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## Polymetallic mineralization of the Boranja orefield, Podrinje Metallogenic District, Serbia: zonality, mineral associations and genetic features

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### Abstract

The Serbo-Macedonian Metallogenic Province, part of the Alpine metallogenic belt, hosts several ore deposits in mainly three geotectonic units: the Vardar Zone, the Serbo-Macedonian massif, and to a lesser extent the Dinarides. This metallogenic province includes the most significant Pb-Zn and Sb deposits in Serbia, as well as smaller Bi, Mo, Cu, Fe, Sn, Au and minor U, W and Hg deposits, which are genetically related to emplacement of granitoids. The Podrinje Metallogenic District belongs to the Serbo-Macedonian Metallogenic Province and incorporates several smaller orefields: Cer (Northwest Serbia), Boranja (West Serbia), and Srebrenica (East Bosnia and Herzegovina). Polymetallic deposits in the Boranja orefield are genetically related to the emplacement of the Tertiary Boranja granodiorite complex. The orefield contains a large number of sulfide deposits with Pb-Zn, and Sb with subordinate Cu, As, Bi and Ag. Small magnetite deposits connected to pyrometasomatic (skarn) stage are also significant. Skarns are of calcic type, and were formed along contacts of Triassic limestones and quartz diorites. Ore minerals are similar among the various types of orebodies in the Boranja orefield and consist of sulfides, sulfosalts [Pb-Bi-(Ag)-Te-Cu, Pb-Sb-(As), Sb-Cu-(Ag, Fe, Zn)], tellurides, native metals and alloys, oxides and complex-oxides, and gangue minerals. Minerals of the Boranja orefield were formed in several successive stages, which together correspond to a single regional-scale mineralization event that is genetically related to the subvolcanic-plutonic intrusion of the Neogene-aged magmatic Boranja complex. This can be best demonstrated by the zonal arrangement of several metallic mineral associations [Fe-Cu(Bi) → Pb(Ag)-Zn → Sb(As) → CaF<sub>2</sub>(Pb-Zn)], with increasing distance from the Boranja granodiorite. Silver occurs as a minor metal principally as Ag-tetrahedrite, with subordinate native silver, Ag-bearing gold and pyrargyrite. Significant quantities of Ag can also be accommodated in galena as it is found to contain varied amounts of Ag, Bi and Sb

(0.001-0.936, 0-3.345, and 0.012-0.510 wt%, respectively). The presence of both Ag and Bi in significant amounts in a Pb-rich sulfide system is essential for development of galena [solid solution  $\alpha$ -(Pb<sub>2</sub>, AgSb, AgBi)S<sub>2</sub>]. This study demonstrates that silver, the most economic metal in Boranja orefield, is mainly accommodated in the galena structure, with lesser amounts present in the form of visible and/or invisible Pb-Bi-(Ag) sulfosalts.

*Key words:* polymetallic ore; sulfosalts; native metals; Boranja orefield; Serbo-Macedonian Metallogenic Province.

## Introduction

The Podrinje Metallogenic District (PMD) extends over a large territory on both sides of the Drina River (Figure 1). Administratively, it belongs to the Podrinje (Serbia) and Zvornik (Bosnia and Herzegovina) regions. The major industrial and cultural centers are Šabac, Loznica, Mali Zvornik, Krupanj and Ljubovija. Most of the district's economic activities are based on production and processing of ores and metals. Mining production in this part of Serbia has generally been very active, since the Roman Empire, through the medieval, to the present day. The PMD has great economic importance for recovery Sb, Pb-Zn and other metals (e.g. Ag, Cd, Cu). Within the district, there are three spatially separated orefields: Cer (Northwest Serbia), Srebrenica (East Bosnia and Herzegovina), and Boranja (West Serbia).

The Cer orefield is developed within granitoids, and involves small pegmatite orebodies and occurrences of greisen mineralization (Sn and Nb-Ta).

The Srebrenica orefield includes numerous hydrothermal and greisen orebodies, hosted in Tertiary subvolcanic rocks (mainly dacite, and lesser andesite), and sporadically in Paleozoic slate and Tertiary pyroclastic rocks. Two different types of mineralization constitute the Srebrenica orefield: (i) greisen-type mineralization is related to quartz-tourmaline-muscovite facies of greisen, with cassiterite; (ii) hydrothermal-type ore-veins with Pb-Zn sulfides as the principal ore,

containing variable concentration of Ag, Sn, Sb (Janković et al., 1992; Radosavljević et al., 2005).

Mineralization of the Boranja orefield is concentrically distributed around the Tertiary granodiorite of Boranja (Figures 1 and 2). In the skarn alteration halo surrounding the intrusion, several small Fe (magnetite and pyrrhotite), less frequently Bi, W and Mo (Velika Reka, Vranovac) and the Kram and Mlakva Cu skarn deposits occur. Outwards from the granodiorite, the Pb-Zn Veliki Majdan ore zone consists of carbonate-hosted orebodies in contact with quartz latite and Paleozoic slate. The main mineral association includes pyrrhotite, pyrite, sphalerite, galena, chalcopyrite, and in lesser amounts Pb-Sb-(Ag) sulfosalts. The outermost halo hosts several Sb deposits. The most important are situated in the Brasina-Zajača-Stolice (BZS) intrusive-volcanic zone with the following main ore elements Sb, Pb, Zn, Fe, Ba, F and in that of the Rujevac-Crvne Stene-Brezovica (RCB) volcanogenic-sedimentary zone of the Diabase-Chert Formation (DCF) with following metals: Sb, Pb, Zn, Fe, As, Ba and Hg. The orebodies occur as irregular pipes and lenses in silicified Carboniferous limestones (Đuričković, 2005).

The aims of the present study are to evaluate the mineralogical and chemical characteristics of the Boranja orefield, to obtain information regarding paragenetic relationships and depositional order of minerals. Mineralogical and chemical analyses of principal sulfide minerals were used to define the ore-forming

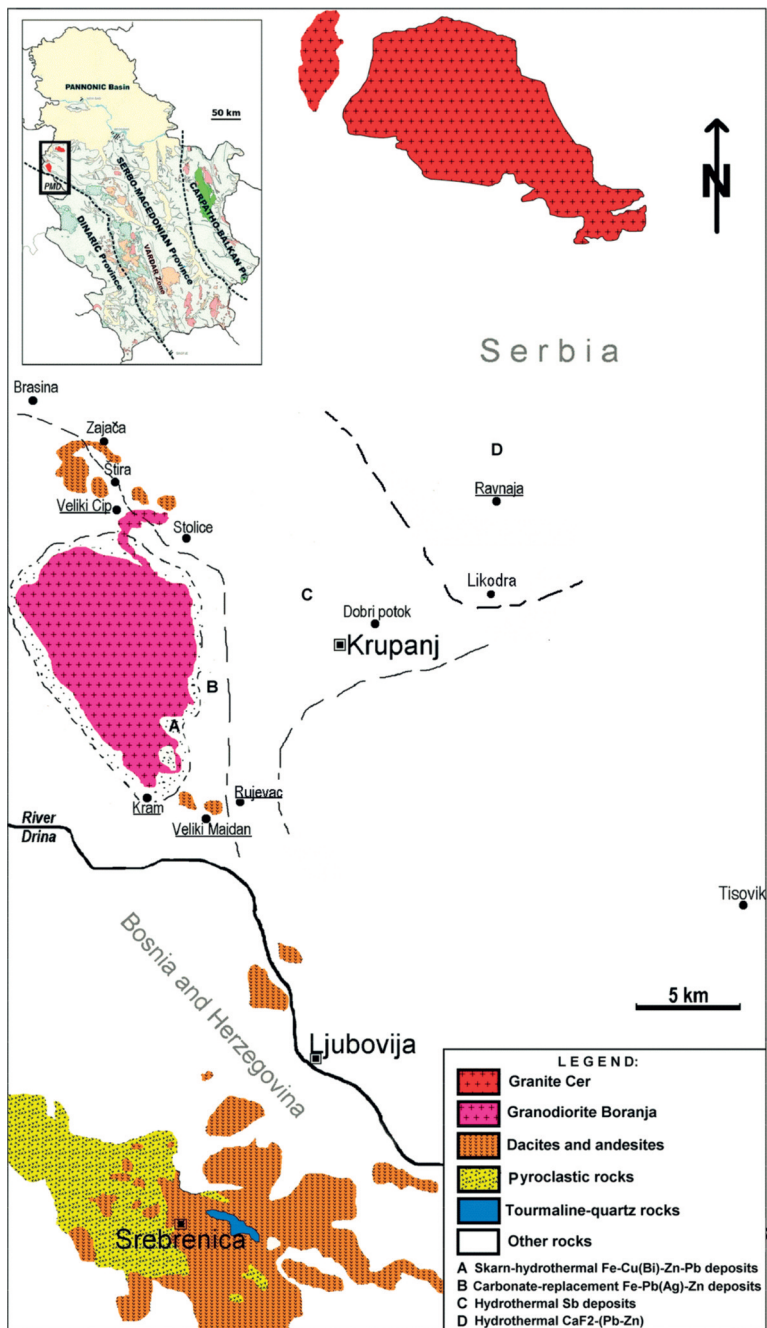


Figure 1. Detailed geological map of Tertiary magmatism of PMD (modified according to Basic Geological Map of Serbia-1:100,000) with structural geological map (Monthel et al., 2002).

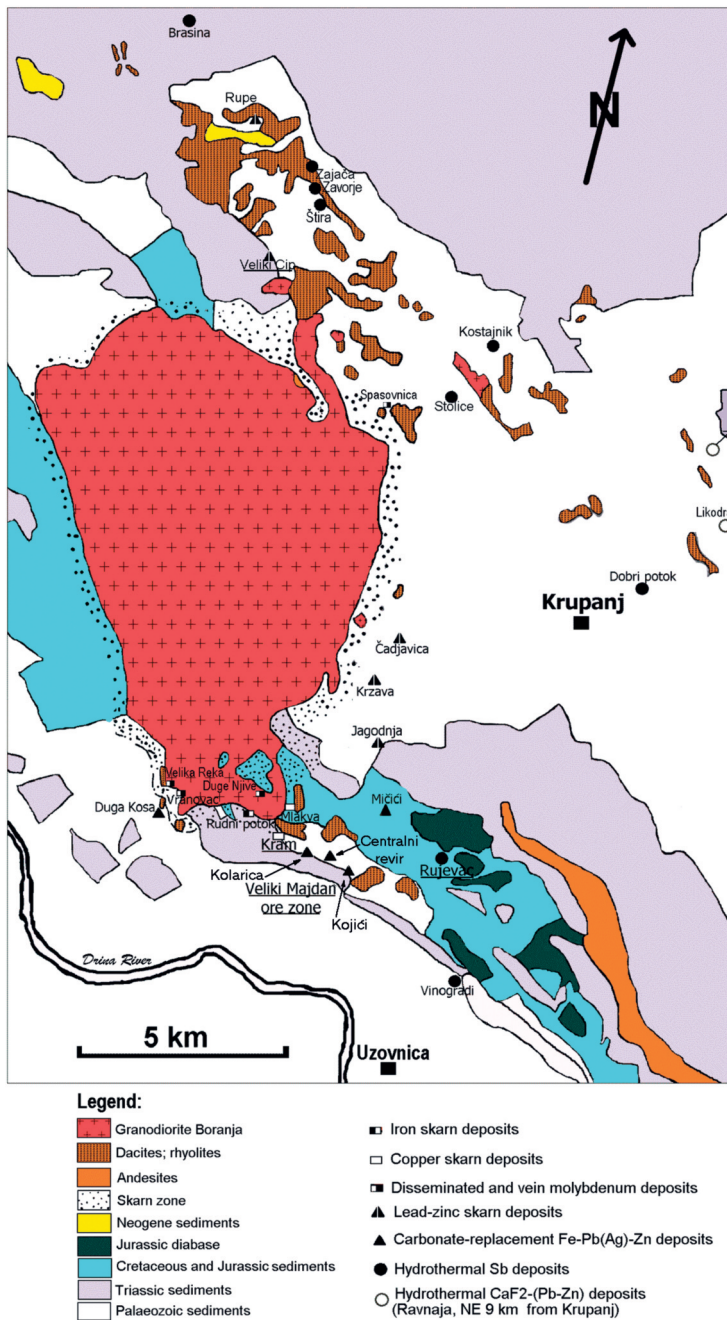


Figure 2. Detailed geological map of Boranja orefield (modified according to Basic Geological Map of Serbia-1:100,000, Monthel et al., 2002).

conditions (Kram, Štira, Veliki Cip, Veliki Majdan ore zone, Rujevac, Ravnaja, Tisovik - Figure 1). Comparison has been made with the adjacent orefields in the Alpine metallogenic province. It should be noted that mineralogical studies focused on the Cu-Fe, Pb-Zn-Fe and Sb-Zn-As mineral associations revealed the presence of several previously not described Pb-Bi-Ag sulfosalts in the Boranja orefield. Based on new compositional data on silver-bearing minerals we evaluated the mode of occurrence of silver in galena in the orefield.

### Geology and metallogeny

The Serbo-Macedonian Metallogenic Province (SMMP) covers the portions of Bosnia and Herzegovina, Serbia, FYRM, Bulgaria and Greece. The Serbian portion of the SMMP covers about 30,000 km<sup>2</sup>, within which includes the following metallogenic districts: Fruska Gora, Šumadija, Podrinje, Golija, Kopaonik, Merdare and Bujanovac (Janković, 1990).

The SMMP extends over three major geotectonic units: Inner Dinarides, Vardar Tectonic Zone and the Serbo-Macedonian massif (Figure 1). This province mainly hosts deposits of Tertiary age, although some Mesozoic and Late Paleozoic deposits are also present (Steiger et al., 1989; Karamata et al., 2000; Neubauer, 2002; Vukašinović and Stefanović, 2003).

Volcanic activity took place during the Late Eocene to Early Neogene within the entire zone. Pb and Zn are the most widespread metals related to this Tertiary metallogenic province. Locally, in some parts of the Serbian metallogenic districts other metals have significant abundance: Sb (Podrinje), Mo (Besna Kobila), Cu (Podrinje), Fe (Podrinje, Kopaonik), Hg (Šumadija), Sn (Podrinje, Šumadija), and W (Šumadija) (Janković, 1990).

Paleozoic and Mesozoic complexes have a Dinaric direction, which is of equatorial elongation in West Serbia. Paleozoic and partially

Mesozoic formations were defined as the "Drina-type" series (Đoković, 1985). Paleozoic formations consist of low metamorphosed slate and sandstone of Lower to Middle Carboniferous age. The Triassic sediments (mostly composed of clastic rock and a lesser degree slate and limestone) are very important regarding Pb-Zn mineralization (Čikin et al., 1980). Jurassic and Cretaceous volcanic-sedimentary associations are well-known as DCF.

The PMD consists of lithostratigraphic units of Paleozoic to Cenozoic age. Paleozoic (Lower and Middle Carboniferous) and Mesozoic low-grade metamorphosed pelite-psammite sediments and limestones are intruded by mafic-ultramafic bodies oriented parallel to the sediments. Triassic units are mostly clastic rocks with subordinate slates and limestones with different metamorphic grades. The Tertiary is represented with Neogene acid magmatism (dacite, andesite, quartz latite), related to lavobreccias, hornfels, and skarn formation (Karamata, 1955; Divljan et al., 1978). The granodiorites of Boranja and Cer, dacite-andesite volcanism of West Serbia (BZS) and East Bosnia and Herzegovina (The Srebrenica orefield) are of great metallogenic importance. Skarn mineralization along longitudinal dislocations within the Triassic series took place as a result of heat and fluid transfer from the Tertiary Boranja granodiorite. Polymetallic mineralization in the Boranja orefield is genetically related to the emplacement of the Tertiary granodiorite magmatic complex.

Several stages of ore deposition genetically related to the Boranja Magmatic Complex (BMC) are characterized by different mineral parageneses including monomineral and polymetallic mineral associations. The main metallogenic belts are as follows (Figure 1):

A - The contact aureole of the Tertiary Boranja granodiorite; predominantly skarn with transitions into hydrothermal deposits - skarn-replacement Fe-Cu-(Pb-Zn) belt.

B - Hydrothermal Pb-Zn zone followed by



local concentrations of Sb - carbonate-replacement Pb-Zn belt.

C - Hydrothermal Sb belt with significant occurrence of Pb, Zn and As.

D - Hydrothermal fluorite belt with Pb-Zn mineralization.

#### *A-belt Skarn-replacement Fe-Cu-(Pb-Zn) belt*

This corresponds to the Tertiary granodiorite of the Boranja contact zone, with predominantly skarn with transition in hydrothermal deposits. The A-belt deposits are typically sited near the contact of the granodiorite of Boranja with surrounding rocks. The width of the mineralized contact zone varies from several hundred of meters to 1-2 km. Numerous small-scale deposits are located in limestone-hosted Ca-skarns. Ore mineralization is localized in the northern, eastern and southern margins of the intrusive, while the western part of the Boranja granodiorite contact aureole is largely barren of mineralization. The areal extent over which ore deposits occur is about 40 km<sup>2</sup>. Based on mineral parageneses the skarn deposits and occurrences can be determined as follows: magnetite deposits (e.g. Majdan, Duge Njive, Vranovac); Cu deposits (e.g. Kram, Mlakva, Lom); powellite stockwork-impregnation occurrences (Rudni Potok); scheelite mineralization (Turski Grob, Duge Njive); Pb-Zn deposits (e.g. Veliki Cip, Dugi Potok, Rupe, Štira); and a cassiterite occurrence (Spasovnica). Among them, magnetite and Cu deposits are to the most important. The Kram and Veliki Cip deposits were selected as a polymetallic ore example (Figure 2).

The Kram deposit Cu-Fe-Bi(Ag) is situated on the southern slopes of Boranja Mountain, in the contact aureole of the Boranja granodiorite and 2-3 km to the NW of the Veliki Majdan ore zone (Figure 2). The Kram deposit has a NE-SW orientation and is also marked by quartz latite intrusions. Calcium skarn-hosted orebodies occur at the contact of clay sediments with limestone.

The skarn composition consists mainly of zonal garnets (andradite-grosular), pyroxene, epidote, wollastonite and calcite. Massive chalcocopyrite-pyrite-prevailing mineralizations, and Pb-Bi sulfosalts-prevailing (+ Ag, Te) impregnation mineralizations have been distinguished, being the first one is of greatest economic importance (Rakić et al., 1984).

The Pb-Zn-Fe ± Au ± Bi ± Ag Veliki Cip deposit is located on the NW slopes of Boranja, a few kilometers from the contact zone (Figure 2). The mineralization is found in the contact of Carboniferous and Triassic limestones with the granodiorite and with quartz latite dykes. Relatively small tubular, stockwork and lens-like orebodies were situated partially in Ca-skarn and partially in contact of limestones and dykes (Đuričković, 1982). The most significant and of economic importance is a massive mineralization pyrite-galena, Au, Ag, Te-containing, mineral paragenesis.

#### *B-belt Carbonate-replacement Pb-Zn belt*

The B-belt refers to a hydrothermal Pb-Zn zone followed by local concentrations of Sb. The carbonate-replacement Pb-Zn hydrothermal deposits, which were developed during metasomatic processes in the Triassic limestones, are the next most dominant mineralization type in the Boranja area. Besides Pb and Zn, significant amounts of Sb occur in the form of Pb-Sb sulfosalts and minor as stibnite. In the N-NE parts of the belt, polymetallic deposits are more common than large Pb-Zn deposits; the latter are being abundant at the SE rim of the Boranja granodiorite. The Veliki Majdan ore zone hosting active Kolarica and Kojići mines and covering an area of some 30 km<sup>2</sup>, is very complex and the most examined of the belt.

The Veliki Majdan Pb-Zn ± Ag ore zone is located on the SE slopes of Boranja and has been in exploitation for over than 50 years (Figure 2). The deposit, which is located a few kilometers from the contact halo, consists mostly of

Paleozoic schists ("Drina-type") and Middle Triassic limestone, in which Neogene dacite-andesite and quartz latite were embedded as small intrusions, dykes and eruptive breccias. Carbonate-replacement Pb-Zn deposits are hosted in limestones which are in contact with either quartz latite or Paleozoic slate. The dimensions of irregular, tubular and NW-trending orebodies are variable (varying from 10 to 100 m<sup>2</sup>). The Veliki Majdan ore zone consists of three major districts, i.e. Kolarica (NW part), Centralni revir (central part), and Kojići (SE part), conneted via mineshaft workings (gallery 271). Small vein-like and tubular orebodies at Kolarice were deposited at the contacts of the footwall and hanging wall with quartz latite dykes. Spiral-tubular orebodies in the central parts of the Veliki Majdan ore zone were located along hanging wall contacts of quartz latite and limestone. Small vertical tubular orebodies of the Kojići deposit were directly sited in the contact of limestone and quartz latite (Čikin et al., 1980). The orebodies consist mainly of Fe-Pb-Zn (sulfide) ores, with Ag-minerals associated with Pb-Zn mineralization. The Pb-Zn ore is characterized by a Sb > Bi > Ag ratio. The most significant mineralization of economic point of view is massive sulfide galena-sphalerite-pyrite (Radosavljević, 1988).

#### *C-belt Hydrothermal Sb belt*

This ore zone including numerous Sb deposits is of major economic importance. BZS and RCB ore zones cover an area of some 200 km<sup>2</sup>. Monomineral Sb deposits and in a lesser degree polymetallic mineralization represents metallogenic products of Neogene magmatism (Đuričković, 1982; 2005; Janković, 1979; Mudrinić, 1984). The Rujevac mine was chosen for studying as a characteristic and specific polymetallic deposit of the Sb-belt.

The Rujevac Zn-Sb-As mine, located on the SE slopes of Boranja a few kilometers from the contact halos, has been in exploitation for a

decade (Figure 2). The hostrocks of the deposit are Jurassic and Triassic limestones, slates, marls, sandstones and cherts, as well as Tertiary dacite-andesite dykes. Lens-like orebodies hosted in silicified limestones and slates, ore veinlets within dacite and locally impregnations, breccias and stockworks are the main mineralization types. Sphalerite-Sb-Pb sulfosalt ore is the most economically important, and is a breccia-impregnation mineralization type (Radosavljević et al., 1986).

#### *D-belt Hydrothermal fluorite belt with Pb-Zn mineralization*

Several fluorite ( $\pm$  Pb-Zn sulfides) deposits and occurrences have been determined NE from the Sb-zone (C-belt) in an area extending for over of tens of square kilometers (Bastav, Belotić, Pantelići localities). The most important mineralization occurs east of Krupanj, and the F-Pb-Zn Ravnaja mine (far NE of the Boranja orefield) is the most important and represents an example of polymetallic deposit of the fluorite-belt hosted in Carboniferous limestones (Figure 2).

Vein-like orebodies, whose thickness varies between 0.5 to 10 m, extend over 1.5 km, and decline up to 300 m. Three mineral parageneses were recognized in this locality, sphalerite-galena-fluorite (the main ore and of vein type, Stefanović et al., 1986), galena and calcite-fluorite.

### **Methods**

Samples were collected mainly from underground locations in the seven selected deposits in the Boranja orefield (Kram, Štira, Veliki Cip, Veliki Majdan ore zone, Rujevac, Ravnaja, and Tisovik). Seven hundred and fourteen polished-sections of sulfide mineralization were studied by optical microscopy and a JEOL JSM 610LB SEM, equipped with back-scattered imaging capabilities.

The chemical compositions of sulfides, sulfosalts and native elements were determined by a Cambridge M-9 Microscan equipped with two WDS analytical systems, using PbS, (Zn, Fe)S, Sb<sub>2</sub>S<sub>3</sub>, Bi<sub>2</sub>S<sub>3</sub>, CuFeS<sub>2</sub>, InAs, CdS, and pure metals as standards. The results were corrected, for absorption and atomic number effects, using a program for ZAF corrections.

Mass spectrometric analyses (MSA) on bursaitite aggregates and galena grains were made by a 01MB mass spectrometer (analytical range 1000-0.01 ppm). Galena was taken from Veliki Cip mine, Veliki Majdan ore zone (Kolarica, Centralni revir, Kojići), Ravnaja and Tisovik in order to compare quantities of trace elements.

X-ray powder diffraction (XRPD) technique was used for phase identification. XRPD analyses were performed using a Philips model PW1710 diffractometer; with Cu K $\alpha$  radiation (40 kV, 30 mA), step scan 16 s, 0.02° 2 $\theta$ ,  $d$  range from 10 to 100° 2 $\theta$ .

In addition, the content of Ag, Sb, As, Bi and Cu extracted from selected galena grains was obtained by Atomic Absorption Spectroscopy method (AAS-Perkin Elmer AA-300).

Selective solution of EDTA with the addition of NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> was used for a precise definition of the nature of silver hosted in the galena lattice and its mode to substitute into galena. Using this solvent, Pb (and Ag) in galena is 100 % soluble, together with silver contained within the galena structure. Microscopically "visible and invisible" Ag minerals (e.g. native silver, Ag-bearing gold, argentian tetrahedrite) stay insoluble in a residue (Bespaev and Pronin, 1975).

### Ore mineralogy

The following main ore minerals were described in respect to their genesis and paragenetic relations in the mineralization. Mineral composition of the Boranja orefield is given in Table 1, while Table 2 reports stages, paragenetic sequences and deposits.

### Sulfides

Pyrrhotite occurs in the A- and B-belt, in various concentrations. It commonly occurs as tabular and elongated aggregates and is usually transformed into marcasite and finally pyrite by hydrothermal processes. In the Kram deposit and the Veliki Majdan ore zone, pyrrhotite is the most abundant metallic mineral. In the first generation of sphalerite, it occurs as a product of decomposition of high-temperature exsolution. Partition is mainly in the form of rectangular or oval cross-section cuprian pyrrhotite and chalcopyrite, when properly oriented along the crystallographic directions of sphalerite. The final transformation of pyrrhotite through secondary changes in marcasite and pyrite decomposition resulted in typical "bird's eye" structure. EPMA shows that pyrrhotite has up to 0.04 wt% Co, up to 0.18 wt% Ni, up to 0.2 wt% Cu contents, whereas As was not detected in this mineral.

Pyrite is dominant and formed throughout the paragenetic sequence and is the dominant sulfide mineral in the orefield. Pyrite from the A- and B-belt is mainly a product of hydrothermal transformation of pyrrhotite. Minor pyrite can be deposited directly from hydrothermal solutions. In the Veliki Majdan ore zone, relic pyrite occurs in large crystals (up to 10 cm in pentagondodecaeder forms), and is a product of pyrrhotite recrystallization. In recrystallized pyrite, a "wreath" made of small green anatase crystals rims the pyrite aggregates. Spongy pyrite  $\pm$  marcasite form colloidal aggregates, with intergrowths of idiomorphic arsenopyrite. Hydrothermal pyrite is commonly associated with younger sphalerite, stibnite, and sulfosalts. Finally, in the C- and D-belt fine-grained pyrite occurs. EPMA data show that pyrite is stoichiometric and has up to 0.03 wt% Co, up to 0.01 wt% Ni, up to 1.5 wt% As and up to 0.07 wt% Cu.

Chalcopyrite locally occurs in the A-, B-, and sporadically in the C-belt. The first generation is



Table 1. Mineral composition of the Boranja orefield.

Mineral groups	Minerals
Sulfides, complex sulfides	pyrrhotite, pyrite, marcasite, chalcopyrrhotite, chalcopyrite, cubanite, mackinawite, valleriite, covellite, chalcocite, molibdenite, bismuthinite, sphalerite, mercurian sphalerite, greenockite, galena, arsenopyrite, stibnite, duranusite, realgar, orpiment, cinnabar, metacinnabar
Sulfosalts	bursaitite, cannizzarite, cosalite, aikinite, ustrasite, tetradymite, Fe-tetrahedrite, Ag-tetrahedrite, pyrargyrite, diaphorite, freieslebenite, schirmerite, phiselyte, stannite, jamesonite, boulangerite, bournonite, As-bournonite, falkmanite, zinkenite, fuloppite, robinsonite, pligionite, twinnite, geocronite, gratonite
Tellurides, native metals and alloys	calaverite, gold, silver, electrum, bismuth, arsenic, stibarsen
Oxides, tungstates, molybdates	magnetite, hematite, cassiterite, rutile, anatas, scheelite, powellite, arsenolite, zincite, valentinite, senarmonite, kermesite, adamite
Gangue minerals	quartz, chalcedony, contact silicates, silicates, calcite, dolomite, siderite, Mn-Zn siderite, fluorite, apatite, malachite, azurite, barite, anglesite, cerussite, smitsonite, otavite, scorodite, limonite, organic matter

related to the skarn-hydrothermal stage, in association with pyrite, pyrrhotite, magnetite, and Pb-Bi-(Te) sulfosalts. Chalcopyrite represents the most important ore mineral at Mlakva and Kram. It occurs as coarse-grained aggregates, which cement or replace older contact silicates, oxides, and sulfides. It contains numerous star-shaped grains of sphalerite and cuprian pyrrhotite. Cubanite lamellae with sporadic mackinawite and valerite were observed as open space fillings between chalcopyrite aggregates. The second generation chalcopyrite appears as inclusions in sphalerite II along with pyrrhotite II. Contact of sphalerite with other minerals is locally cemented with exsolved chalcopyrite. Blebs of pyrite-marcasite and arsenopyrite occur as inclusions in galena. Third generation chalcopyrite is represented by a chalcopyrite-tetrahedrite-bournonite mineral

assemblage connected to the galena-sphalerite-pyrite mineral association.

Several generations of sphalerite are ubiquitous, like pyrite. The older generation is very high in iron and black in colour ("marmatite"). It commonly contains numerous inclusions of cuprian pyrrhotite, pyrrhotite and chalcopyrite oriented along crystallographic directions. Sphalerite occurs in traces in the A-belt and as a main mineral in the B-belt. A younger generation of reddish, yellowish or colorless sphalerite is characterized by a low content of iron ("cleophane"). No inclusions were detected, while cloud-like zones composed of white and yellow internal reflections are quite common. Fractures are often filled with younger Pb-Sb sulfosalts occurring as lath- to needle-like aggregates. They occur in traces in the B- and as a main mineral in the C- and D-belt. EPMA show

Table 2. Stages and paragenetic sequences of ore and gangue minerals in various deposits of the Boranja orefield.

<i>Stage</i>	<i>Paragenetic sequence</i>	<i>Deposit</i>
Relict	sandstone - limestone - silicates - apatite - rutile - organic matter	Rujevac**
Greisen	quartz I - tourmaline - muscovite - cassiterite - rutile	Veliki Majdan ore zone*
Pyrometamorphic (skarn)	calcite I - garnet - axinite - anatase - vesuvianite - epidote - zoisite - orthorhombic pyroxene - tremolite - actinolite - pyrite I quartz II - magnetite I - scheelite - $\pm$ powellite	Kram***, Veliki Cip***, Kolarica*
High-temperature hydrothermal	pyrrhotite I - $\pm$ molybdenite - bismuthinite - sphalerite I - cuprian pyrrhotite - chalcopyrite I - native gold I - vallerite - cubanite - galena I - calaverite - sylvanite - ustarasite - schirmerite - diaphorite - freieslebenite - fizelyite bursaitite - cannizzarite - tetradymite - native bismuth - magnetite II - chalcopyrite II - native gold II - aikinite - cosalite - quartz III	Štira***, Veliki Cip**, Veliki Majdan ore zone** Kram*** Kolarica*
Transformation-hydrothermal	marcasite I - pyrite II - hematite	Veliki Majdan ore zone***, Kram**
Medium-temperature hydrothermal	sphalerite II - pyrrhotite II - chalcopyrite II - stannite - arsenopyrite I - galena II - Ag-bearing gold-electrum - native silver - pyrargyrite - jamesonite - falkmanite As-bournonite - bournonite - ferrian tetrahedrite - argentian tetrahedrite - geocronite - boulangerite I - siderite	Veliki Majdan ore zone***
Low-temperature hydrothermal	quartz IV - arsenopyrite II - pyrite III - sphalerite III - chalcopyrite III - tetrahedrite I - stibnite I - $\pm$ barite I - $\pm$ cinnabar - chalcedony quartz V - mercurian sphalerite - zinkenite - duranusite - fuloppite - robinsonite - pligionite - native silver - pyrite IV - dolomite I native arsenic - stibarsen - twinnite - gratonite - calcite I	Brasina-Zajača-Stolice***, Rujevac**, Kojići* Rujevac***
	sphalerite IV - stibnite II - realgar - orpiment - barite II - quartz VI - calcite II - $\pm$ Mn-Zn siderite - dolomite II.	Rujevac**, Brasina-Zajača-Stolice***
	quartz VII - sphalerite IV - chalcopyrite IV - tetrahedrite II - galena III - fluorite - calcite III	Ravnaja***
Cementation-oxidation	$\pm$ mackinawite - chalcocite - covellite - galena IV - $\pm$ greenockite - $\pm$ metacinnabar - pyrite V - marcasite II $\pm$ kermesite - valentinite - senarmontite - smithsonite - $\pm$ otavite - anglesite - cerussite - malachite - azurite - $\pm$ arsenolite - zincite - $\pm$ scorodite - $\pm$ adamite - limonite	Veliki Majdan ore zone**, Kram**, Rujevac**, Tisovik***, Brasina-Zajača-Stolice**

Note: \*\*\* Main; \*\* Weak; \* Trace

that sphalerites contain from 0.1 to 22 mol% FeS. In "marmatite" FeS content ranges from 19 to 22 mol% (up to 1.6 wt% Mn, up to 0.6 wt% Cd, content of In, Ge and Sn is under detection limits), while in "cleophane" the FeS content ranges from 0.1 to 2.5 mol% (up to 2.7 wt% Cd, up to 0.05 wt% Mn, content of In, Tl, Ge, and Sn is under detection limits). Furthermore, frequent zoning with rhythmical replacement of Zn by Fe, Cd and Hg is noted in sphalerite from the Rujevac deposit. In the aggregate cores of sphalerite, narrow zones are enriched with mercury (up to 6.5 wt% Hg) (Radosavljević et al., 2012).

Galena occurs throughout the entire paragenetic sequence, like pyrite and sphalerite. Galena from the A- and B-belts, is in association with sphalerite, chalcopyrite and pyrrhotine. Early galena (I generation) usually replaces silicates and pyrrhotine along cleavage directions and embeds sphalerite and chalcopyrite. Exsolutions of native bismuth, tetradymite and Pb-Bi sulfosalts are quite common. Late galena (II generation) is very abundant and is mainly present in the B-belt. It occurs as coarse-grained aggregates with characteristic cubic perfect cleavage and octahedral shape. Typically native silver exsolutions, tetrahedrite, Pb-Sb sulfosalts and rarer pyrrhotite occur in galena. Furthermore, it is partially replaced by anglesite and cerussite being products of oxidation processes. The youngest generation of galena, characterized by massive monomineral orebodies, is mostly present at the D-belt and to a lesser degree at the C-belt. Chemical, physical and genetic features of galena are shown in detail in the following part of the study.

Arsenopyrite occurs throughout the entire mineralization process. The first generation is deposited during and after the hydrothermal transformation of pyrrhotine into marcasite and pyrite. It intensively replaces pyrite and contains zonally arranged relicts of older sulfides and silicates. Arsenopyrite of the second generation is distinguished by large and well-developed

crystals of prismatic habitus (up to 1 cm), but without inclusions. The third generation of arsenopyrite, connected to the polymetallic deposit Rujevac, is characterized by small idiomorphically developed crystals within the quartz matrix. Decomposition processes of arsenopyrite most probably resulted in the formation of native arsenic in reduction zones, realgar in sulfidization zones, and scorodite in oxidation zones (Vink, 1996). EPMA data of arsenopyrite from the Rujevac deposit yielded presence of Zn (up to 2.7 wt%).

Stibnite occurs as lath-like crystals which form radial, ribbon-like, and fan-like aggregates. In oxidation zones stibnite alter in secondary products: valentinite, senarmontite, and kermesite. Moreover, it is replaced in various degrees by Pb-Sb sulfosalts. EPMA data yielded stoichiometric composition, without arsenic.

Realgar is a rare mineral situated in the rims of orebodies filling fissures and open spaces in the surrounding rocks of the C-belt (Rujevac). EPMA data yielded stoichiometric composition of realgar, without presence of any other element. Orpiment is exceptionally rare.

### *Sulfosalts*

Sulfosalt-group minerals occur throughout the entire paragenetic sequence. Based on chemical composition they are divided into three major groups: (i) the  $Pb \pm (Fe,Cu)-As-Sb \pm S$  system, (ii) the  $(Cu,Ag)-(Fe,Zn)-(Sb,As)-S$  system (iii) the  $Pb(Ag)-(\pm Cu)-Bi-(S,Te)$  system. The first and second group is more common with several mineral species (Radosavljević, 1988).

Pb-Sb(As) sulfosalts are associated to the B- and C-belt. Within the Veliki Majdan ore zone, these minerals include jamesonite, boulangerite, geocronite, bournonite, and As-bournonite and accompany the pyrite-galena-sphalerite mineral paragenesis. The most abundant sulfosalt is jamesonite. It occurs as short-prismatic crystals, deposited in the interspaces of chalcopyrite and calcite aggregates (Figure 3d, Dimitrijević and

Rakić, 1978; Radosavljević et al., 1993). Bournonite most frequently occurs at the boundaries between galena and chalcopyrite replacing galena. It is Ag-free, and contains As from 0.5 to 7.7 wt%. The higher As content, the thicker and narrower the twin lamellae become.

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 (Table 3). A wide spectrum of various Pb-Sb(As)

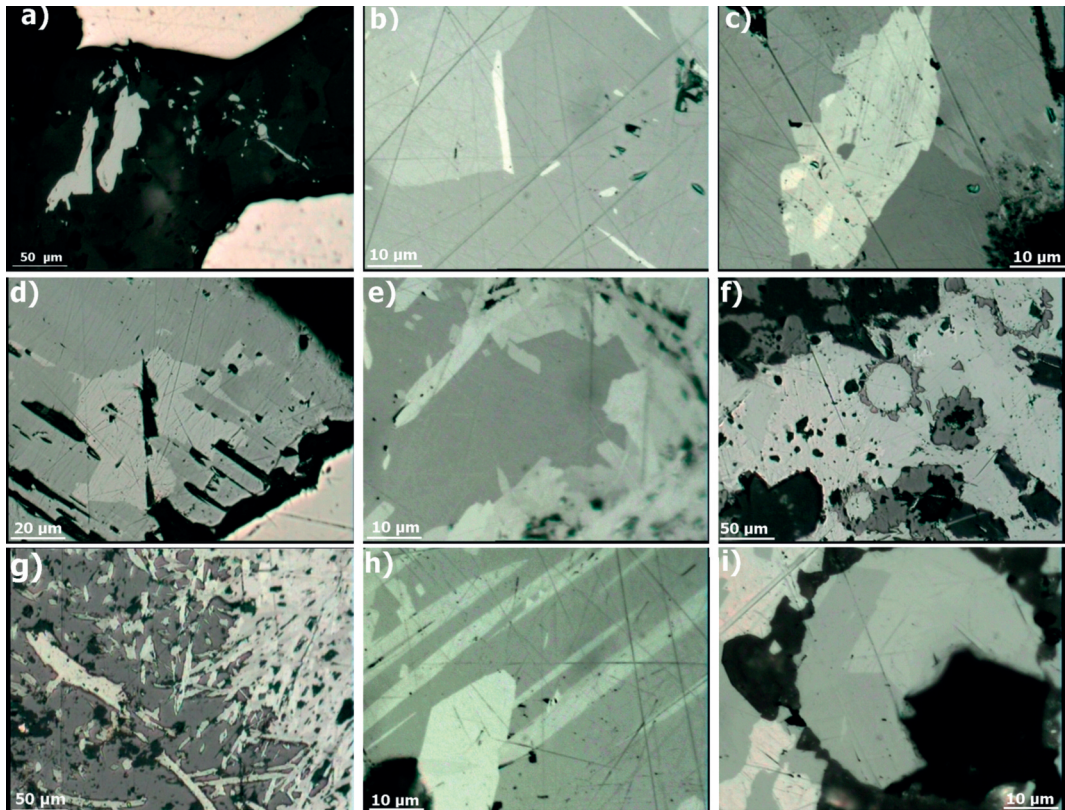


Figure 3. a) Spindle-shaped crystals of ustarasite embedded in carbonate martix, Kolarica (reflected light, in air, N II); b) bursaitite (dark gray) and cannizzarite (light gray) aggregate accompanied with needle-like tetradymite, Kram (reflected light, in oil, N II); c) Crystal of aikinite (light gray) with native bismuth (white) located in a contact of bursaitite (dark gray) and cannizzarite (light gray), Kram (reflected light, in oil, N II); d) Aggregate of jamesonite (gray greenish) with galena relict (white), Centralni revir (reflected light, in air, N II); e) Ag-tetrahedrite (olive gray) pushed down by needle-like boulangerite, Centralni revir (reflected light, in oil, N II); f) Complex aggregates composed of Pb-Sb sulfosalts (gray greenish), native arsenic (white) and colloform sphalerite (dark gray) embedded in quartz matrix (black), Rujevac (reflected light, in air, N II); g) Intensive replacement of sphalerite (gray) by needle-like zinkenite (creamy gray), Rujevac (reflected light, in air, N II); h) Polysynthetic growing of fulloppite (creamy gray) and zinkenite (gray), Rujevac (reflected light, in oil, N II); i) Filling gel rings of sphalerite (black) with zinkenite (gray greenish), plagiogonite (light gray), and native arsenic (white), Rujevac (reflected light, in oil, N II).

sulfosalts associated with the sphalerite-antimonite mineral association occur in the Rujevac deposit. The following minerals have been determined: zinkenite, fuloppite, twinnite, plagionite, robinsonite, and gratonite. The most abundant Pb-Sb(As) sulfosalts are zinkenite and fuloppite (Figure 3g, 3h, 3i). Zinkenite occurs in lath-, needle- to wool-like aggregates situated into interspaces of the quartz matrix. Furthermore, zinkenite and fuloppite crosscut and replace cataclastic sphalerite grains, and contain quartz and duranusite inclusions. Zinkenite and fuloppite are usually cemented and crosscut by coarse-grained, euhedral dolomite. Twinnite, characterized by polysynthetic twinning, is the youngest sulfosalt (Janković et al., 1977; Moëlo et al., 1983; Zarić et al., 1993). EPMA data yielded presence of As (up to 8 wt%), Ag (up to 0.04 wt%), Cu (up to 0.03 wt%) and Fe (up to 0.01 wt%), while Hg, Zn, Cd, Bi and Tl were not detected (Table 3). Among Sb-Ag sulfosalts, only pyrargyrite, which is a very rare mineral usually, associated with galena, was determined optically (Veliki Majdan ore zone).

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 association. Furthermore, they usually cement older cataclastic pyrite aggregates. Tetrahedrite-group minerals rim galena aggregates and are also replaced by boulangerite (Figure 3e, Radosavljević et al., 1986). 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. EPMA data showed that they belong to the tetrahedrite and freibergite solid solution series (Fe- and Ag-bearing tetrahedrites, respectively). Microhardness of tetrahedrite-group minerals increases with increasing content of Fe and decreasing content of Ag (Table 4). Tetrahedrite

fills fissures within cataclastic pyrite. Tetrahedrite show variable Zn and Fe content (2.2-4.2 and 3.4-5.4 wt%, respectively), whereas some grains contain up to 13.1 wt% Ag (Table 4). Argentian tetrahedrite is characterized by a  $\text{Ag}/(\text{Ag} + \text{Cu})$  molar ratio between 0.33 and 0.34. The tetrahedrite-group minerals display  $\text{Sb}/(\text{Sb} + \text{As})$  and  $\text{Zn}/(\text{Zn} + \text{Cu} + \text{Fe} + \text{Ag})$  ratios between 0.89 and 1.00 and between 0.05 and 0.10, respectively. The highest Ag content is measured in argentian tetrahedrite from the Veliki Majdan ore zone which is in good accordance to the observation of Sack et al. (2003). Following Sack and Goodell (2002) this solid-state reaction produced a distinct population of argentian tetrahedrite found in galena-rich samples, quantitatively removed Ag (in an  $\text{AgSbS}_2$  component) from galena, and accounts for all of the bournonite mineralization.

Pb-Bi sulfosalts, occurring in the Kram ore deposit and related to the pyrite-chalcopyrite mineral association, are represented by lillianite homologues (bursaite and cannizzarite), cosalite, aikinite, ustarasite, and tetradymite (Figure 3b i 3c). These cannot be mutually macroscopically distinguished owing to their very small grain-size. Aggregates were embedded in a garnet-calcite matrix. Well-developed crystals have not been observed, only spheroidal and spindle-like forms up to 10  $\mu\text{m}$  long. In addition, fewer occurrences of these sulfosalts were also determined in the Kolarica locality, associated with pyrrhotite-sphalerite-galena mineral paragenesis (Tables 2 and 3). Bursaite characterizes complex intergrowths where it covers an area from 50 to 80% of polished sections. Noticeable bireflectance (light gray to gray with violet tint), weak pleochroism (distinct only at grain boundaries, strong in oil), and visible anisotropy (only strong in oil) are the main optical features. It occurs in lath-like grains, mutually parallel along their elongation. Sometimes, triangular sections and polysynthetic lamellae are observed. In comparison to the other accompanying Pb-Bi



Table 3. Representative average electron microprobe analyses and atomic proportions of bursaitite (1), cannizzarite (2), cosalite (3), aikinite (4), tetradymite (5), geocronite (6), boulangerite (7), bournonite (8), As-bournonite (9), ustarasite (10), twinnite (11), plagiönite (12), zinkenite (13) and fulopptite (14) from polymetallic deposits of the Boranja orefield.

Elements	A-belt			B-belt				C-belt						
	1 (9)	2 (3)	3 (3)	4 (3)	5 (3)	6 (3)	7 (12)	8 (7)	9(2)	10 (1)	11 (2)	12 (3)	13 (9)	14 (2)
wt%	16.07	16.32	16.69	17.08	5.11	17.33	18.18	19.81	20.45	19.62	23.37	21.69	23.43	23.73
S	0.33	b.d.	n.a.	n.a.	36.98	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
Te	0.07	b.d.	b.d.	0.15	0.01	b.d.	0.02	0.03	0.21	0.07	b.d.	0.01	0.01	b.d.
Fe	0.24	b.d.	0.49	10.80	0.08	b.d.	b.d.	13.02	13.15	0.24	b.d.	b.d.	b.d.	b.d.
Cu	0.01	b.d.	b.d.	b.d.	b.d.	n.a.	n.a.	n.a.	n.a.	n.a.	b.d.	b.d.	b.d.	b.d.
Zn	0.80	0.14	0.04	0.96	0.04	b.d.	b.d.	b.d.	b.d.	0.12	b.d.	0.04	0.03	b.d.
Ag	b.d.	b.d.	0.12	0.17	b.d.	8.73	26.44	23.66	13.94	16.49	31.54	35.20	40.09	42.46
Sb	n.a.	n.a.	n.a.	n.a.	n.a.	4.82	0.00	0.89	7.75	b.d.	8.25	2.01	4.01	3.43
Pb	45.49	36.01	41.58	35.04	2.10	69.19	54.42	42.62	44.23	15.15	36.73	40.83	32.18	29.47
Bi	36.91	47.71	41.28	35.04	55.58	b.d.	b.d.	b.d.	b.d.	48.09	n.d.	n.d.	n.d.	n.d.
Σ	99.92	100.18	100.12	99.89	99.90	100.08	99.05	100.03	99.72	99.78	99.89	99.78	99.75	99.78
Atomic proportions														
S	10.99	8.93	5.05	3.03	1.10	23.00	10.83	3.00	2.99	9.84	4.00	17.05	42.02	15.06
Te	0.06	-	-	-	1.99	-	-	-	-	-	-	-	-	-
Fe	0.03	-	-	0.02	-	-	0.01	-	0.02	0.02	-	-	0.01	-
Cu	0.08	-	0.08	0.97	0.01	-	-	1.00	0.97	0.06	-	-	-	-
Zn	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ag	0.16	0.02	-	0.05	-	-	-	-	-	0.02	-	0.01	0.02	-
Sb	-	-	0.01	-	-	3.05	4.15	0.94	0.54	2.18	1.42	7.29	18.94	7.01
As	-	-	-	-	-	2.74	-	0.06	0.48	-	0.60	0.68	3.08	1.07
Pb	4.81	3.05	1.95	0.98	0.07	14.21	5.02	1.00	1.00	1.18	0.97	4.97	8.93	2.86
Bi	3.87	4.00	1.92	0.95	1.83	-	-	-	-	3.70	-	-	-	-
Number of atoms	20	16	9	6	5	43	20	6	6	17	7	30	73	26

Note: 1-5 Kram deposit; 6-10 Veliki Mjajdan ore zone; 11-14 Rujevac deposit; (n) number of analysis; b.d. below detection limit; n.a. not analyzed.

Table 4. Representative electron microprobe analyses and atomic proportions of Fe-(1-4) and Ag-tetrahedrite (5-6) from the Veliki Majdan ore zone.

Elements	B-belt					
	1	2	3	4	5	6
wt%						
S	25.58	25.71	25.36	25.84	23.55	23.74
Fe	5.00	5.34	5.02	5.14	3.44	3.43
Cu	35.26	34.26	35.97	35.34	26.85	26.56
Ag	3.98	4.33	3.39	3.80	12.98	13.33
Sb	25.75	26.24	26.98	26.99	28.58	28.84
As	1.92	1.63	0.67	0.69	b.d.	b.d.
Zn	2.24	2.20	2.68	2.39	4.16	4.19
Cd	0.12	0.11	0.10	0.11	0.13	0.13
Bi	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
$\Sigma$	99.85	99.82	100.17	100.30	99.69	100.22
	Atomic proportions					
S	13.21	13.30	13.10	13.30	13.00	13.05
Fe	1.48	1.59	1.49	1.52	1.09	1.08
Cu	9.19	8.94	9.38	9.17	7.48	7.37
Ag	0.61	0.67	0.52	0.58	2.13	2.18
Sb	3.50	3.57	3.67	3.66	4.15	4.17
As	0.42	0.36	0.15	0.15	-	-
Zn	0.57	0.56	0.68	0.60	1.13	1.13
Cd	0.02	0.02	0.01	0.02	0.02	0.02
Bi	-	-	-	-	-	-
Number of atoms	29	29	29	29	29	29

Note: b.d.-below detection limit

sulfosalts, it is harder. It often contains inclusions of native bismuth and tetradymite as exsolution decomposition products. According to Burke (2006) and Moëlo et al. (2008) bursaitite has been discredited as a mineral species. From In the Sn-W deposit (Shumilovskoe locality) Mozgova et al. (1988) described an almost identical to Kram deposit Pb-Bi sulfosalt mineral paragenesis. In their detailed mineralogical work on bursaitite and cannizzarite they proposed that bursaitite should be retained as a variety of lillianite. Minerals of bursaitite composition from four known localities (Uludag-Turkey, Shumilovskoe-Russia, Cofer-Virginia and Kram-Serbia) still have a problem of unsolved crystal structure. However, our new

evidences, led to confirm that bursaitite is undoubtedly a distinct mineral (Radosavljević-Mihajlović et al., 2007). Unfortunately, numerous attempts to determine the crystal structure using X-ray diffraction on both single-crystal and powdered samples of bursaitite grains from the Kram locality were not successful, due to a very low degree of crystallinity. Cannizzarite reflectance is moderately high, but lower than bursaitite. Reflection pleochroism is distinct light gray to creamy. The anisotropy is strong; similar to bursaitite, but its hardness is considerably lower and similar to galena. Cosalite is less abundant than bursaitite and cannizzarite. It occurs along sulfosalt aggregate rims as corroded intergrowths.

It is white, very similar to galena with only a trace of cream. Reflection pleochroism is weak (light gray to light green) and only distinctive in oil. The anisotropy is noticeable, and very distinct in oil with strong illumination. Reflectance and hardness are lower in comparison to bursaite and cannizzarite. Aikinite is the least abundant phase. It occurs as elongated crystals, in contact to bursaite and chalcopyrite. It is the hardest among the sulfosalts of this group. It is white with a light cream tint. Reflection pleochroism (light yellow to grey) is distinct in air and in oil it is very striking. Anisotropy is also distinct in air and in oil it is high. Ustarasite occurs only in the Kolarica locality mostly as mutually parallel thin needle-like crystals (up to 100  $\mu\text{m}$  in length), and rarely as rhombohedral crustals embedded in older galena and carbonate matrix (Figure 3a). It is a product of decomposition of galena solid solution and Bi-Sb-Ag complex compounds. Bireflectance is distinct, // strong luster like galena,  $\perp$  darker with gray tint (quite to that of falkmanite), microhardness similar to cosalite,

and anisotropy is strong without internal reflections. According to EPMA analyses the Bi/Sb atomic ratio amounts to 1.7 (Table 3). Qualitative determination using X ray diffraction method of ustarasite crystals obtained after galena dissolution resulted in the following  $d$ -values (3.531; 3.060; 2.506; 1.914; 1.730, 1.480  $\text{\AA}$  - Table 5). Tetradymite accompanies the Bi-sulfosalts aggregates and form fine needles. It is white, with faint yellowish tint. Light yellow to creamy bireflectance is weak, hardly visible at grain boundaries, anisotropy is distinct, reflectance is high ( $R \sim 60\%$ ).

#### Native metals

Native gold is rare and characteristic only for the Veliki Cip polymetallic deposit. It appears in the form of isometric grains (up to 15  $\mu\text{m}$  in length) included in pyrite (Radosavljević et al., 2008). Gold also appears in the form of the telluride (most probably calaverite or sylvanite) forming small grains (up to 10  $\mu\text{m}$ ) included in galena. The telluride was determined using

Table 5. Transfer of silver contained in galena to solution using EDTA with qualitative identification of insoluble residue by the XRD method from the Veliki Majdan ore zone.

1 g PbS + solution (100 ml 2 % EDTA + 5 ml conc.  $\text{H}_2\text{O}_2$  + 5 ml conc.  $\text{NH}_4\text{OH}$ )

	Ag (ppm) in galena			Time minute	Degree of Ag transfer in solution (%)			
	Min	Max	average		Min	Max	average	
	1,800	3,130	2,370	6	45	11.4	16.5	15.0
Ag-minerals:	<i>diaphorite</i> (3.282; 2.812*; 2093), <i>fizelyite</i> (3.342; 3.478; 2.896; 2.822*), <i>freieslebenite</i> (3.478; 2.896; 2.822*), <i>schirmerite</i> (2.020; 3.209*; 2.812*; 2.786; 2.369), <i>Ag-tetrahedrite</i> (3.026; 2.601; 1.839; 1.568)							
Other minerals:	<i>ustarasite</i> (3.531; 3.060*; 2.506; 1.914; 1.730, 1.480), <i>boulangerite</i> (3.714; 2.812*; 3.209*; 3.900), <i>bournonite</i> (3.817; 2.724; 4.396), <i>sphalerite</i> (3.130; 2.711; 1.915; 1.632), <i>pyrite</i> (2.694; 2.422), <i>quartz</i> (3.334), <i>calcite</i> (3.040*)							

Note: (n) number of analyses; \* the strongest diffraction maximums.

optical criteria (light-yellow to creamy-white color, reflectance from 55 to 60%).

Native silver is the most widespread among Ag minerals. In the Veliki Majdan ore zone it is associated with older galena. Most of native silver is detected in the Štira locality accompanying Ag-bearing gold and native bismuth replacing galena and considered to be decomposition product of a galena solid solution. EPMA data yielded up to 98 wt% Ag with small amounts of Bi (up to 3.1 wt%) and Sb (up to 0.03 wt%).

Native bismuth is spatially associated with Pb-Bi sulfosalts in the A-belt, where it occurs as exsolution in bursaites aggregates (Figure 3c). It was also found as exsolved grains in galena from the pyrite-galena-sphalerite mineral association of the Veliki Cip and Štira.

Native arsenic is deposited mainly in the central parts of subvertical tubular orebodies within the Rujevac polymetallic deposit. It occurs in the form of spheroidal aggregates (Figure 3f, Radosavljević, 1986). In fresh surfaces the native arsenic is opaque, tin white and has a strong metallic luster. It is very liable to oxidation, and change gradually to grey-brown, dark-gray or grey-black when exposed in air. Zonal lamellae with radial-transverse contraction cracks and presence of spear- and needle-like sulfosalt (according to optical features correspond to gratonite) embedded in native arsenic are quite common (Zarić et al., 1985). Higher content of Sb increases its stability towards oxidation (Ramdohr, 1980). EPMA data yielded up to 98% As with small amounts of Sb (up to 1.35 wt%) and Tl (up to 2.01 wt%). Stibarsen, the SbAs alloy, is rather rare. It occurs as isolated droplets in quartz matrix up to 5  $\mu\text{m}$  (high reflectance  $R \sim 60\%$ , grayish-pink bireflectance weak, moderate microhardness).

#### **Genetic characteristics of silver in galena from the Boranja orefield**

Numerous articles have been published

dealing with the occurrence of minor and trace elements like silver, bismuth and antimony in galena (e.g., Ontoyev et al., 1960; Paronikyan, 1967; Bespaev and Pronin, 1975; Blackburn and Schwendeman, 1977; Foord and Shawe, 1989; Schaefer et al., 2004; Pitcairn et al., 2010).

Galena has the NaCl (cubic) type of crystal structure. The increasing amounts of Ag, and AgSbS<sub>2</sub>-AgBiS<sub>2</sub> solid solutions decrease its unit-cell. A wide range of solid solutions of PbS with AgSbS<sub>2</sub>, AgBiS<sub>2</sub>, PbSe, Tl<sub>2</sub>S, Cu<sub>9</sub>S<sub>5</sub>, Sb<sub>2</sub>S<sub>3</sub>, SnS, MnS was determined during processes of hydrothermal synthesis (Chvilyova et al., 1988). High-temperature galena solid solution decomposed during decreasing temperature of crystallization forming micron and submicron lamellae of high-temperature miargyrite, matildite, etc. (Wernick, 1960).

In polymetallic deposits of the Boranja orefield, galena is the main Ag-bearing mineral. It is a significant mineral from the genetic frame because it occurs during the whole hydrothermal stage in a wide temperature range (from high-, medium-, to low-temperatures, as well as a product of supergene oxidation). The silver content of galena was obtained from grains carefully separated under the stereo-microscope. The occurrence of impurities like sphalerite, pyrite, arsenopyrite, tetrahedrite, sulfosalts, carbonates and quartz were determined by microscope, XRD and/or EMPA, and/or AAS, as impurities (up to 2 wt%). Finally, solid solutions of galena with high-temperature isostructural minerals of Ag, Bi, Sb-bearing minerals were determined as optically "invisible" mineral impurities.

Average Ag contents of galena occurring within the studied belts are reported in Table 6, which also shows Bi and Sb contents. They vary in a range from 0.001 to 0.936, 0.000 to 3.345, and 0.012 to 0.510 wt%, respectively. Cu and As occur in traces.

Galena from A-, B- and D-belts was analyzed by mass spectrometric methods aiming to

Table 6. Average contents of trace elements in galena and other main sulfides from all four mineralized belts.

Elements *wt%	A-belt			B-belt		C-belt	D-belt
	bursait <sup>1</sup>		Kolarica (15)	galena		**stibnite <sup>2</sup> (ppm)	galena
	Kram (1)	V. Cip (1)		Centralni revir (31)	Kojići (30)	Rujevac (1)	Ravnaja (6)
Ag	0.39	0.30	0.28	0.22	0.26	> 1,000.00	< 0.01
Sb	0.05	0.05	0.21	0.27	0.31	> 1,000.00	0.01
As	0.01	0.05	0.01	0.05	< 0.01	> 1,000.00	< 0.01
Bi	37.11	0.71	0.19	0.01	0.01	3.73	n.d.
Cu	1.17	0.01	< 0.01	< 0.01	0.04	n.a.	0.01
**ppm	(1)	(1)	(3)	(3)	(2)	(1)	(1)
Na	n.d.	27.55	55.58	27.55	68.24	337.39	80.50
K	20.00	89.26	65.84	89.26	71.43	n.a.	165.41
Rb	n.d.	+	0.72	+	+	24.53	n.d.
Cs	0.02	+	0.09	+	+	n.a.	n.d.
Sr	+	+	1.75	+	0.34	963.62	14.57
Ba	n.d.	0.07	1.95	1.49	5.96	76.13	18.42
Hg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	+
Tl	n.d.	0.35	4.27	3.80	+	155.12	n.d.
La	n.d.	n.d.	0.08	0.39	0.01	n.d.	n.d.
Ce	n.d.	n.d.	0.22	0.22	+	n.d.	n.d.
Pr	n.d.	n.d.	0.03	0.08	+	n.d.	n.d.
Nd	n.d.	n.d.	+	+	n.d.	n.d.	n.d.
Sn	+	15.94	79.86	15.94	16.39	n.d.	n.d.
Nb	n.d.	n.d.	0.49	n.d.	n.d.	n.d.	n.d.
Se	50.00	50.00	148.15	37.04	240.99	> 1,000.00	n.d.
Te	>1,000.00	200.50	116.11	50.07	234.35	n.a.	n.d.
Mo	n.d.	n.d.	1.40	n.d.	n.d.	19.13	+
W	n.d.	n.d.	3.96	+	n.d.	132.26	n.d.
F	n.d.	0.55	0.82	0.55	9.38	10.60	> 1,000.00
Cl	5.00	162.49	48.69	92.42	26.96	322.06	38.54
I	n.d.	0.78	1.14	0.78	0.12	n.a.	+
Br	n.d.	+	+	+	+	n.a.	+
Co	6.00	+	2.96	+	+	19.73	n.d.
Ni	60.00	+	+	+	+	> 1,000.00	n.d.
Pt	n.d.	n.d.	+	n.d.	n.d.	n.a.	n.d.
Pd	n.d.	n.d.	+	n.d.	n.d.	n.a.	n.d.
Au	n.d.	1.14	+	+	+	n.d.	n.d.

Note: <sup>1</sup>Radosavljević-Mihajlović et al., 2007; <sup>2</sup>Mudrinić, 1984; \* AAS method; \*\* MSA method; (n)-number of analyses; n.d.-not detected (AAS < 0.001 wt%; MSA < 0.01 ppm); +-qualitative detected; n.a.-not analyzed.



determine regularities essential for typomorphism and genetic models of formation. All examined galena contain traces to ultratraces of Na, K, Sr, Ba, F, Cl, Br and I (Ge was not determined). Na/K atomic ratio is < 1. In addition, Tl, Sr and Ba progressively increase in deposits distal to the Tertiary granodiorite of Boranja. Moreover, Se also increases and Te decreases from A- to C-belts, while in the D-belt they are absent (Table 6).

From the geochemical abundances found in this study, galena from the A-belt shows distinctive high content of Te and Bi. Galena from the B-belt shows a decreasing Bi content with increasing distance from the Boranja granodiorite, while Ag and Sb are approximately the same (Figure 4). In general Tl, Sn, Nb, Mo and W follow the same phenomenon. Rare Earth Elements (REEs, La → Nd series), as well as Pt, Pd and Au is also detected in galena from the B-belt (Table 6). Antimonite from the the C-belt is characterized by high contents of alkaline and

alkaline earth metals, as well as Tl, Se, W and Cl (REE, Sn, Nb and Te not detected) (Rujevac deposit-Mudrinić, 1984). High contents of halogens as well as Hg, characterize the D-belt (all other elements are absent) (Table 6).

According to the Ag-, Bi-, and Sb content in galena, as well as the spatial distribution of the metallogenic belts, four genetic types of galena can be pointed out. They practically overlap with the paragenetic sequence and mineralization. The first type refers to galena with high Bi- and Ag-content occurring at the A- and B-belt in a lesser extent. In the Veliki Majdan ore zone Bi decreases from NW to SE (Kolarica-Centralni revir-Kojići). In the D-belt Ag and Sb appear in trace amounts while Bi is completely absent (Figure 4). Supergene galena formation associated with cerusite is observed at Tisovik, and less commonly as a decomposition product in the rims of Pb-Sb sulfosalts at Rujevac.

This galena type has Bi/Ag, Sb/Ag, and Bi/Sb

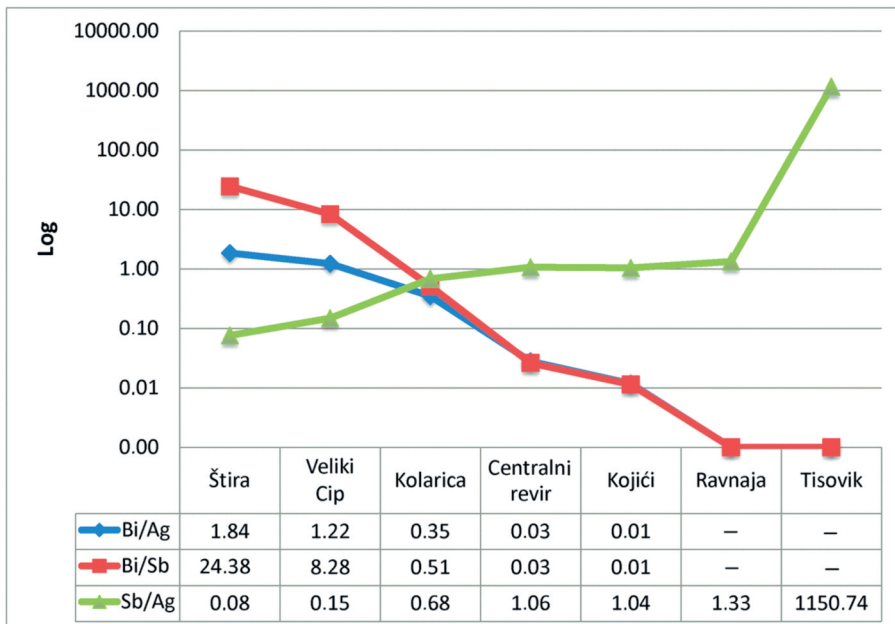


Figure 4. Bi/Ag, Sb/Ag and Bi/Sb atomic ratios in galena from polymetallic deposits related to the Tertiary granodiorite of Boranja (note: galena without Bi in the log-scale is given as 0.01 ppm).

atomic ratios in the range of 1.2-1.8, 0.08-0.15 and 8.3-24.4, respectively (Figure 4). It is commonly associated with pyrrhotite-chalcopyrite and less commonly to Pb(Ag)-Bi sulfosalts. It can be considered a residual phase in transformation products of pyrrhotite or it is distributed along cracks in silicates. Moreover, it is usually replaced by younger sulfides. Three electron microprobe analyses yielded the following amounts for Ag, Bi, and Sb: (0.00-0.80, avrg. 0.33), (0.03-2.03, avrg. 0.59), and wt% (0.00-0.08, avrg. 0.01), in wt% respectively.

The second generation of galena has Bi/Ag, Sb/Ag, and Bi/Sb atomic ratios in the range 0.01-0.35, 0.68-1.06 and 0.01-0.51, respectively (Figure 4). The Bi content is low and fluctuating, while Sb and Ag are uniform without oscillation. Galena of this type is usually associated with pyrite-sphalerite, tetrahedrite-chalcopyrite and Pb(Ag)-Sb sulfosalts. It is the most abundant galena type with a very large areal distribution mainly in the B-belt (Veliki Majdan ore zone).

The third generation of galena is characterized by absence of Bi and low content of Ag and Sb. Sb/Ag atomic ratio amounts to 1.33 (Figure 4). It is usually deposited in the form of massive monomineralic orebodies of small dimensions and associated with pyrite-sphalerite-fluorite. It is moderately abundant, mainly present in the D-belt (Ravnaja).

The fourth galena generation, which is a product of decomposition of Pb-Sb sulfosalts (neomineralization of galena), occurs in the Rujevac deposit. Previous work by Borodaev (1978) suggested for that deposit a paragenetic paragenetic order of deposition with early antimonite followed by Pb-Sb sulfosalts and then by galena, which is opposite to that proposed by Ramdohr (1980). Detailed mineralogical investigation by Janković et al. (1977) described galena as a mineral deposited after Pb-Sb sulfosalts and filling fissures in Sb-oxides. Our studies consider this type of galena as a secondary mineral (product of decomposition of

Pb-Sb sulfosalts) accompanied by kermesite and other Sb-oxides. Its intensity and areal extend is low. Colloform galena associated with clear sphalerite (cleophane) and boulangerite is found in the Tisovik cerussite deposit. The fourth generation galena is without detectable Bi, Ag is in trace amounts and has a high content of Sb. Sb/Ag atomic ratio amounts to 1,152 (Figure 4).

Besides galena, other important Ag-bearing minerals are of the tetrahedrite group (Table 3) and Pb-Bi sulfosalts (according to AAS and EPMA data Ag ranges from 0.27-1.06, and 0.62-1.10 wt%, respectively - Radosavljević-Mihajlović et al., 2007). Trace Ag is finally found in sphalerite (up to 120), pyrite (up to 120), pyrrhotite (up to 30), arsenopyrite (up to 75), and chalcopyrite (up to 700 ppm). Most silver originated from galena inclusions. As found by Radosavljević (1988), correlation analysis between silver and lead resulted in *r* values of 0.87 and 0.91 (significant at the 95% confidence level).

#### **Solid-solution $\alpha$ -galena phase (Pb<sub>2</sub>, AgSb, AgBi)S<sub>2</sub>**

Results of study of silver-bearing minerals included in galena yielded low solubility of Ag<sub>2</sub>S, that varies at around 0.1 at high and 0.01 mol% at low temperatures. These inclusions are in the form of various Ag-sulfosalts and not as argentite as it was considered by previous research (Ramdohr, 1980). Their orientation along crystallographic directions in galena suggest these inclusions to be exsolution products. Very early studies showed that using extrapolation of unit-cell shifting of Ag<sub>2</sub>S-AgBiS<sub>2</sub>-PbS ternary solutions, Van Hook (1960) approximated solubility of Ag<sub>2</sub>S in PbS at around 0.4 mol% at 600 °C. Then, Hutta and Wright (1964) studied the solubility of Ag<sub>2</sub>S during hydrothermal synthesis of galena in the temperature range from 215 to 615 °C and at pressure of around 1300 bar. They concluded

that the solubility of  $\text{Ag}_2\text{S}$  in  $\text{PbS}$  at 300 and 600 °C amounts 0.03 and 0.53 mol%, respectively. Wernick (1960) was the first who experimentally proved that at high temperatures  $\text{AgSbS}_2$  and  $\text{AgBiS}_2$  (high-temperature modifications of miargyrite and matildite respectively) have galena crystal structure type. They are characterized by unlimited mixing and formation of solid solutions with galena. All these isostructural phases have great influence on unit-cell reduction of galena. These data have been confirmed and supplemented in detail by Craig (1967), Nenasheva (1971), Hoda and Chang (1975), Chang et al. (1980; 1988), Wu (1987) and Wang (1999). Finally, Chutas et al. (2008) found that significant quantities of Ag can be accommodated in galena as a coupled substitution with  $\text{Ag} + \text{Sb}$  and/or  $\text{Ag} + \text{Bi}$  for 2 Pb atoms. The limitations of this solubility are quantified experimentally for the cubic ( $Fm\bar{3}m$ )  $\alpha$ -galena phase. Above 442 °C, the  $\alpha$ -galena phase has complete solid solution across the  $\text{Pb}_2\text{S}_2$ - $\text{AgSbS}_2$ - $\text{AgBiS}_2$  (galena-miargyrite-matildite) ternary. Galena from the Boranja orefield was singled out directly from polished sections. In order to determine the nature and way of occurrence of Ag in galena, as well as its relation between Ag incorporated in the structure of galena and Ag as inclusions, selective solvent (mixture of EDTA, hydrogen peroxide and ammonia) was used (Bespaev and Pronin 1975). Advantages of this method over others (e.g. EPMA, AAS) is in using larger amounts of galena (1 g) as well as collecting “hidden” minerals from insoluble residue (optically “visible” and “invisible”). Ag content in filtrate was measured in order to determine the degree of solubility of Ag incorporated in the structure of galena, whose percentage ranged from 11.4 to 16.6 wt%. Pb from galena was completely transferred into a solution (Table 5). According to the results of these analyses, Ag content incorporated in the structure of galena amounts approximately 15 wt%, while the rest 85 wt% is

in a form of micron (“visible”) and/or submicron (“invisible”) particles of Ag minerals. Furthermore, these values are approximately equal independent from the total Ag content in galena. The following Ag minerals: diaphorite, fizelyite, freieslebenite, schirmerite, argentine tetrahedrite, as well as ustarasite, boulangerite, bournonite, sphalerite, pyrite, quartz, calcite found among other minerals were qualitatively determined into the insoluble residue using XRPD method (Table 5).

### Paragenetic analysis and conclusive remarks on the Boranja orefield genesis

The A-belt is dominated by the pyrometasomatic (skarn) stage, which includes deposition of calcite I, silicate, magnetite, scheelite and powellite. The following high-temperature hydrothermal stage, which corresponds to the sulfide-sulfosalt mineral paragenesis, is subdivided in several paragenetic sequences. The following mineral parageneses are recognized at the Kram deposit: *i.* garnet-calcite with magnetite, *ii.* pyrrhotite-chalcocopyrite, *iii.* pyrite-chalcocopyrite-sulfosalts with Te and Ag, *iv.* hematite-carbonate-limonite-Cu.

Chalcocopyrite occurs in coarse-grained aggregates, which cement or replace older contact silicates, oxides, and sulfides. It contains numerous star-shaped inclusions of sphalerite and cuprian pyrrhotite. An intensive hydrothermal transformation of pyrrhotite (“bird’s eye structure”) was observed (pyrrhotite → marcasite → pyrite). During the high-temperature hydrothermal stage various Pb-Bi sulfosalts were formed, yielding bursaite and cannizzarite after decomposition. Sphalerite-galena containing Ag and Bi sulfosalts occur rarely in the Kram deposit; however, they are very common in the Veliki Cip and Štira deposits.

The hydrothermal stage is the most representative of the B-belt, while the

pyrometasomatic (skarn) stage occurs only sporadically on the rims of the belt (Kolarica). The hydrothermal stage is subdivided in several mineral sequences, corresponding to high-, medium- and low-temperature mineral assemblages. The following mineral parageneses were identified: *i.* pyrrhotite-galena-sphalerite with magnetite and chalcopyrite, *ii.* pyrite-arsenopyrite, *iii.* pyrite-galena-sphalerite-sulfosalts, *iv.* pyrite, *v.* antimonite. The pyrite-galena-sphalerite-sulfosalts and the pyrrhotite-galena-sphalerite with magnetite and chalcopyrite are the main mineral parageneses and have great economic importance. The pyrite paragenesis occurs at the most distal NW parts of the Kolarica area and is spatially related to the pyrite-galena-sphalerite-sulfosalts mineral paragenesis. At depth, the pyrite orebodies grade into the pyrite-galena-sphalerite-sulfosalt mineral paragenesis and consequently the ore content in useful metals increases. All of the pyrite orebodies were formed through the process of alteration of pyrrhotite. According to the present knowledge of mineral parageneses, the ore deposits within the B-belt are characterized by enrichment of several metallic elements. Besides the main elements Fe, Zn, Pb and S, special role in the formation of these deposits have As, Sb, Cu, Bi and Ag, while the rest are rare and have contents of less than 0.01%.

In the C-belt only the hydrothermal stage is present. It corresponds to low-temperature mineral parageneses and is subdivided in several mineral sequences. The following mineral parageneses were recognized in the Rujevac polymetallic deposit: *i* relict (quartz, calcite, silicate, Ti-minerals, apatite, organic matter), *ii* quartz-sphalerite-arsenopyrite-antimonite, *iii* sulfosalt-arsenic-carbonate, *iv* sphalerite-pyrite-antimonite-realgar, *v* Sb-As-oxide-sulfide (product of oxidation processes, Radosavljević et al., 2012).

In the D-belt, similarly to the C-belt, only the hydrothermal stage, characterized by monomineral and polymetallic fluorite-bearing

deposits, took place. The Ravnaja deposit, typical for vein-like orebodies where minerals were deposited from low-temperature hydrothermal fluids, belongs to this belt. The following mineral parageneses were recognized at Ravnaja: *i* calcite-fluorite, *ii* sphalerite-galena-fluorite, *iii* galena. The fluorite-pyrite-sphalerite-galena is the main mineral paragenesis and has great economic importance.

Temperatures of deposition of Pb-Zn mineral associations in the Boranja orefield range from 480-160 °C (Radosavljević et al., 2012), and this is in a good agreement to the paragenetic analysis given in Table 2. Galena and sphalerite genesis spans all high- to low-temperature hydrothermal stages, while the Pb-Zn mineral associations of the Veliki Cip and Ravnaja deposits correspond to the high- (480 °C) and low-temperature hydrothermal stages (230 °C), respectively. In addition, the Veliki Majdan ore zone corresponds to a temperature range from 450 to 367 °C that is between high- and medium-temperature hydrothermal stages. Temperatures of ore formation gradually decrease moving further away from the Tertiary Boranja granodiorite according to the following sequence: Kolarica → Centralni revir → Kojići. Moreover, in the Ravnaja deposit, Nikolić and Gatter (1986) determined two temperature intervals of formation of fluorite (275-245 °C and 205-160 °C), and density of fluids (0.98-0.80 g/cm<sup>3</sup>). In addition, temperature range of deposition from 280 to 160 °C was obtained on quartz and cleophane using a cryometric method in the Rujevac deposit (Mudrinić, 1984). Cryometric measurements yielded that ore-bearing solutions were mainly NaCl and alkaline CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> but to a lesser extent. Presence of gaseous inclusions with volume participation from 5 to 25% was determined (equivalent percentage content of NaCl range from 3 to 10%).

The presence of widespread exsolved minerals evidences found in all levels of ore deposits is

indicative that the temperature of crystallization of all skarn-metasomatic, high-, and medium-temperature hydrothermal associations was identical to the formation of the host coarse-grained metallic minerals. Low-temperature hydrothermal associations are fine-grained colloform and gel-like and usually recrystallized.

Based on paragenetic relationships of the polymetallic deposits at the Boranja orefield it can be concluded that the beginning of crystallization started in a low sulfur partial pressure (low  $fS_2$ ) environment, and resulted to the deposition of minerals of low- to partly intermediate sulfidation states (e.g. pyrrhotite, Fe-rich sphalerite, tetrahedrite group minerals, Pb-Bi sulfosalts, etc.). Minerals of higher sulfidation state (pyrite, Fe-poor sphalerite, antimonite, realgar etc.) began to crystallize with decreasing temperature, increasing  $fS_2$  - values, and increasing distance from the Boranja granodiorite. Hostrocks were mostly Triassic limestones and partly silica-bearing rocks (e.g. dacite, andesite, slates). The Pb content prevails over Zn, although in the Srebrenica orefield this ratio is reversed (Radosavljević, 1988).

Silver is an important and genetically significant metal in the Boranja orefield with a content varying from 10 to 820 g/t. Its transport is achieved by polysulfide solutions with Pb, Bi, Sb and As. However, a possibility of carbonate-bicarbonate and halogen complex solutions should not be excluded (Hemley et al., 1992; Hemley and Hunt, 1992). There exists a very good correlation between Ag and Pb ( $r = 0.828$  significant at the 95% confidence level), while silver poorly correlates with other elements. This is expectable since galena is the main Ag-bearing mineral, while other Ag-bearing minerals (e.g. Ag-tetrahedrite, pyrargyrite, Ag-bearing gold and native Ag) occur in lesser amounts (Radosavljević, 1988).

Besides Ag, the elements Bi and Sb are significantly abundant in galena (Table 6 and Figure 4). Multianalytical investigations of

galena from various deposits at the Boranja orefield yielded that it frequently occurs in a form of isostructural solid solutions with diaphorite, fizelyite, freieslebenite and schirmerite in accordance to previous work (e.g. Wernick, 1960; Ontoyev and Korsakova, 1967; Hoda and Chang, 1975; Wang, 1999; Chutas et al., 2008 - Table 5).

In addition, galena from the A- and B-belt contains traces of W, Nb, Se and Te. Other elements detected in galena (e.g. Si, Al, Ca, Mg, Na and K with very minor presence of Ti, Cr, V, Zr, Rb and Cs) may represent impurities and are only of petrogenetic significance.

The crystallization of minerals in the Boranja orefield occurred at several successive stages, probably corresponding to a single regional metallogenetic event. According to the mineral assemblage, it can be concluded that hydrothermal solutions ascended from common magmatic source and this is believed to be the Tertiary granodiorite of Boranja. The following genetic interpretation can be made for the Boranja orefield:

Ore deposits at the Boranja orefield are genetically related to the Upper Oligocene to Lower Neogene subvolcanic-plutonic intrusions of the Boranja magmatic complex.

The mineralizing processes occurred in several hydrothermal stages and are characterized by a well-developed lateral zonality and regular distribution of several mineral associations. The lateral zonality is generally represented by the spatially and genetically simplified sequence: Fe-Cu(Pb, Zn) belt → Pb(Ag)-Zn belt → Sb(As) belt →  $CaF_2$ (Pb, Zn) belt. This sequence is controlled by change of temperature, pressure and chemical characteristics of the ore fluids, due to various degree of interaction with hostrocks and fluid differentiation (similar to hydrothermal systems of Bingham, Bowman et al., 1987; Kloppenburg et al., 2010).

Besides the PMD, similar Pb-Bi sulfosalts mineral parageneses have been determined in the



Šumadija Metallogenic District, Rudnik orefield in Central Serbia (Stojanović et al., 2006). In comparison to the other districts in the SMMP (e.g. Kopaonik, Rogozna, Golija), the mineral association of the Boranja orefield is characterized by significant amounts and varieties of Pb-Bi sulfosalts. Similar Pb-Bi sulfosalt mineral parageneses are also reported from neighbouring areas belonging to the Alpine metallogenic province, e.g. the Uludag orefield, Bursa Province, Turkey (Van der Kaaden, 1958; Makovicky and Karup-Møller, 1977), the Lavrion ore district, Greece (Voudouris et al., 2008a,b) and the Larga hydrothermal system in Romania (Cook and Ciobanu, 2004).

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