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-FeS₂ Veliki Majdan (Kolarica–Centralni revir–Kojići); Sb-Zn-Pb-As Rujevac; and Pb-Zn-FeS₂-BaSO⁴ 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.

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...
thioarsenic acids (e.g., HSbS₂, H₁₈As₄S₁₅, H₃AsS₄). 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; Sb₂S₃) 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 (MOELO et al. 2008).

These minerals were formed under the mutual influence of different sulfantimonide, sulfarsenide, sulfstibate, sulfbismuthinite, etc. anions (e.g. SbS₂, As₂S₃, Bi₂S₃), with metal ions (e.g., Cu⁺, Fe²⁺, Pb²⁺). These reactions occur only in mineralized solutions with increased alkalinity and high concentration of H₂S. Deposition of miargirite Ag₅Sb₃S₁₀, pyrogaryrite Ag₅Sb₂S₁₀ and stephanite Ag₉Sb₈S₂₁, occur during mutual influence of sulfantimonide anions with Ag⁺. Interactions between already deposited sulfides (galena, chalcopyrite, etc.) and mineralized solutions (ascendant and/or descendant) may result in the formation of younger sulfosalts. The typical example of this reaction crystallization is contact between galena-chalcopyrite with sulfantimonide solutions when bornonite PbCuSbS₃ was deposited. The corrosive reaction is characteristic for influence of sulfantimonide solutions along galena surfaces thus creating wool-like varieties boulangerite Pb₄Sb₃S₁₁ and/or semseyite Pb₉Sb₈S₂₁ (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 sulfbismuthinite when complex exsolutions with lamellae structures were deposited (i.e., phases along the lillianite-gustavite solid solution Pb₃Bi₂S₇AgPbBi₃S₉) (COOK 1997).

Although under exceptional circumstances some sulfosalts may constitute Ag ores (i.e., proustite, pyrogaryrite, 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; TOMIC 1962; BORODAEV 1978; JANKOVIC 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: FeS₂ (FeKα, SKα), ZnS (ZnKα, SKα), Mn (MnKα), Ni (NiKα), Co (CoKα), Cu (CuKα), InAs (AsKα), InSb (SbLα), SnO₂ (SnLα), AgTe (AgLα), CdS (CdLα), HgS (HgMα), PbS (PbMα), and Bi (BiMα). EDX detection limits were 2σ ~ 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) (VANDEL 1978; JANKOVIC 1990). The Boranja orefield (BOF) covers an area of about 200 km². It is situated on the SE margin of the Oligocene granodiorite pluton of Boranja (DELAJOYE 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 Jadarc block terrane (FILIPPOVIĆ 2005), the Varad 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, lime-
stones, 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 Brasića–Zajaća–Stolice–Dobri potok intrusive-volcanic zone with the following leading ore elements Sb, Pb, Zn, Fe, Ba, and F; in the Rujevac–Crvene stene–Vujanović–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; Đurčiković 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
zonal arrangement of several metallic mineral associations (Fe-Cu(Bi) → Pb(Ag)-Zn → Sb(As)-Pb-Zn → CaF₂(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 FeS₂-Pb-Zn-Cu elongated lens-like ore bodies. Massive barite ore bodies are consisted of 50 to 90 wt% of BaSO₄ (RADOŠA VLJEVIĆ 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; filöppite, plagionite, robinsonite, boulangierite, 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 n Huffeldite, and fizzleite; (iv) Pb-Bi(STe)-system – burrsalite, canniżzarite, cosalite, aikinite, ustarasite, and trtadymite. 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-FeS₂ Veliki Majdan (Kolarica–Centralni revir–Kočiće), Sb-Zn-Pb-As Rujevac, and Pb-Zn-FeS₂-BaSO₄ 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 (BORODA EV 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) sulfosalts-As mineral assemblage, which are very dominant. So far, the following sulfosalts have been determined: zinkenite – Pb₈.₉₃(Sb₁₈.₉₄,As₁₀.₈₈)Σ₂₉.₈₂S₂₂.₀₂S₂₂.₀₂; filöppite – Pb₃.₈₆(Sb₇.₀₁,As₁.₀₇)Σ₈.₀₈S₁₅.₀₆; plagionite – Pb₄.₉₇ (Sb₁.₉₂,As₀.₇₆)Σ₉.₀₂S₁₅.₀₀; robinsonite (?); twinnite – Pb₀.ₐ₇(Sb₁.₄₂,As₀.₆₀)Σ₂.₀₂S₄.₀₀; and gratonite (determined only microscopically, RADOSAVLJEVIĆ 1988, 2012).

The most abundant sulfosalts of the sphalerite-Pb-Sb(As) sulfosalts-As mineral assemblage is zinkenite. It was first discovered by JANKOVIĆ et al. (1977) and MOĐO et al. (1983), and later supplemented by new data by RADOSAVLJEVIĆ (1988), ŽARIĆ 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, duranisute, 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 duranisute. 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%), Cu (up to 0.04 wt%), Zn (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 – Pb₃.₉₉(Fe₁.₀₀, Cu₀.₀₁)Σ₁.₀₁S₈.₀₀; boulangierite – Pb₂.₀₂Sb₄.₁₅ S₁₀.₈₃; geoconrite – Pb₁.₄₁(Sb₃.₉₅,As₂.₇₄)Σ₅.₇₉S₂₃.₀₀ (Fig 2a); bournonite – Pb₁.₀₀Cu₁.₀₀(Sb₀.₉₄,As₀.₀₆)Σ₁.₀₀ S₃.₀₀; As-bournonite – Pb₀.ₐ₀(Cu₀.₉₇,Fe₀.₀₂)Σ₂.₀₀S₈.₀₀(Sb₀.₅₄, As₀.₄₈)Σ₂.₀₂S₂₉.₉₉; and accompanying the pyrite-galenaphalerite mineral assemblage (ĐIMITRIJEVIĆ & RAKIĆ 1978; RAKIĆ et al. 1984; RADOSAVLJEVIĆ et al. 1993; RADOSAVLJEVIĆ et al. 2013a).

The most abundant sulfosalts 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: \( \text{Pb}_2 \text{Sb}_{4.97} \text{S}_{15.01} \) (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: \( (\text{Cu,Ag})_{10} \text{Fe}_2 \text{Sb}_4 \text{S}_{13} \). 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 geo- cronite 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.]

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*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})\text{Sb}_{3.68}\text{As}_{0.27}\text{Fe}_{2.33}\text{Sb}_{4.16}\text{S}_{13.02} \text{(4 analyses). According to these analyses Cu has been 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 moderate (~35–45 %), microhardness is higher than 50 H. This group belongs to Ag-rich sulfosalts (pyrrhotite family) and ternary sulfosalts (freieslebenite family) (Møelø et al. 2008). Within the Veliki Majdan ore zone, pyrrhotite 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})\text{Sb}_{3.68}\text{Bi}_{1.01}\text{Fe}_{2.01}\text{S}_{17.98} \text{(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})\text{Sb}_{0.54}\text{Bi}_{0.21}\text{S}_{1.01}\text{Bi}_{2.00}\text{S}_{17.98} \text{(4 analyses). According to these analyses Cu has been completely substituted by Ag and Fe (Møelø 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* - \((\text{Pb}_{0.81}\text{Fe}_{0.03}\text{Cu}_{0.08}\text{Ag}_{0.16})\Sigma_{2.06}\text{Bi}_{0.38}(\text{S}_{0.10}\text{Te}_{0.08})\Sigma_{1.15}\); *cannizzarite* - \((\text{Pb}_{3.05}\text{Ag}_{0.02})\Sigma_{3.07}\text{Bi}_{4.00}\Sigma_{8.93}\); *cosalite* - \((\text{Pb}_{1.95}\text{Cu}_{0.08})\Sigma_{2.03}(\text{Bi}_{1.92}\text{Sb}_{0.01})\Sigma_{1.93}\text{S}_{0.05}\); *akitine* - \((\text{Cu}_{0.97}\text{Fe}_{0.02})\Sigma_{0.99}(\text{Pb}_{0.98}\text{Ag}_{0.05})\Sigma_{1.03}\text{Bi}_{1.95}\text{S}_{3.05}\); *ustarasite* - \((\text{Pb}_{1.16}\text{Ag}_{0.02})\Sigma_{1.20}(\text{Bi}_{1.70}\text{Sb}_{2.18}\text{Cu}_{0.06}\text{Fe}_{0.02})\Sigma_{5.96}\text{S}_{9.84}\); and *tetradymite* - \((\text{Bi}_{1.83}\text{Pb}_{0.07}\text{Cu}_{0.01})\Sigma_{1.91}\text{Te}_{1.95}\text{S}_{1.10}\).

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 of these sulfosalts were also determined in the Kolarica locality (Veliki Majdan ore zone), associated with pyrrhotite-sphalerite-galena mineral assemblage (RADOSAVLJEVIĆ-MIHAILOVIĆ 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 MOELLO et al. (2008), bursaite has been discredited as a mineral species. From the Sn-W deposit (Shumilovskoe locality) MOŽGOVA 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 EMPA composition, which represents a composite of two phases, indicates a Pb deficiency \((n \approx 3.83)\). Minerals of bursaite composition from four known localities \((\text{Uludag-Turkey, Shumilovskoe-Russia, Cofer-Virginia, and Kram-Mlakva-Serbia})\) still have a problem of unsolved crystal structure. However, our new evidences, led to confirm that bursaite is undoubtedly 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 crystalinity degree (RADOSAVLJEVIĆ-MIHAILOVIĆ 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 sulfosalts corresponds to cannizzarite. It is determined on a basis of optical, crystallographic and chemical measurements (RADOSAVLJEVIĆ-MIHAILOVIĆ 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 \((up to 100 \mu m in length)\), 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, ⊥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 sulfosalts 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 \((R \approx 60 \%)\). It is determined on a basis of optical and chemical measurements (RADOSAVLJEVIĆ-MIHAILOVIĆ 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-FeS₂ Veliki Cip and CaF₂-Pb-Zn Ravnaja deposits unquestionably correspond to the high- \((480^\circ C)\) and low-temperature hydrothermal stage \((230^\circ C)\), respectively. In addition, the Pb(Ag)-Zn-FeS₂ 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 \((275–245^\circ C and 205–160^\circ C)\), and density of fluids \((0.98–0.80 \text{ g/cm}^3)\). In addition, temperature range of...
deposition from 280 to 160 °C 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 (RADOŠA VLJEVIĆ 1988).

Based on paragenetic relations into the polymetallic deposits of the BOF, the beginning of crystallization is connected to the low partial pressure $f_{S_2}$, 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 crystallize with temperature decrease, partial pressure $f_{S_2}$ increase, and spatial distancing from the Tertiary granodiorite of Boranja. Deposition areas were carbonates (mostly Triassic limestones) and siliicates (dacite, andesite, slates), but in a lesser extent (RADOŠA VLJEVIĆ 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, pyrrargyrite, electrum, and native Ag) is limited (RADOŠA VLJEVIĆ 1988). Besides Ag, polymorphic 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, fizeslitye, 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 (RADOŠA VLJEVIĆ 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, wolframites, 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(Fe)-Zn-Sb(S)-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 (Rajičeva Gora, Belo Brdo, Rogozna, etc.), Kratovo–Zletovo, Toranica, Sasa, Bučim, Alšar, etc. (e.g. JANKOVIĆ & ŽARIĆ 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; RADOŠA VLJEVIĆ & DIMITRIJEVIĆ 2001; VOUĐURIΣ et al. 2008; RADOŠA VLJEVIĆ & STOJANOVIĆ 2013; RADOŠA VLJEVIĆ 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 (STAJEVIC & ŽARIĆ 1984). According to the mineral compositions, they are close to the Uludag orefield, Bursa Province, Turkey (VAN DER KAADEN 1958; MAKOVIĆ & KARUP-MOLLER 1977), the Stanos shear-zone related deposit, Chalkidiki, Northern Greece (VOUDOURIS et al. 2013), and in the Trepča deposit, Stari Trg, Kosovo, Serbia (KOLODZIEJCZYK 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 & COIBANU 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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A review of Pb-Sb(As)-S, Cu(Ag)-Fe(Zn)-Sb(As)-S, Ag(Pb)-Bi(Sb)-S and Pb-Bi-S(Se) sulfosalt systems from the ...


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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(Se) системима са рудног поља Борање, Западна Србија

У Српско-македонској металогенетској provincији (СММП), која просторно захваћа мањи део Источне Босне, веће делове Србије и Македоније, и наставља даље према Бугарској и Грчкој, јављају се простране масе вулкано-плутонских комплекса калко-алкалне магме. Површина њихова развоја у Србији износи око 30.000 km² и простире се преко три крупне геотектонске јединице: унутрашњег Динарида, Вардарске тектонске 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 већег броја сулфидних лежишта са Pb-Zn, и Sb; у мањој мери са Cu, As, Bi и Ag. Међу њима, јављају се мања значајна лежишта магнетита, која су у вези са скарновском етапом. Скрајни су калијуски тип, а формирани су дуж контаката тријаских кречњака и кварцичних диорита. У рудном пољу Борање, рудни и нерудни минерали одликују се огромним вариететима и формама из посебне групе Ag(Pb)-Bi(Sb) сулфосоли.

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.

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