.92},Sb_{0.01})_{\Sigma 1.93}S_{5.05}$; *aikinite* - $(Cu_{0.97},Fe_{0.02})_{\Sigma 0.99}(Pb_{0.98},Ag_{0.05})_{\Sigma 1.03}Bi_{0.95}S_{3.03}$; *ustarasite* $(Pb_{1.16},Ag_{0.02})_{\Sigma 1.20}(Bi_{3.70},Sb_{2.18},Cu_{0.06},Fe_{0.02})_{\Sigma 5.96}S_{9.84}$; and *tetradymite* $(Bi_{1.83},Pb_{0.07},Cu_{0.01})_{\Sigma 1.91}Te_{1.99}S_{1.10}$. These cannot be mutually macroscopically distinguished owing to their very small grain-size. Aggregates were embedded in garnet-calcite matrix. Well-developed crystals have not been observed, only spherical and spindle-like forms up to 10 µm in length. In addition, fewer occurrences of these sulfosalts were also determined in the Kolarica locality (Veliki Majdan ore zone), associated with pyrrhotite-sphalerite-galena mineral assemblage (Radosavljević-Mihajlović *et al.* 1998, 2007; Radosavljević *et al.* 2013a).

Bursaite is characterized by complex intergrowths that appear along cracks and fissures of chalcopyrite and silicates in a form of lath-like grains (Fig. 2i). In comparison to the other accompanying Pb-Bi sulfosalts, it is harder. It often contains inclusions of native Bi as exsolution products. According to Moelo *et al.* (2008), bursaite has been discredited as a mineral species. From the Sn-W deposit (Shumilovskoe locality) Mozgova *et al.* (1988) described an almost identical mineral to the one from the Kram-Mlakva ore zone. In their detailed mineralogical work on bursaite and cannizzarite the authors proposed that bursaite should be retained as an intergrowth of two lillianite-related phases, each with distinct unit-cell parameters. The EPMA composition, which represents a composite of two phases, indicates a Pb deficiency ($n \approx 3.83$). Minerals of bursaite composition from four known localities (Uludag-Turkey, Shumilovskoe-Russia, Cofer-Virginia, and Kram-Mlakva-Serbia) still have a problem of unsolved crystal structure. However, our new evidences, led to confirm that bursaite is undoubtfully a distinct mineral. Unfortunately, numerous attempts to determine the crystal structure using XRD on both single-crystal and powdered samples from the Kram–Mlakva ore zone were not successful, due to a very low crystallinity degree (Radosavljević-Mihajlović*et al.* 2007).

Cannizzarite reflectance is moderately high, but lower than bursaite (Fig. 2i). Reflection pleochroism is distinct, light gray to creamy. The anisotropy is strong, similar to bursaite, and hardness is considerably lowered (similar to galena). According to optical (reflectance, bireflectance, anisotropy) and physical (hardness) characteristics the investigated sulfosalt corresponds to cannizzarite. It is determined on a basis of optical, crystallographic and chemical measurements (Radosavljević-Mihajlović *et al.* 2007). Cosalite is less abundant than bursaite and cannizzarite. It occurs along sulfosalt aggregate rims as "jaggy" intergrowth forms. It is white, very similar to galena with trace of cream. Reflection pleochroism is weak and distinct only in oil, light gray to light green. The anisotropy is noticeable, but very distinct in oil with strong illumination. Reflectance and hardness are lower than in bursaite and cannizzarite (Radosavljević 1988).

Aikinite is the least abundant. It occurs in a form of elongated crystals, in a contact with bursaite and chalcopyrite. Hardness is the highest of all sulfosalts of this group. It is white with a light tint of cream. Reflection pleochroism is distinct in air, in oil very striking, light yellow to gray. Anisotropy is also distinct in air, in oil rather high. It is determined on a basis of optical and chemical measurements (Radosavljević 1988).

Ustarasite occurs only in the Kolarica locality (Veliki Majdan ore zone) mostly as mutually parallel thin needle-like crystals (up to 100 µm in length), and rarely as rhombohedral crystals embedded in older galena and carbonate matrix (Fig. 2g). It is an exsolution product of galena and Bi-Sb-Ag complex compounds. Bireflectance is noticeable, //N strong luster like galena, $\perp$ N darker with gray tint (quite to that of falkmanite), microhardness similar to cosalite, and anisotropy is strong without internal reflections (Radosavljević *et al.* 2013a).

Tetradymite also occurs in sulfosalt aggregates in form of fine needles. It is white, with faint yellowish tinge (Fig. 2i). Bireflection is weak, hardly visible at grain boundaries, light yellow to creamy. The anisotropy is distinct, and reflectance is high (R ~ 60 %). It is determined on a basis of optical and chemical measurements (Radosavljević-Mihajlović *et al.* 2007).

General genetic and paragenetic characteristics

Temperature of deposition of Pb-Zn mineral associations in the BOF range from 480–160 ºC (Radosavljević *et al.* 2012). Galena and sphalerite of this orefield were formed in high-, middle- and low-temperature hydrothermal stage, while Pb-Zn mineral associations of the Pb(Au)-Zn-FeS_2 Veliki Cip and CaF_2-Pb-Zn Ravnaja deposits unquestionably correspond to the high- (480 ºC) and low-temperature hydrothermal stage (230 ºC), respectively. In addition, the Pb(Ag)-Zn-FeS_2 Veliki Majdan ore zone corresponds to the temperature range from 450 to 370 ºC that is between high- and medium-temperature hydrothermal stages. Temperature decreases moving further from the Tertiary granodiorite of Boranja according to the following sequence: Kolarica–Centralni revir–Kojići. Moreover, in the Ravnaja deposit, Nikolić & Gatter (1986) determined two temperature intervals of formation of fluorite (275–245 ºC and 205–160 ºC), and density of fluids (0.98–0.80 g/cm^3). In addition, temperature range of deposition from 280 to 160 ºC was obtained on quartz and sphalerite from the Sb-Pb-Zn-As Rujevac deposit using cryometric method (Mudrinić 1984).

Judging by the look of the exsolution structures of various compositions established in all levels of ore deposits, the temperature of crystallization of all skarn, high-, and middle-temperature hydrothermal associations was identical to formation of isometric coarse-crystalline grain-like structures. However, low-temperature hydrothermal associations characterize fine-grained colloform and gel-like textures with regular appearance of recrystallization (Radosavljević 1988).

Based on paragenetic relations into the polymetallic deposits of the BOF, the beginning of crystallization is connected to the low partial pressure fS_2, and deposition of low sulfidization minerals (pyrrhotite, Fe-rich sphalerite, tetrahedrite group of minerals, Pb-Sb and Pb-Bi sulfosalts, etc.). Minerals of high sulfidization (transformation of pyrrhotite into pyrite, pyrite, Fe-poor sphalerite, antimonite, realgar, etc.) began to crystalize with temperature decrease, partial pressure fS_2 increase, and spatial distancing from the Tertiary granodiorite of Boranja. Deposition areas were carbonates (mostly Triassic limestones) and silicates (dacite, andesite, slates), but in a lesser extent (Radosavljević *et al.* 2013a).

Silver is important and genetically significant metal which content varies from 10 to 820 g/t in the BOF. Its transport was achieved by polysulfide solutions enriched with Pb, Bi, Sb, and As. However, a possibility of carbonate-bicarbonate and halogen complex solutions should not be excluded. The best correlation is between Ag and Pb (r=0.828 significant at the 95 % confidence level), while among other elements it does not exist. This is expected since galena is the main Ag-bearing mineral, while occurrence of Ag minerals (Ag-tetrahedrite, pyrargyrite, electrum, and native Ag) is limited (Radosavljević 1988). Besides Ag, typomorphic elements as Bi and Sb are significantly abundant in galena. Complex investigations of galena from various deposits yielded that it frequently occurs in a form of isostructural solid solutions with diaphorite, fizélyite, freieslebenite, and schirmerite (e.g. Wernick 1960; Ontoyev & Korsakova 1967; Hoda & Chang 1975; Wang 1999; Chutas *et al.* 2008).

Crystallization of minerals in the BOF occurred in several successive stages, which together correspond to the unique mineralization cycle. According to the deposited minerals it can be concluded that hydrothermal solutions descend from common magmatic chamber connected to the Tertiary granodiorite of Boranja (Radosavljević *et al.* 2013a).

Conclusions

The areal extent of the SMMP covers around 30,000 km^2 in the territory of Serbia and extends over the three major geotectonic units: the Vardar ophiolite zone, the Serbo-Macedonian massif, and the inner Dinarides. It covers a small part of eastern Bosnia and Herzegovina (B&H), larger parts of Serbia and the Former Yugoslav Republic of Macedonia (FYRM), and also extends towards Bulgaria and Greece. The SMMP contains numerous volcanic-intrusive complexes of calcalkaline and shoshonitic affinity. These igneous complexes are directly associated with the development of numerous deposits and metal occurrences; primarily as Pb, Zn, Sb, then Cu and Mn, and to a lesser extent Fe, Bi, Ag, Hg, U, Sn, and W.

Polymetallic deposits of the BOF are genetically connected to the Tertiary granodiorite complex. It consists of a large number of Pb-Zn and Sb sulfide deposits, and in a lesser extent Cu, As, Bi and Ag. Magnetite deposits of lesser importance, connected to Ca-skarn stage, were formed along the contact of Triassic limestones and quartz diorite. Minerals of the BOF are characterized by very diverse types and are consisted of sulfides, sulfosalts, native metals, wolframates, molybdates, oxides, silicates and hydroxides.

The sulfosalts of the BOF can be divided in four main groups: (i) Pb-Sb(As)-S system, with ±Fe and ±Cu; (ii) Cu(Ag)-Fe(Zn)-Sb(As)-S system; (iii) Ag(Pb)-Bi(Sb)-S system; (iv) Pb-Bi-S(Te) system. These are most abundant in following polymetallic deposits and ore zones: Cu(Bi)-FeS Kram–Mlakva, Pb(Ag)-Zn-FeS_2 Veliki Majdan (Kolarica–Centralni revir–Kojići), Sb-Zn-Pb-As Rujevac, and Pb-Zn-FeS_2-$BaSO_4$ Bobija. Among over a hundred ore and rock-forming minerals from this area a considerable number of new minerals from the aspects of supplementing systematics of mineralogy of Serbia have been discovered.

Pb-Sb sulfosalt mineral assemblages are widespread throughout SMMP, where following orefields and ore zones are distinguished by its diversity: Kopaonik (Rajićeva Gora, Belo Brdo, Rogozna, etc.), Kratovo–Zletovo, Toranica, Sasa, Bučim, Alšar, etc. (e.g. Janković & Zarić 1980; Janković 1993; Serafimovski & Aleksandrov 1995; Aleksandrov *et al.* 1990a; Aleksandrov *et al.* 1990b; Serafimovski *et al.* 1990; Serafimovski *et al.* 2006; Serafimovski *et al.* 2013; Serafimovski *et al.* 2015; Radosavljević & Dimitrijević 2001; Voudouris *et al.* 2008; Radosavljević & Stojanović 2013; Radosavljević *et al.* 2014b). Besides the BOF, similar Pb-Bi(Sb) sulfosalt mineral assemblages have been determined in the Central Serbia, the Šumadija Metallogenic District, Rudnik orefield (Stojanović *et al.* 2006) and Golija orefield (Stajević & Zarić 1984). According to the mineral compositions, they are close to the Uludag orefield, Bursa Province, Turkey (Van der Kaaden 1958; Makovicky & Karup-Møller 1977), the Stanos shear-zone related deposit, Chalkidiki, Northern Greece (Voudouris *et al.* 2013), and in the Trepča deposit, Stari Trg, Kosovo, Serbia (Kołodziejczyk *et al.* 2015), belonging to the Alpine metallogenic belt.

Also, these mineral assemblages are very similar to the Larga hydrothermal systems in Romania (Carpathian-Balkan metallogenic province - COOK & CIOBANU 2004). Moreover, in comparison to the other metallogenic district within the SMMP, the mineral associations of the BOF are distinguished by a variety of Ag(Pb)-Bi(Sb) sulfosalts.

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Резиме

Преглед сулфосолне групе минерала у Pb-Sb(As)-S, Cu(Ag)-Fe(Zn)-Sb(As)-S, Ag(Pb)-Bi(Sb)-S и Pb-Bi-S(Te) системима са рудног поља Борање, Западна Србија

У Српско-македонској металогенетској провинцији (СММП), која просторно захвата мањи део Источне Босне, веће делове Србије и Македоније, и наставља даље према Бугарској и Грчкој, јављају се бројне и пространe масе вулкано-плутонских комплекса калко-алкалне магме. Површина њиховог развића у Србији износи око 30.000 km^2 и простире се преко три крупне геотектонске јединице: Унутрашњи Динариди, Вардарска тектонска зона и Српско-македонска маса. У вези са овим магматским комплексима, директним или индиректним, дошло је до стварања бројних лежишта и појава метала, у првом реду Pb, Zn, Sb, затим Cu, Mn, у мањој мери Fe, Bi, Ag, Hg, U, Sn и W.

Подрињска металогенетска област припада СММП. Мање металогенетске јединице су издвојене у оквиру следећих рудних поља: Цер (Северна Србија), Борања (Западна Србија) и Сребреница (Источна Босна). Полиметалична лежишта у рудном пољу Борање генетски су везана за терцијарни гранодиоритски комплекс. Састоје се од великог броја сулфидних лежишта са Pb-Zn, и Sb; и у мањој мери са Cu, As, Bi и Ag. Међу њима, јављају се мања значајна лежишта магнетита, која су у вези са скарновском етапом. Скарнови су калцијског типа, а формирани су дуж контаката тријаских кречњака и кварц диорита. У рудном пољу Борање, рудни и нерудни минерали одликују се веома разноврсним врстама и састоје се од сулфида, сулфосоли, самородних метала, волфрамата, молибдата, оксида, силиката и хидроксида.

Минерале из групе сулфосоли, који се јављају у лежиштима и појавама рудног поља Борање, могу се поделити у четири веће групе, са следећим до сада одређеним минералима: (i) систем Pb-Sb(As)-S, са ±Fe и ±Cu – цинкенит, филопит, плагионит, робинсонит, буланжерит, џемсонит, бурнонит, As-бурнонит, твинит, геокронит и гратонит; (ii) систем Cu(Ag)-Fe(Zn)-Sb(As)-S – тетредрит, тенантит, и Ag-тетредрит; (iii) систем Ag(Pb)-Bi(Sb)-S – пираргирит, дифорит, фрајслебенит, Sb-ширмерит, Ag-њуфилдит и физелит; (iv) систем Pb-Bi-S(Te) - бурсаит, каницарит, козалит, ајкинит, устарасит и тетрадимит.

Ове сулфосоли су просторно широко распрострањене у оквиру рудног поља Борање, међутим, оне су најзаступљеније у следећим полиметаличним лежиштима и рудним зонама: Cu(Bi)-FeS Крам-Млаква; Pb(Ag)-Zn-FeS_2 Велики Мајдан (Коларица–Централни ревир–Којићи); Sb-Zn-Pb-As Рујевац; Pb-Zn-FeS_2-$BaSO_4$ Бобија. Осим ових, до сада откривених сулфосоли, са сигурношћу постоји вероватноћа откривања и нових минерала из ове групе, а нарочито треба очекивати код познатог сулфосолног система Pb-Ag-Bi-Sb-S. Од преко стотинак одређених рудних и нерудних минерала на овом подручју, откривен је и знатан број нових минерала са аспеката допуњавања систематике минералогије Србије, и шире. У овој студији изложена је синтеза досадашњих резултата истраживања на минералима из групе сулфосоли, која су већим делом публикована од стране аутора, међутим, овде су дати допуњени, а такође, и нови подаци.

Pb-Sb сулфосолне минералне парагенезе најзаступљеније су у скоро целој СММП, где се по својој разноликости ових минерала издвајају: рудно поље Сребренице, Копаоничка рудна зона (Рајићева Гора, Бело Брдо, Црнац, и др.), рудна поља Кратово-Злетово, Тораница, Саса, Бучим и Алшар (Македонија), и друга. Поред рудног поља Борање, сличне Pb-Bi сулфосолне минералне парагенезе утврђени су у рудним пољима Рудника (Шумадија) и Голије (Копаоник).

Поред рудног поља Борање, сличне Pb-Bi(Sb) сулфосолне минералне парагенезе утврђене су у рудним пољима Рудника и Голије. Према минералном саставу, она су у веома сличне рудном пољу Улудаг (Бурса, Турска), минерализацијама на Станос (Халкидики, Северна Грчка) и рудном пољу Трепча (Стари Трг, Косово, Србија), која су такође део алпске металогенетске јединице. Такође, ове Pb(Ag)-Bi сулфосолне минералне парагенезе веома су сличне хидротермалним системима Ларга у Румунији (Карпато-балканска металогенетска провинција). На крају, у поређењу са осталим областима у СММП, минералне асоцијације рудног поља Борања одликује се са јединственим минералима и варијететима из посебне групе Ag(Pb)-Bi(Sb) сулфосоли.