A review of the Pb-Zn-Cu-Ag-Bi-W polymetallic ore from the Rudnik orefield, Central Serbia

JOVICA N. STOJANOVIĆ1, SLOBODAN A. RADOSAVLJEVIĆ2, RADULE D. TOŠOVIĆ3, ALEKSANDAR M. PAČEVSKI4, ANA S. RADOSAVLJEVIĆ-MIHAILOVIĆ5, VLADAN D. KAŠIĆ1 & NIKOLA S. VUKOVIĆ5

Abstract. The Rudnik orefield is one of the well-known skarn-replacement and high-temperature hydrothermal Pb-Zn-Cu-Ag-Bi-W polymetallic sulfide deposits, and is a part of the Šumadija Metallogenic District, Serbia. It comprises ore bodies grouped into several major ore zones. The pseudostratified and plate-like ore bodies have relatively high content of valuable metals. The average content varies in wide ranges: Pb (0.94–5.66 wt%), Zn (0.49–4.49 wt%), Cu (0.08–2.18 wt%), Ag (50–297 ppm), Bi (~100–150 ppm), and Cd (~100–150 ppm). Generally, a complex mineral association has been determined. Iron sulfides, arsenopyrite, chalcopyrite, sphalerite, galena and sulfosalts are abundant minerals in the ore. Carrier minerals of Bi and Ag are Bi-sulfosalts, such as galenobismutite, cosalite, Ag-bearing aschamalmite, vikingite, schirmerite and gustavite. Copper, Ag and Pb-Sb sulfosalts have been found only locally. Complex Ni-minerals (sulfides, arsenides and sulfosalts) with Fe, Co and Ag were formed under the influence of present serpentine rocks and their yield of Ni, Co and Cr in the hydrothermal ore-bearing solutions. Significant scheelite mineralizations have been found in the Nova Jama, Gušavi Potok and Azna ore zones. The presence of Bi-sulfosalts and argentopenlandite suggests formation temperatures higher than 350, and lower than 445°C, respectively. Therefore, the mineralization was formed in the temperature range 350 to 400°C. The continuity of pyrite, pyrrhotite and siderite colloform bands in relic aggregates shows frequent changes of \( f_{O2} \) and \( f_{S2} \) in hydrothermal solutions. Isotopic composition of sulfur also confirms that the source of the ore-bearing fluids was magmatic. In addition, the enrichment of Bi and Ag indicates a magmatic origin. The appearance of Bi-minerals represents a significant genetic indicator for detection of increased Ag concentrations within the ore mineralizations. Typical gangue minerals are quartz, silicates, carbonates, oxides and different oxy-hydroxides. Special attention is given to the paragenetic relationships and the genetic significance of mineral associations as indicators of ore-forming conditions.

Key words: ore mineralogy, Pb-Zn-Cu-Ag-Bi-W polymetallic ore, sulfosalts, Rudnik orefield, Serbia.

Апстракт. Полиметалично Pb-Zn-Cu-Ag-Bi-W лежиште Рудник највеће и најдетаљније истражено лежиште у шумадијској металогенетској области. Састоји се од система рудних тела, која су груписана у неколико већих рудних зона. Рудна тела су псеудо-стратификована и плочастих форми, са релативно високим садржајем корисних метала. Средњи садржај главних рудних елемената у оквиру целог лежишта варира у широким границама: Pb (0.94–5.66%), Zn (0.49–4.49%), Cu (0.08–2.18%), Ag (50–297 ppm), Bi (~100–150 ppm), Cd (~100–150 ppm). Генерално, одређена је сложена Pb-Zn-Cu-Ag-Bi-W полиметалична минерална асоцијација. Најчешће распрострањени сулфидни минерали су Fe-сулфиди, арсено- пирит, халкопирит, сфалерит, галенит и сулфосоли. Водећи минерали Bi и Ag су Bi-сулфосоли. Одређене су: галенобизмутит, козалит, Ag-ашамалмит, викингит, ширмерит и густавит. Локално је утврђена...
Introduction

The Rudnik orefield (ROF) is one of the numerous Pb-Zn polymetallic deposits belonging to the Serbo-Macedonian Metallogenic Province (SMMP), located in the central part of the Balkan Peninsula (Southern Europe) (JANKOVIĆ, 1990). The mineralizations of Tertiary magmatism are related to hydrothermal activity. Lead-zinc polymetallic mineralizations are known from different metallogenic districts, e.g., Podrinje (Central Serbia and Bosnia & Herzegovina), Šumadija (Central Serbia), Rogozna (Central Serbia), Stari Trg (Serbia-Kosovo province), Zletovo-Kratovo (FYR of Macedonia), Lavrion (Greece), and many other (e.g., SMEJKAL & RAKIĆ, 1957; ALEKSANDROV et al., 1990a,b; DANGIĆ, 1993; TOŠOVIĆ, 1997, 2000; SERAFIMOVSKI et al., 1990; SERAFIMOVSKI & ALEKSANDROV, 1995; SERAFIMOVSKI et al., 2006a,b; SERAFIMOVSKI et al., 2013, 2015; RADOŠAVLJEVIĆ-MIHAILOVIĆ et al., 2007; VOUDOURIS et al., 2008a,b; KOLODZIEJCZYK et al., 2015, 2016, 2017; RADOŠAVLJEVIĆ et al., 2014a,b, 2015, 2016a).

The aim of this study is to discuss some key questions regarding mineralogical characteristics (mineral associations and parageneses), and genesis of the skarn-replacement and high-temperature hydrothermal polymetallic ores of the ROF.

Geological settings and description of the ore zones

Since the Eocene, the migrating subduction wave has interfered with non-coaxial extension in the Aegean area (Aegean rift). Magmatism in this period was initially characterized by calcalkaline–shoshonitic products and, especially since the Oligocene–Miocene, by the coexistence of “slab-related” cal-

calkaline–shoshonitic and “slab-unrelated” alkaline magmas (Čvetković et al., 2004; Marchev et al., 2005; Agostini et al., 2010; Nimis & Omnetto 2015). The ore deposits of the SMMP are spread within three main geotectonic units: a small part of the Dinarides, the Vardar zone, and the Serbo-Macedonian massif (Janković, 1990; Jelenković et al., 2008). This metallogenic province is located in the tectonic–magmatic zone formed during the Cenozoic, when tectonic activities and associated magmatism in Serbia are expressed by emplacement of two groups of igneous rocks: i) granitoids (e.g. Cer, Bukulja); and ii) multi-stage granodiorite volcanogenic-intrusive complex (e.g. Podrinje, Šumadija, Kopaonik). The second group is genetically related to economically significant deposits of Pb–Zn, Sb, Cu, Mo, Au, and Fe (Petković, 1997). Volcanic/plutonic magmatism with an absolute age of 31.9 to 26.1 Ma in the ŠMD was initiated by one of the orogenic phases during the Oligocene (Čvetković et al., 2004), and covers a relatively narrow area (up to 30 km in width) that extends from Belgrade to Kraljevo. The ŠMD is constituted of the several small ore fields (Janković 1990): Avala-Kosmaj, Bukulja-Brajevac, Rudnik and Kotlenik (Fig. 1a).

The area of the ROF is of oval shape, elongated in NW–SE direction, and covers approximately 35 km² in areal extent (Fig. 1a). Sedimentary rocks are represented by sandstone, siltstone, limestone, Upper Cretaceous flysch, and marly limestone. The beginning of Oligocene dacite and quartz latite volcanic activity has an absolute age of 31.9–30.0 Ma (K–Ar on associated high-K volcanics – Čvetković et al., 2004). The volcanic complex of the ROF was formed in two successive events, the first before 30 Ma, and the second at 23 Ma. This magmatism produced various products of quartzlatitic magma, while vein-like equivalents of granitoid rocks of quartz monzonite and granodiorite composition occur to a lesser extent. Marly-clayey sediments of low-grade metamorphism, sandstones, conglomerates, schist hornfels, and Ca-skarns represent contact-metamorphic rocks (Čvetković et al., 2016). The origin of these rocks is closely related to the emplacement and crystallization of
igneous rocks, which provided both the heat for their metamorphism and the differential pressure at impact-ated alteration of host rocks.

The name of the Rudnik deposit and the mountain where it is located originates from the Serbian word for mine—“rudnik". This polymetallic deposit comprises over 90 skarn-replacement and hydrothermal ore bodies, and is mainly hosted by Cretaceous sediments, occasionally by Oligocene dykes and sills (dacite, less quartz latite), and contact-metamorphic complex rocks. The dominant lithostratigraphic units, in which the ore bodies lie, include various sedimentary, metamorphic and magmatic lithologies (clastic sediments, low-grade metaclastics, carbonate sediments, olistolith limestones, breccia-filled volcanic pipes formed by gaseous explosions and volcanics of quartz latite and latite composition (POPOVIĆ & UME-LIĆ, 2015). The ore bodies are oriented NW–SSE on area of approximately 6 km². The ROF is divided into several ore zones named after nearby localities. These ore zones are located between the Prlovski (NW) and the Bezdan (SE) (Fig. 1b).

According to Tošović (1997, 2000), ore bodies within the ROF can be classified in the two morphogenetic types: (i) skarn plate-like, and (ii) hydrothermal plate-like. They have massive to brecciated textures and stockwork/disseminated and disseminated mineralization types with extremely variable sizes. The thickness of ore bodies ranges up to 12 m, while length is up to 50 m along strike and depth. Mass of mineralization types with extremely variable sizes.

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Sampling and analytical methods

The samples, collected from all main levels of the ROF, as well as from the borehole No 197/12 (between the Gušavi Potok and Bezdan ore zones), have been analyzed by ore microscopy, chemistry, mass spectrometry and electron microprobe. Over 80 polished sections were prepared for study using microscopy in reflected light and electron probe microanalysis (EPMA) (Picot & Johans 1982). A CARL-ZEISS polarizing microscope, model JENAPOL-U, equipped with 10x, 20x, 50x, air medium, 100x, immersion medium (cedar oil), objectives and a system for photomicrography (AXICAM 105 color camera equipped with CARL ZEISS AIXOVISION SE64 REL. 4.9.1. software package) was used.

The EPMA were carried out in the Laboratory of Electron Microscopy (University of Novi Sad, Serbia) and in the Laboratory for Scanning Electron Microscopy, Faculty of Mining and Geology (University of Belgrade, Serbia). The analytical spots were marked on Backscattered Electron Images (AIXICAM 105 color camera equipped with CARL ZEISS AIXOVISION SE64 REL. 4.9.1. software package) was used.

The EPMA were carried out in the Laboratory of Electron Microscopy (University of Novi Sad, Serbia) and in the Laboratory for Scanning Electron Microscopy, Faculty of Mining and Geology (University of Belgrade, Serbia). The analytical spots were marked on Backscattered Electron Images (BEI). The chemical compositions were determined using 1) a LINK AN 1000 EDS microanalyser attached to a JEOL JSM-6460LV scanning electron microscope (SEM) at accelerating voltage 15 kV at counting time 250 using the ZAF-4/FLS software (Novi Sad); and 2) a JEOL JSM-6610LV SEM connected with an INCA energy-dispersion X-ray analysis unit at accelerating voltage 20 kV for counting time 60 s (Belgrade). The following X-ray lines and standards (both natural (n) and synthetic (s)) were used 1) - SKα (n-CuFeS₂), FeKα (n-CuFeS₂), PbMα (n-PbS), CuKα (n-CuFeS₂), AsKα, La (n-FeAsS), SbLβ (n-Sb₂S₃), ZnKα (n-ZnS); pure metals for AgLα, BiLα, CdLα, and MnKα; 2) - FeKα, SKα (FeS₂), AsKα (InAs), SbLα (InSb), AgLα (Ag₆Te), PbMα (PbS); pure metals for NiKα, CoKα, CuKα and BiMα. EDX detection limits are σ ~ 0.3 wt%.

Mass Spectrometric Analyses (MSA) of pure pyrrhotite grains and ore samples were carried out by JEOL, model 01MB mass spectrometer with an analytical range from 1,000 to 0.01 ppm. Iron content, determined by AAS, was used as an internal standard.

Chemical analyses of ore samples, obtained by different methods (gravimetry, cupellation, volumetry, AAS, and ICP-OES), carried out in the Institute of Technology of Nuclear and Other Mineral Raw Mate-
Results and discussion

Bulk ore geochemistry

The ore bodies from the ROF characterize complex chemical compositions ranging from Pb-Zn ores with enriched Ag content to Pb-Zn-Cu ores with increased amounts of Ag, Bi, and W.

The content of valuable and other metals obtained from the representative technological sample of the Prlovi 2 ore body amounts to (in wt%): Pb=7.18, Zn=3.47, Fe= 3.00, S=0.25, Mn=0.57, WO3= <0.02, Sb=0.01; Ag=29.3 ppm, Au=0.44 ppm (RADOŠAVLJEVIĆ et al. 2002). According to Tomanec & Lazić (2012), contents of Pb and Zn from the same sample amount to: 4.06 and 3.02 wt%, from which 1.89 and 1.58 wt% is sulfide part, and 2.17 and 1.44 wt% is oxide part, respectively.

In the Azna ore zone the average content of valuable metals amount to (in wt%): Pb=0.90, Zn=0.59, Cu = 1.12; Ag = 91ppm. According to ZARIĆ et al. (1992b) significant variations of chemical composition of the polymetallic ore were determined (11 samples): Pb 0.61-9.23, Zn 0.88-14.13, Cu 0.05-4.21, and As 0.12-0.69 wt%; Cd 76-168, Bi 76-1610, Ag 31-602, and Au <0.5 ppm. The chemical composition of the representative technological sample of the scheelite mineralization is as follows: Pb= <0.01, Zn=0.01, Cu =<0.01, S=0.25, WO3=0.15 wt%; Ag=2.3, Au=0.3, Bi=90, Mo= <10, Sn=40 ppm.

According to the Pearson coefficient, a positive correlation has been determined between Ag and Pb (r= 0.561), while it is absent between all other metals within the Azna ore zone. In the representative composite sample following trace-elements were determined (MSA in ppm): F 79, P 332, Cl 98, V 69, Cr 726, Co 199, Ga 49, Rb 220, Y 17, Zr 248, Ag 16, Cd 12, In 3, Sn 33, Sb 53, Te 5, Cs 28, Ba 159, Rare Earths (La 19, Ce 24, Pr 4, Nd 17, Gd 2) Σ 66, Bi 150, Th 1.4. Elements >1000: Fe 78, Pb 2.99, Zn = 2.71, Cu = 0.21 wt%; and Ag = 76 ppm. According to ZARIĆ et al. (1992b) significant variations of chemical composition of the polymetallic ore were determined (9 samples): Pb 2.19-6.61, Zn 0.86-3.31, Cu 0.09-0.66 and As 0.12-0.30 wt%; Cd 89-170, Bi 101-807, Ag 60-347 and Au <0.5 ppm.

Significant variations in contents of WO3 have been determined in the scheelite ore (Z-1): 0.03-4.48 wt%, while in the mineralized zone (Z-2) WO3 has the uniform low content (~ 0.03 wt%). Silver slightly increased in three samples labelled 5, 6 and 9 (Fig. 2). In addition, the EPMA confirmed a permanent presence of Ag in the galena and Bi-sulfosalts (Table 1). These Ag-bearing minerals are unevenly distributed within the polymetallic ores and mineralizations. Average chemical composition in the representative composite sample is as follows: Pb= 0.59, Zn= 1.13, Cu= <0.01, S= 1.20, WO3= 1.22 wt%; Ag= 20, Au= <0.5, Bi = 500, Mo= 200, Sn= 10 ppm.

According to the Pearson coefficient, a strong positive correlation has been determined between Bi and Ag (r = 0.947) and high between Pb and Ag (r = 0.624), while these are absent between all other metals within the Nova Jama ore zone. In the representative composite sample following trace elements were determined (MSA in ppm): Be 1, B 9, F 300, P 800, Cl 100, Ti 1000, Sc 70, V 20, Cr 200, Mn 400, Co 40, Ni 600, Ga 40, Se 20, Rb 1000, Sr 300, Y 5, Zr 300, Nb 100, Mo 60, Ag 40, Cd 10, In 0.8, Sn 10, Sb 20, Te 60, Cs 70, Ba 500, Rare Earths (La 8, Ce 20, Pr 3, Nd 20, Sm 5, Eu 1, Gd 10, Tb 1, Dy 5, Ho 0.3) Σ73.3, Hf 5, Ta 1, Tl 10, Th 2. Elements >1000: Na, Al, Si, S, K, Cu, Zn, Pb and W. Qualitatively detected: Mg, Ge, Se, Sr, Nb, Mo, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Au, Tl, while following were not detected: Br, Ru, Rh, Pd, I, Re, Os, Ir, Pt, Hg (<10 ppb). Standard Fe = 10.47 wt% (ZARIĆ et al., 1992b).

In the Nova Jama ore zone the average content of valuable metals is as follows: Pb = 2.99, Zn = 2.71, Cu = 0.21 wt%; and Ag = 76 ppm. According to ZARIĆ et al. (1992b) significant variations of chemical composition of the polymetallic ore were determined (9 samples): Pb 2.19-6.61, Zn 0.86-3.31, Cu 0.09-0.66 and As 0.12-0.30 wt%; Cd 89-170, Bi 101-807, Ag 60-347 and Au <0.5 ppm.
Tm, Yb, Lu and U while following were not detected: Ge, Br, Ru, Rh, Pd, I, Re, Os, Ir, Pt, Au and Hg (<10 ppb); Standard Fe = 2.62 wt% (STOJANOVIĆ 2005). The core samples from borehole No 197/12, located between the Gušav Potok and Bezdan ore zones, yielded following chemical composition: Pb = 0.12, Zn = 1.35, As = 0.11–5.35 wt%, Ag = 37–162 ppm, and Au = 0.8–3.3 ppm (POPOVIĆ & UMELJIĆ, 2015).

Ore mineralogy

Based on the microscopy study and EPMA, the following list of minerals was established: sulfides; sulfoarsenides and arsenides (pyrrhotite, pyrite, colloform pyrite, framboidal pyrite, marcasite, arsenopyrite, chalcopyrhytite, chalcopyrite, cubanite, mackinawite, sphalerite, galena, bismuthinite, molybdenite, pentlandite, argentopentlandite, gersdorffite, and nickel); sulfosalts (gallenobismutite, cosalite, Ag-bearing aschamalmite, gustavite, schirmerite, vikingite, Ag-bearing tetrahedrites, and semseyte); native metals (bismuth, silver, gold, and PGE – Rh, Pd, Pt); oxides (magnetite, hematite, rutile, anatase, tenorite, cuprite, massicot, minium, scrutinyite, and zincite); wolframate (scheelite); gangue (quartz, sanidine, adularia, andesine, amphiboles, biotite, chlorites, clinohumosite, hedenbergite, garnets, axinite, epidote, clay minerals, apatite, zircon, monazite-(Ce), sphene, leucoxene, calcite, siderite, aragonite, anglesite, cerussite, smithsonite, willemit, hydrohaetaerolite, zinc(II) metasilicate, limonite, goethite, lepidocrocite, hydrohematite, and malachite). The main ore and gangue minerals are briefly described according to their genetic status and paragenetic relations in the mineralization cycle.

Sulfide, sulfoarsenide and arsenide minerals

The Fe sulfides are the most common constituents of the sulfide massive ore and occur in the all ore zones of the ROF. Major Fe sulfide mineral is pyrrhotite, which occurs as characteristic coarse-crystalline tabular aggregates. Based on the optical characteristics it responds to the hexagonal and monoclinic polytypes. Pyrrhotite, occurring in several generations, is commonly in plate-like chunky crystals (Fig. 3a). It is often overgrown by Bi-sulfosalts, chalcopyrite, arsenopyrite and partially transformed into pyrite (Fig. 3b). The first generation of pyrrhotite was formed in early skarn-hydrothermal mineralization stage. The cracks and fractures were filled-up with native bismuth and Bi-sulfosalts (Fig. 3c). It commonly contains inclusions of very fine PGM grains (Fig. 3d) and silicates (Fig. 3e). This generation is commonly followed by intensive

Fig. 3. Optical microscopy images showing the textural features of ore and gangue minerals of the ROF: a) tabular sections of pyrrhotite crystals (air, //N) – Nova Jama; b) pyrrhotite overgrown by Ag-bearing aschamalmite, galena and chalcopyrite (air, //N) – Azna; c) cracks and fractures of pyrrhotite cemented with native bismuth and Bi-sulfosalts (oil, //N) – Nova Jama; d) the inclusion of PGE-mineral embedded in pyrrhotite (oil, //N) – Nova Jama; e) newly formed hedenbergite penetrates through pyrrhotite (air, //N) – Azna; f) pyrrhotite overgrown by galena and pyrite (air, //N) – Azna. Abbreviations: Po – pyrrhotite, Py – pyrite, Cp – chalcopyrite, Sp – sphalerite, Gl – galena, Ash – aschamalmite, Gb – galenobismutite, Bi – native bismuth, Sch – scheelite, Ru – rutile, Sd – siderite, Si – silicate, Qz – quartz (RADOŠAVLJEVIĆ & STOJANOVIĆ (2003, 2006)).
silification manifested by appearance of quartz meta-
crystals. The younger generation of pyrrhotite was
formed in high-temperature hydrothermal mineraliza-
tion phase in association with sphalerite, galena, chal-
copyrite, pyrite, arsenopyrite and quartz (Fig. 3f).
The most abundant ore minerals of the Gušavi
Potok and Azna ore zones (level 815) are Fe sulfides
(up to 65 mass%) (ZARIĆ et al., 1992b; STOJANOVIĆ et
al., 2016; RADOVALEVIĆ et al., 2006c, 2016). Although
its presence is determined in the surround-
ing silicate matrix, isolated droplets of native bismuth
occur rarely along aggregate boundaries. The central
parts of spherulitic aggregates are composed of
pyrrhotite, while peripheral parts are characterized by
rhythmic, elliptical, broad, annular zones of colloform
pyrrhotite relic (Fig. 4a). These aggregates are often
fractured or translationally shifted. Siderite occurs
along colloform pyrrhotite–pyrite contacts (Fig. 4b).
Pyrite is partly a product of hydrothermal transforma-
tion of pyrrhotite. It is related to the hypogenic trans-
formation process of pyrrhotite established by RAM-
DOHR (1980): pyrrhotite $\rightarrow$ marcasite $\rightarrow$ pyrite. Aggre-
gates that have “bird’s-eye” structure are less affected
by alteration processes, which are similar to appear-
ce of the colloform pyrite although they are com-
pressed and oriented along of the pyrrhotite cleavage.
Pyrite appears in several generations in all ore zo-
nes. In the altered volcanic rocks, pyrite occurs in

Fig. 4. Optical microscopy images in reflected light and BEI showing the textural features of ore and gangue minerals of the ROF: a) pre-
served forms of relic colloform pyrite, pyrrhotite and siderite cemented with galena (air, //N) – Azna; b) microscopic occurrence of a zonal
colloform pyrite aggregate with various sulfides (light) (BEI) – Azna; c) a relic of colloform pyrite, pyrrhotite and siderite cemented with
mixture of galena, native bismuth and Bi-sulfosalts (air, //N) – level 815; d) the annular forms of a colloforms pyrite relic (oil, //N) – level
815; e) anisotropic circular zone corresponds to the mix of marcasite-pyrite (oil, ×N) – level 815; f) a relic of colloform pyrite and siderite
(Figures 4a-h - RADOVALEVIĆ & STOJANOVIĆ (2006); Figures 4c-h - ZARIĆ et al. (1992b); Figure 4i - this study).
Colloform pyrite is the most common in the levels 815 and 720 (NW part of the ROF). Macroscopically, colloform pyrite occurs in the form of black to yellowish black globules, 10–15 mm in diameter, forming irregular botryoidal clusters. Microscopically, it is commonly elliptical to circular filled with colloform bands of Fe-sulfides forming sections consisted of marcasite–pyrite and/or pyrite–pyrrhotite and/or pyrite–pyrrhotite–siderite (Figs. 4b–h). Sometimes they form rhythmical zones cemented with siderite. Colloform pyrite is quite abundant mineral and is commonly cataclasied and as relics embedded in younger sulfides in a form of “isolated islands”.

Tomanec & Lazić (2012) and Popović & Umeljić (2015) unintentionally wrongly named these sections of colloform pyrites as “oolites relicts of pyrites” (Figs. 4a–h). According to Gao et al. (2016), colloform pyrite is a special form of nano-micro polycrystalline aggregation growth, for which a suitable term is “aggregates of nano-micro crystals”. There appears to be three main mechanisms of formation of colloform pyrite: pseudomorphic replacement; biogenic precipitation; and inorganic precipitation. This kind of colloform texture is observed in various geological bodies, such as ancient sedimentary rocks, modern marine and lake sediments, various types of ore deposits, and modern seafloor hydrothermal vents. The morphology, particle size, trace element content and preferential growth orientations of colloform pyrite microcrystals can be important indicators for sedimentary environments, hydrothermal activity, and ore-forming processes. According to Parr (1994), colloform banding textures of pyrite from the Broken Hill-type Pinnacles deposit, New South Wales, Australia, are somewhat similar to those observed in supergene alteration zones, textural relationships in fresh rocks suggest that these are pre-metamorphic and that pyrite was formed as the result of depositing from hydrothermal fluids in open veins, vugs and fissures. Based on the above-mentioned, genesis of the colloform Fe-sulfides in the ROF is undeniably of hydrothermal origin, and colloform growth bandings are due to the frequent changes of precipitation conditions as well as fluctuations and rapid changing of concentrations of ore-bearing fluids.

Relicts of framboidal pyrite in the mineralized Upper Cretaceous sandstones were determined at the level 815 (Zarić et al., 1992b). A similar occurrence was observed in sediments of the Jurassic Diabase-Chert Formation in the Rujevac Sh-Pb-Zn-As polymetallic deposit, Boranja ore field, western Serbia (Radosavljević et al., 2014a). According to this, it is not likely that framboidal pyrite from the ROF is genetically related to the metallogeny of Neogene magmatism as stated in literature data (Popović & Umeljić, 2015).

Arsenopyrite was deposited in forms of coarse idioblastic crystals throughout the ROF (Fig. 5a). It is commonly associated to pyrite, chalcopyrite, sphalerite, Bi-sulfosalts, native bismuth and gangue minerals. The second generation appears in forms of small euhedral crystals or/and complex rosettes in quartz and galena matrix accompanied with younger chalcopyrite. Arsenopyrite is commonly related to the arsenization process of parent igneous rocks, although it is less abundant than Fe-sulfides in NW parts of the ROF. It is also deposited along cracks and fissures as crystal druses composed of radially-twinned, euhedral crystals. Mineralized rocks have brecciated textures as a result of crushing during tectonic processes and later cementation with sulfide-carbonate mineralization, which is typical for the upper parts of ore bodies from the level 815 (Fig. 4h). Finally, arsenopyrite occurs in the form of anhedral to subhedral grains or with skeletal marcasite–pyrite mix-aggregates in the polymetallic ore (borehole No 197/12; Fig. 4i).

Chalcopyrite displays diversity in its appearance within the Gušavi Potok and Nova Jama ore zones. The older generation is always associated with pyrrhotite, sphalerite, arsenopyrite, native bismuth and Bi-sulfosalts (Figs. 5b and 5d), while the younger mainly replaces all the other sulfides. Regularly, it contains skeletal portions of sphalerite, and commonly cemented cracks and fractures in pyrrhotite. Chalcopyrite occurs also as an exsolution oriented along the crystallographic directions in sphalerite (Fig. 5c). Chalcopyrite is the principal valuable mineral in the Azna ore zone. It either forms large masses or occurs as cement into cataclasied Fe-sulfides and arsenopyrite. It occasionally forms complex intergrowths with galena overgrowing the siderite matrix. Galena, galenobis-mutite and native bismuth of acicular mix-aggregates as products decomposition of solid solution Bi2S3–PbS system frequently intersperse large chalcopyrite surfaces (Fig. 5d). Inclusions of sphalerite skeletal crystals in chalcopyrite are widely spread as the result of high-temperature exsolution processes (“sphalerite stars”), locally form dense arrays along crystallographic directions. Chalcopyrite additionally displays strong polysynthetic lamellae having distinct anisotropy (“parquet-like twinning”), suggesting its crystallization at very high temperatures (Fig. 5e). Moreover, it often occurs as cement in pyrrhotite fissures, cataclasied and fragmented pieces of older sulfides, and/or suppresses pyroxene along cleavage planes. Chalcopyrite, Bi-minerals and scheelite are characteristically concentrated in the lower parts of the Azna ore zone (level 720). Also, chalcopyrite appears with the same characteristics in the polymetallic ore from borehole No 197/12 (Fig. 5f). Cubanite also occurs in the form of thin lamellae in chalcopyrite and pyrrhotite, and represents exsolution from a more compositionally permissive chalcopyrite. EPMA showed that chalcopyrite has a typical stoichiometric chemical composition.
Galena was formed in the high-temperature hydrothermal stage in the all ore zones. It occasionally replaces older pyrrhotite, but sometimes is replaced by younger pyrrhotite and chalcopyrite. The main characteristic of native bismuth is that it fills gaps between galena-pyrite contacts. It also forms free surfaces deposited in interspaces of pyrrhotite and silicates containing oriented inclusions of native silver and bismuth along crystallographic directions of galena. Galena is widespread in the Azna ore zone, but its relative abundance varies. It occurs as small “toothed” patches associated with pyrrhotite and silicates. To a lesser extent, galena is accompanied with pyrrhotite and chalcopyrite, and locally with native bismuth. Relics of spherulitic chalcopyrite and chalcopyrrhotite occur along sphalerite grain boundaries extensively overgrown by galena. Galena, embedded into chalcopyrite, is commonly replaced by Ag-bearing tetrahedrite and semseyite in the polymetallic ore from borehole No 197/12. (Figs. 6h-i). Galena sometimes has a fine mixture of exsolution of Ag-Pb-Bi sulfosalts with emulsions and droplets of native bismuth thus forming irregular “spongy” segments of up to 100 µm². AAS showed that galena commonly contains Ag between 0.10 and 1.70 wt% (argentiferous galena). Bismuth and Sb are below detection limits (< 0.01 wt%).

Sphalerite appears in several generations in all ore zones. The first generation from the skarn-replacement hydrothermal stage contains exsolution of chalcopyrite, chalcopyrrhotite and pyrrhotite. These inclusions are square-like, hexagonal and rhombohedral oriented along crystallographic directions of sphalerite (Fig. 5c). Oriented sphalerite “stars” in chalcopyrite are characteristic for the younger generations of are hydrothermal stage (Fig. 5d). Sphalerite is less abundant than galena in the Azna ore zone. It occurs in coarse-crystalline aggregates (Fig. 3g), belonging to the Fe-bearing variety (marmatite). Irregular, band-like intergrowths of pyrrhotite and chalcopyrite sometimes occur in the form of square, hexagonal, and rhombohedral sections replaced by galena. EPMA showed that sphalerite contains up to 18.4 mol% FeS and belongs to the Fe-bearing variety (marmatite), up to 0.30 wt% Mn, and up to 0.52 wt% Cd. Copper, In, Ge, and Sn are below detection limits of <~0.3 wt%.

CVETKOVIĆ (2001) described the occurrence of Ni-minerals (pentlandite, gersdorffite, and nickeline) in the footwall of the ROF (400 m beneath the surface). They are associated with the nickel-pyrrhotite mineral.
paragenesis into serpentinite matrix. Moreover, gersdorffite has been microscopically discovered in the association with pyrrhotite, galena, Bi-sulfosalts, native bismuth, scheelite, Ti-minerals and quartz in the Nova Jama and Azna ore zones (Fig. 6a). Argentopentlandite, determined in the Azna ore zone, accompanied by native silver appears in a form of elongated crystals (90–115 µm in length), filling cracks and fissures in pyrrhotite (Fig. 7c). The chemical formula of argentopentlandite is as follows Ag1.03(Fe4.81Ni3.14)Σ=7.95S8.02 (STOJANOVIĆ et al., 2016).

Bismuthinite is rare in the Nova Jama and Azna ore zones. It appears along grain boundaries as needle-like, fibrous, and woolly crystalline aggregates overgrowing native bismuth. According to EPMA, it is of typical stoichiometric chemical composition (STOJANOVIĆ et al., 2016). The occurrence of molybdenite was observed only in the Nova Jama ore zone in association with scheelite-sulfide ore.

Bi-sulfosalts minerals

The Ag-Pb-Bi-S system is fairly disseminated throughout the ROF, and includes galenobismutite, cosalite and lillianite homologous series (Ag-bearing aschamalmite, gustavite, schirmerite and vikingite). They are defined in the Ag-Pb-Bi ternary system with no noticeable Sb or As substitution (Fig. 6). The complexity of sulfosalts within the ROF, originally reported by RAKIĆ (1958), has been confirmed by finding these new rare sulfosalts. These are commonly disseminated in the massive sulfide ore bodies or as an exsolution in Ag-bearing galena with native bismuth, or in lesser extent in axinite-epidote rocks. These Bi-sulfosalts regularly contain Ag in the range from 0.44 to 9.30 wt%. Chemical composition of Bi-sulfosalts is shown in Table 1.

Macroscopically, galenobismutite occurs in needle-like to lath-like crystals, common in radial aggregates in the Nova Jama ore zone. Microscopically, color of galenobismutite is pale grey to white; bireflectance is strong, particularly in oil: white, grey-white with a brown-rose tint (Fig. 3c). Anisotropic effects are strong but not strikingly colorful (Figs. 7f-g). EPMA (6 analyses) gave average chemical formula (Pb0.97Cu0.05Ag0.03)Σ=1.05Bi1.97S3.97 (Table 1). Galenobismutite contains noticeable Cu and Ag, and is also associated with chalcopyrite, Ag-bearing galena and native bismuth (STOJANOVIĆ et al. 2006). Lath-like to elongated aggregates composed of galena, galenobismutite, and native bismuth occur in chalcopyrite in the Azna ore zone (Fig. 5d).

Cosalite regularly appears in association with pyrrhotite, galena, chalcopyrite, native bismuth, arsenopyrite and pyrite (STOJANOVIĆ et al., 2006). Microscopically, the color of cosalite grains is light grayish-white to pale greenish. It is columnar to needle-like and elongated along c-axis or radial. Bireflectance and anisotropy of cosalite is weak and only distinct in oil immersion. These minerals filled-up interspaces between grains of older sulfides and cracks in scheelite. EPMA (4 analyses) yielded following average chemical formula (Pb1.91Cu0.08Ag0.05)Σ=2.04Bi1.94S5.02. Similar Ag and Cu contents to those from the ROF have been reported by several authors (TERZIĆ et al., 1974, 1975; RADOSAVLJEVIĆ-MIHAILOVIĆ et al., 2007; VOUDOURIS et al., 2013; KOŁODZIEJCZYK et al., 2017).
Sulfo salts of lillianite homologous series, namely Ag-bearing aschamalinite, gustavite, schirm erite and vikingite, occur moderately in polymetallic ores of the ROF. Minerals from the mentioned group are very rare and further accumulation of mineralogical data should be valuable to assess their systematics and to understand their crystallochemical relationships.

Aschamalinite was mistakenly described as heyrovskyite in the study by Dimitrijevic et al., (1992). Aschamalinite from the Azma ore zone (Z1 ore body) is exceptional rare as it was found only in one polished section, occurring as coarse-grained aggregates. These aggregates are generally embedded within colloform Fe-sulfides matrix, and to a lesser extent in silicates and chalcopyrite. Microscopically, it occurs in a form of large irregular aggregates (>100 µm) cementing colloform Fe-sulfides, chalcopyrite, galena, and arsenopyrite (Fig. 3b). Aschamalinite has inclined extinction when sections are parallel to the elongation. It is characterized by moderately high luster (like galena), white to creamy-white with a slight grayish tint, weak bireflectance, noticeable anisotropy (Fig. 3b). Gangue minerals are represented by carbonates (siderite), quartz and silicates. The average chemical formula of Ag-bearing aschamalinite (6 analyses) amounts to: (Pb5.82Ag0.20)Σ=6.02Bi2.03(S8.93Te0.02Se0.01)Σ=8.96 (Table 1). Silver content ranges between 1.03 and 1.32 wt%. It is important to to emphasize that this is the first confirmed discovery of Ag-bearing aschamalinite (Stojanovic et al., 2016).

Microscopically, vikingite from the Nova Jama ore zone is white to creamy-white with moderately high luster, unnoticeable bireflectance and hardly noticeable anisotropy. The measured values of reflected light \( (Y \%) = R_1 38.1; R_2 36.9 \) and the microhardness (97.6 kg/mm²) correspond to the vikingite, with minor deviations (Stojanovic, 2005). EPMA of a single grain gives following chemical formula: \( \text{Ag}_{4.43}\text{Pb}_{8.12}\text{Bi}_{13.49}\text{S}_{29.96} \) (Table 1). It belongs to Bi-bearing vikingite and illustrates the coupled substitution of \( \text{Ag}^{1+} + \text{Bi}^{3+} \leftrightarrow 2\text{Pb}^{2+} \) found in several Bi-sulfosalts (Makovicky et al., 1992). From the borehole No 197/12, it always occurs in association with native bismuth as exsolution on the grain boundary of Ag-bearing galena (1.50 wt% Ag) (Fig. 7b). EPMA of a single grain gives following chemical formula: \( \text{Ag}_{5.01}\text{Pb}_{8.03}\text{Bi}_{13.00}\text{S}_{29.95} \) (Table 1). Due to the very small grain size, it is not confirmed by XRD.

Schirmite from the borehole No 197/12 always appears in mineral association with native bismuth as well as the exsolution in Ag-bearing galena. Microscopically, it is white with weak bireflectance and gray anisotropy (distinct to strong in oil). EPMA of a single grain gives chemical formula \( \text{Ag}_{9.98}\text{Pb}_{9.59}\text{Bi}_{7.05}\text{S}_{18.06} \) (Table 1) and belongs to the last member of the solid solution \( \text{Ag}_n\text{Pb}_n\text{Bi}_n\text{S}_{18} \) to \( \text{Ag}_9\text{Pb}_9\text{Bi}_9\text{S}_{19} \). Due to the small grain size, it is not confirmed by using XRD. The identical sulfosalts occur within the polymetallic Pb(Ag)-Zn Veliki Majdan ore zone, Boranja ore field, West Serbia (Radosavljevic et al., 2016c).

Microscopically, gustavite from the borehole No 197/12 is always associated with native bismuth as exsolution on the grain boundary of Ag-bearing galena (1.70 wt% Ag). It is white to grayish-white in tabular to chunky forms with white to greenish-gray bireflectance and moderate anisotropy (Fig. 7e). EPMA of a single grain gives following chemical formula: \( \text{Ag}_{9.83}\text{Pb}_{1.30}\text{Bi}_{2.85}\text{S}_{6.00} \) (Table 1). Similarly to schirmite, it is not confirmed by XRD due to the small grain size. The lillianite–gustavite series with intermediate phases occur within the Stari Trg Pb(Ag)-Zn polymetallic deposit, Trepa ore field, Serbia (Kolodziecyk et al., 2017).

Sb-sulfosalts

Sb-sulfosalts from the SE part of the ROF, associated with Fe-sulfides, arsenopyrite, chalcopyrite, sphalerite, and galena, are extremely rare and include the tetrahedrite-group and semseyite. This is the first discovery of semseyite within the ROF. It is very interesting that tetrahedrite-group and semseyite are widespread into Pb-Zn polymetallic deposits of the SMMP (e.g. Srebrenica ore field – Rakic et al., 1978, Radosavljevic & Dimitrijevic, 2001, Radosavljevic et al., 2016a; Boranja ore field – Radosavljevic et al., 2016c; Kopaonik ore zone – Zarić et al., 1984; Rogozna ore field – Radosavljevic et al., 2014b, 2015).

Microscopically, solid solution series \( \text{Cu}_{10(\text{Fe,Zn})_2}\text{Sb}_2\text{S}_{13}^-\text{Cu}_{10(\text{Fe,Zn})_2}\text{As}_2\text{S}_{13}^- \) within tetrahedrite-group have some optical distinctions in color, characterized by zonality with dominant tinge from coffee gray in central parts to greenish gray tint in peripheral parts (Fig. 7h). According to optical features, tetrahedrite minerals from the ROF belong to Ag-bearing varieties. They occur to a lesser extent in the form of small patches growing along boundaries of semseyite and galena, embedded in fissures of chalcopyrite. EPMA yielded two types of Ag-bearing tetrahedrite: I) Ag content of 31.10 wt% Ag (Fig. 7b); EPMA of a single grain gives following chemical formula: \( \text{Ag}_{5.47}\text{Cu}_{4.52}\text{Sb}_{4.01}\text{S}_{12.99} \) (I), and \( \text{Cu}_{5.98}\text{Ag}_{4.11}\text{Sb}_{4.01}\text{S}_{12.99} \) (II). Both Ag-bearing types belong to the Sb and Fe end-members without noticeable As and Zn substitution. Due to the small grain size, they are not confirmed by XRD.

Semsyeite belongs to a plagionite group together with fülöppite, plagionite and heteromorphic, forming homologous series. Semsyeite, determined for the first time within the ROF, occurs in a form of isolated...
tabular crystals associated with galena and Ag-bearing tetrahedrite embedded in chalcopyrite matrix (Fig. 7h). EPMA yielded the following chemical formula: \( \text{Pb}_{8.61}\text{Sb}_{8.28}\text{S}_{21.10} \) (Table 2, Fig. 7i). Due to the small grain size, it was not confirmed by XRD.

Native elements

Native bismuth, widespread into the ROF, occurs in several generations, and is commonly associated with Bi-sulfosalts, Ag-bearing galena and pyrrhotite (Figs. 3b-c, 5d). It occurs in a contact with pyrrhotite, rarely silicates as veinlets (Fig. 8a), euhedral hexagonal and oval sections as inclusions in galena and scheelite (Fig. 8b), and as a product of the decomposition of the high temperature solid solution in Ag-bearing galena and Bi-sulfosalts (7b-d). EPMA yielded the following Ag contents: Nova Jama 0.67 wt%; Azna \(<0.3 \text{ wt%}\) with oxygen content from 0.5 to 0.7 wt%; and borehole No 197/12 \(<0.3 \text{ wt%}\). Tellurium, Pb and Sb were below detection limits \(<0.3 \text{ wt%}\).

Native silver appears as exsolution in galena, regularly as submicronic emulsions. It also occurs along fissures of pyrrhotite as cement associated with argentopentlandite (Fig. 8c). Native gold, extremely rare in...
the ROF, occurs as electrum in the chalcopyrite (the Nova Jama ore zone).

Microscopically, extremely rare PGE-minerals characterize inclusions in pyrrhotite and silicates (Fig. 3d). They appear as isometric droplets up to 5 μm; high hardness and relief (>pyrrhotite); high reflectance (R >60 %); white color with yellow tinge; isotropic under ×N. According to ZARIĆ et al. (1992a-b) PGE contents are as follows (in ppb): Pd 100, Pt 20, and Rh 10 (ΣPGE=130). They occur as sub-traces in magnetic (Pd 30, Rh 2 ppb) and nonmagnetic (Pd 10 ppb) fractions of heavy minerals extracted from the flotation tailing (RADOSAVLJEVIĆ et al. 2006b). In addition, CVETKOVIĆ (2001) noted a similar occurrence of PGE-minerals within the nickel-pyrrhotite mineral paragenesis disseminated in the serpentine rocks below the ROF at a depth of 400 m.

Tungstates

RAKIĆ (1958) first described scheelite from the ROF, but only as a rare mineralization. However, ZARIĆ et al. (1992b) found that scheelite mineralization is widespread in the Nova Jama, Gušavi Potok and Azna ore zones. The new scheelite mineralizations in the Nova Jama (gallery HI 672-92) and Azna (levels 815 and 720) ore zones were tested in order to obtain a collective scheelite-sulfide concentrate (combinations of gravity separation and flotation techniques) and finally W, Ag and Bi (Fig. 2), but positive results were obtained only for the Nova Jama scheelite mineralization (ADAMOVIĆ et al., 2000; RADOULJJEVIĆ et al., 2003b, 2006; STOJANOVIĆ, 2005; STOJANOVIĆ et al., 2004, 2006a,b; RADOULJJEVIĆ et al., 2005, 2006; MILANOVIĆ & MARKOVIĆ, 2009a,b; MAGDALI-

Table 2. Representative EPMA of Ag-bearing tetrahedrite I (8), Ag-bearing tetrahedrite II (9-11) and semseyite (12) from the borehole No 197/12 of the ROF (in wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>21.97</td>
<td>22.86</td>
<td>22.46</td>
<td>22.70</td>
<td>19.50</td>
</tr>
<tr>
<td>Fe</td>
<td>5.91</td>
<td>6.15</td>
<td>6.02</td>
<td>5.84</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>15.14</td>
<td>21.70</td>
<td>18.54</td>
<td>21.80</td>
<td>-</td>
</tr>
<tr>
<td>Ag</td>
<td>31.10</td>
<td>22.50</td>
<td>26.50</td>
<td>23.30</td>
<td>-</td>
</tr>
<tr>
<td>Sb</td>
<td>25.74</td>
<td>26.57</td>
<td>26.12</td>
<td>25.80</td>
<td>29.06</td>
</tr>
<tr>
<td>Pb</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>51.40</td>
</tr>
<tr>
<td>Total</td>
<td>99.86</td>
<td>99.78</td>
<td>99.64</td>
<td>99.44</td>
<td>99.96</td>
</tr>
</tbody>
</table>

Note: - <0.3 wt%; n.a. - not analyzed; As, Zn, Cd and Bi analyzed but not detected (<0.3 wt%). General formulae were calculated according to MOËLO et al. (2008).

Fig. 8. Optical microscopy images in reflected light, BEI, and reflected UV-light (short wave) showing the textural features of ore and gangue minerals of the ROF: a) crust of native bismuth along the pyrrhotite-silicate contact (reflected light, oil, //N) – Nova Jama; b) galenobismitite embedded in spherulitic sections of native bismuth in the scheelite matrix (reflected light, oil, //N) – Nova Jama; c) argentopentlandite and native silver filling cracks and fissures in pyrrhotite (BEI) – Azna; d) scheelite crusts and coatings (fluorescent blue) – Nova Jama; e) scheelite veinless (fluorescent blue) – Nova Jama; f) scheelite single crystal embedded in the quartz-silicate matrix (fluorescent blue) – Nova Jama. Abbreviations: Po – pyrrhotite, Gb – galenobismitite, Apd – argentopentlandite, Ag – native silver, Bi – native bismuth, Sch – scheelite, Si – silicates, Qz – quartz. (All figures- RADOSAVLJEVIĆ & STOJANOVIĆ 2003, 2006).
been shown by Popović & Umeljić (2015), describing WO$_3$ <0.30 wt%. Quartz veins, in which scheelite is matrix (the Azna ore zone; Radosa Vljević et al., bedded in the quartz-silicate and/or quartz-sulfide scheelite crystals from 0.02 to 40 mm (Fig. 8f) ememinated in the Nova Jama ore zone (Fig. 8d) in a form of quartz-sulfide minerals (Fig. 2, zone 1); ii) disseminated in the Nova Jama ore zone (Fig. 8d) in a form of small coatings of agglomerated isometric scheelite crystals accompanied by sulfide-silicate-carbonate minerals (Fig. 2, zone 2); and iii) as loosely euhedral scheelite crystals from 0.02 to 40 mm (Fig. 8f) embedded in the quartz-silicate and/or quartz-sulfide matrix (the Azna ore zone; Radosa Vljević et al., 2003b, 2006; Stojanović, 2005; Stojanović et al., 2006).

Scheelite is grey-white to white, sometimes yellowish; with vitreous to diamond luster and white color of streak. Under the UV-short waves it is intense light blue (Figs. 8d-e). The gallery HI 672-92 of the Nova Jama has the “starry night sky” effects when exposed to the UV-short waves. In reflected light, it is dark grey with relatively high relief and strong internal reflections colored whitish. It regularly contains hexagonal-shaped and oval portions of native bismuth and Bi-sulfosalts, as inclusions (Fig. 8b).

In the Azna ore zone scheelite grains are isolated, coarse-grained or in a form of euhedral tabular crystals associated with the sulfide-quartz-silicate minerals (level 720 and partially level 815). High concentrations of scheelite are particularly significant on the level 720 (veinlets of a thickness of up to 10 mm, and isolated crystals from 1 to 5 mm, rarely up to 40 mm (Fig. 8f). Locally it shows high extensities on the 815 level, but is very variable intensities (Zarić et al., 1992b).

The scheelite mineralizations have also been determined in S-7 and G-16 ore bodies (Fig. 1b) embedded in the axinite-epidote-chlorite rocks; and in the heavy mineral fraction from flotation tailings (Zarić et al., 1992b, Radosavljević et al., 2006b).

Paragenetic sequence

The term “paragenesis” refers to the time-successive order of formation of a group of associated minerals within a particular deposit. Since the great majo-

Table 3. Stable isotopic composition of sulfur in the sulfides and sulfoarsenides from the ROF (according to Tošović, 2000).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ore zone (ore body)</th>
<th>Level (m)</th>
<th>$\delta^{34}S$ ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrhotite</td>
<td>Gušavi Potok (G-8)</td>
<td>689</td>
<td>+3.0</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>Mali Do (S-7)</td>
<td>725</td>
<td>+3.5</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>Gušavi Potok (G-9)</td>
<td>644</td>
<td>+3.0</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>Srednji Šturac (SS-20)</td>
<td>715</td>
<td>+2.9</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Azna (Z-1)</td>
<td>725</td>
<td>+3.8</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Azna (Z-2)</td>
<td>725</td>
<td>+2.9</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>Bezdan</td>
<td>600</td>
<td>+3.4</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>Azna (Z-1)</td>
<td>725</td>
<td>+4.6</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>Prlovi (P-12)</td>
<td>720</td>
<td>+3.9</td>
</tr>
</tbody>
</table>

The following mineral paragenetic sequences were determined in the ROF: i) pre-ore (relic minerals and rocks); ii) pyrometasomatic (skarn silicates–quartz–scheelite); iii) high-temperature hydrothermal (pyrrhotite–sphalerite–galena with Pb-Bi(Ag) sulfosalts); iv) micro-skarn (skarn silicates–sulfides–scheelite); v) high-temperature hydrothermal (colloform Fe-sulfides–arsenopyrite–siderite and chalcopyrite–sphalerite–galena with Ag-Pb-Bi-sulfosalts); vi) hypogene (pyrite–marcasite); vii) medium-temperature hydrothermal (sphalerite–chalcopyrite–Sb-sulfosalts with Ag); and viii) supergene. Deposition order of ore and gangue minerals is reported on Table 4.

The pyrometasomatic (skarn) stage, which is widespread throughout ore zones, belongs to the garnet–pyroxene–adularia and/or axinite– epidote–chlorite mineral assemblage associated with Ti-minerals, Fe-sulfides and Fe-oxides. Newly formed euhedral elongated crystals of contact-silicates (such as hedenbergite) penetrated older sulfides (Fig. 3e). This is a very slow process, which can also involve the diffusion of atoms through solid crystals (MEHRER, 2007), and it suggests that the skarn stage occurs in two generations. These features are indicative for a complex event-based stage formation with multiple dissolution-replacement reactions. According to CVETKOVIĆ et al. (2016) magma mixing was crucial for mineralization processes in the ROF volcano-intrusive complex; injected lamproite-like and water-saturated melt provided conditions for a strong hydrothermal phase, formation of hydraulic breccia and precipitation of ore minerals. Such events should explain the formation of the multi-stage skarn-replacement and high-temperature hydrothermal polymetallic mineral parageneses (Table 4).

The scheelite and pyrrhotite–sphalerite–galena with Pb-Bi(Ag)-sulfosalts paragenetic sequence are the most abundant within the ROF. The scheelite mineralization is commonly associated with mineralized silica breccias and/or potassic altered volcanic dykes. Mineral paragenetic analyses revealed at least several stages of skarn and ore formation. The first stage represents early prograde metasomatism, and is characterized by diopside-hedenbergite pyroxenes, and traces of andradite-grossular garnets. The second stage represents main-stage of prograde metasomatism and is characterized by axinite, hedenbergite, epidote, calcite, and quartz accompanied by rutile, anatase, sphenite, scheelite, zircon, magnetite, monazite-(Ce) and apatite. Retrograde alteration caused local replacement of early mineral assemblages by calcite and quartz together with scheelite, hematite, chlorite, and K-feldspars.

The high-temperature pyrrhotite-sphalerite-galena paragenetic sequence is represented by low-sulfidation state minerals deposited from low alkaline fluids (e.g. presence of pyrrhotite, Fe-bearing sphalerite, Ag-bearing tetrahedrite; according to EINAUDI et al., 2003). By changing of pH and temperature, the depo-

Table 4. Stages and paragenetic sequences of the Pb-Zn-Cu-Ag-Bi-W polymetallic ores from the ROF (according to STOJANOVIĆ et al. 2006, updated by this study).

<table>
<thead>
<tr>
<th>Stages</th>
<th>Paragenetic sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrometasomatic (skarnization of sandstone, flysch, and limestones) and pneumatolitic breccia-filled volcanic pipes</td>
<td>Calcite I – garnet (andradite-grossular) – pyroxenes – clinohumite (Fe,Mn)–axinite – epidote I – chlorites – sercite – feldspars (needle-like sandine, adularia) – clay minerals</td>
</tr>
<tr>
<td>Hypogene</td>
<td>Marcasite I – pyrite I – hematite – aragonite</td>
</tr>
</tbody>
</table>
tional environment become more alkaline and led to deposition of Pb-Bi(Ag)-sulfosalts (galenobismutite, cosalite – STOJANOVIĆ et al., 2006). Mixed aggregates composed of galenobismutite, Ag-bearing galena and native bismuth were formed during decomposition of solid solutions from chalcopyrite (Fig. 5d). The change of pH and Eh conditions, as well as the sulfidization of pre-existing sulfides led to hypogene hydrothermal paragenetic sequence of pyrrhotite→marcasite→pyrite (RAMDOHR 1980).

Colloform Fe-sulfides–arsenopyrite–siderite and chalcopyrite–sphalerite–galena with Ag-Pb-Bi-sulfosalts mineral parageneses are widespread, occurring in the NW and central parts of the ROF. Silver bearing aschamalmite belongs to this mineral assemblage, and is most probably deposited as solid solutions from the high-temperature hydrothermal fluids along with Bi, Pb and Ag (STOJANOVIĆ et al., 2016). A significant portion of Ag-Pb-Bi sulfosalts (vikingite, schirmerite, gustavite) and native bismuth originate from exsolution of the high-temperature Ag-bearing galena. Based on the mineral composition, the ROF primarily belongs to the high-temperature mineral assemblage of low (pyrrhotite, Fe-bearing sphalerite, Ag-bearing tetrahedrite, Bi-sulfosalts), and high sulfidization (pyrite, marcasite, arsenopyrite, bismuthinite). As evidenced by aggregates composed of rhythmic, uneven zones of pyrrhotite, pyrite, and siderite, pH and Eh conditions were constantly changing during the period of mineralization. Colloform pyrite can be interpreted either as an intrinsic or an extrinsic occurrence, i.e., relating to crystal growth within a closed, local system, or involving chemical fluctuations in ore-forming fluids. Colloform banding, concentric botryoidal overgrowth of fine radiating crystals is a texture that is commonly encountered in open-space filling ores. Sb-sulphosalts are very poorly represented, and nodular anhedral overgrowths of fine radiating crystals is a texture that is commonly encountered in open-space filling ores. Sb-sulphosalts are very poorly represented, and occur in the SE parts of the ROF (boreshole No 197/12), and are practically without significance.

All paragenetic sequences of the ROF tend to overlap one another, forming complex mineral associations both within the main ore bodies and their mineralized zones. An important feature for the ROF is the occurrence of a various range of Pb–Bi(Ag), Ag–Pb–Bi, and Cu(Ag)–Sb sulfosalts.

Two main types of mineral assemblages (territories of B&H, Serbia, and FYRoM) occur in Pb-Zn deposits associated with Neogene magmatism within the SMMP: i) contact-greisen-metasomatic mineralization (e.g. skarn- and carbonate-replacement types), occurring only in few deposits, and ii) medium- to low-temperature hydrothermal Pb-Zn mineralization (e.g. epithermal vein-type) of significant economic importance (RAKIĆ, 1962). The both types of mineralizations are genetically related to the emplacement of plutonic and subvolcanic bodies.

The metallic mineral assemblages from the Neogene Pb-Zn deposits in Serbia are characterized by regular presence of Cu, As, and Sb minerals, and locally Sn, W, Mo, Bi, Te, Au, Ag, and Ba minerals, as well as minor occurrences of Ni, Co, U and Hg minerals. Some of these elements are associated with specific mineralization types and individual ore fields, but only Pb, Zn, Fe, Mo, Sb, As and Hg deposits are of economic importance. Based on geological and mineralogical relationships, the following ore fields correspond to skarn-carbonate-replacement types, and epithermal vein-type mineralizations: Avala, Rudnik, Cer, Boranja, Kopaonik, Trepcă, Novo Brdo, Karavansalija, Blagodat, Crunch, and Kosmaj, Kotlenik, Koporić, Žuta Prlina, Ajvalija, Kižnica, Lece, Karanmanica, respectively (RAKIĆ, 1962; JANKOVIĆ, 1990).

Ore-forming conditions

Mineral assemblage formation temperatures within the ROF are difficult to establish, although it is possible to determine the temperature interval. Three different events occurred within this timeframe: i) transformation of chalcopyrite from high to low temperature (400 to 550°C, CRAIG & KÜLLERUD, 1969); ii) formation of “sphalerite stars” (400 to 500°C, SUGAKI et al., 1987), and iii) formation of argentopentlandite (<455°C, MANDZIUK & SCOTT, 1977). The isotopic data and the Fe-content of sphalerite, together with geological and mineralogical evidence, indicate a shallow mineralization emplacement and a multistage depositional process developed at decreasing temperatures from about 450° to 350°C according to physico-chemical parameters fluctuations. These fluctuations appear to be restricted to /O2, pH field where H2S and HS, were the prevailing sulfur aqueous species. Therefore, the most probable formation temperature ranges from 450° to 350°C.

Bi-sulfosalts can be valuable indicators of physico-chemical forming conditions due to their sensitivity to changings in temperature, Eh, pH, S2- and /O2 (COOK & CIODANU, 2004). According to LIU & CHANG (1994), aschamalmite is not stable in PbS-PbSe-Bi2S3-Bi2Se3 system at 500°C. This assumption has recently been confirmed by the discovery of heyrovskyite in the fumaroles of Vulcano, Aeolian Islands, Italy, where temperature close to 500°C was measured (BOROAEV et al., 2003). Heyrovskyite is also present in deposits formed in a range from 350 to 400°C (MAKOVICKY et al., 1991). However, aschamalmite crystallizes only at lower temperatures, initially as a partly and then as a completely ordered phase. Experimental studies in CuS–PbS–Bi2S3 system showed that galenobismutite decomposes to bismuthinite and lillianite at 375°C (CHANG & HODA, 1977, 1988). COOK (1997) reported temperatures for Bi assemblages can be 350°C. MÖELO et al. (1987) suggested formation of several lillianite homologues at temperatures of 350–400°C and showed they can be
unstable at lower temperatures. The presence of intermediate phases of solid solution among lillanite homologues with high Ag content at the ROF, may suggest temperatures of 350–400°C, as it was proposed previously for Toroiaga deposit by COOK (1997) and the Stanos mineralization by VOUDOURIS et al. (2013).

According to their mineral composition and MSA, transport of ore metals primarily took place in the form of acid halides (e.g. Zn, Fe, Cd) and basic polysulfide complex (e.g. Fe, Pb, Ag, Bi). However, the scheelite mineralization suggests that the later hydrothermal fluids containing ore elements were largely complexed with halides (mainly Cl). According to MSA halide contents are as follows (ppm): F = 270 and Cl = 45 in pure pyrrhotite (Azna), F = <0.01 and Cl = 700 in pure scheelite (Nova Jama), Br and I not detected (<10 ppb) (ZARIĆ et al., 1992b, STOJANOVIĆ, 2005). However, the transport of ore elements was also possible with other anions (e.g. HS−, H3B2−, H2AsO4−, P2O74−, KWO4−, HWO4−). Ways and directions of movement of the hydrothermal fluids is not definitely known.

MSA showed the presence of all rare earth elements (REEs). Among them, La, Ce, Pr, Nd, Sm, and Gd were found in relatively high concentrations, while the rest were qualitatively determined. The presence of REEs, however, is not unusual for the ROF, although their host minerals still have not been determined with certainty, except for monazite-(Ce). It is well-known in the greisens (quartz-tourmaline-muscovite rocks with cassiterite) from the Srebrenica ore field, B&H (RADOŠAVLJEVIĆ et al., 2011) and in the listwaenites from the Rogozna ore field, Serbia (RADOŠAVLJEVIĆ et al., 2014b, 2015). High contents of Cr, Co, and Ni in the ore are most likely, remobilized from serpentinite in the present ophiolitic zone. The presence of nickel minerals with cobalt was additionally determined by CVETKOVIĆ (2001). According to RADOŠAVLJEVIĆ et al. (2006), dykes of quartz latite composition are extremely rich in potassium, where K2O ranges from 6 to 12 wt%, and measured up to a high of 16 wt%. High contents of Rb, Sr and Ba can be explained by effects of cation exchange in K-feldspar(s) (sannidine, “adularia”). High potassium content is a result of intensive K-metasomatism with adularization.

Arsenic, Sn, and Sb, were also detected, while Hg and Tl were below detection levels. This suggests that all primary minerals in the ROF crystallized at high temperatures either as skarn-replacement or from high-temperature hydrothermal solutions. There is additionally a well-developed zonality of medium- to low-temperature mineral associations within the SMD. Pegmatites and greisens (Bukulja ore field – Sn-W), skarn-replacement, and high-temperature hydrothermal mineralizations (Rudnik ore field – Pb-Zn-Cu-Ag-Bi-W, Kosmaj ore field – Pb-Zn-Cu and Sn) were found in the central parts of the SMD, while the southern and northern parts of the SMD are typified by medium to low temperature hydrothermal mineralizations (Avala ore field – Pb-Zn and Hg; Kotlenik ore field – Pb-Zn and Sb).

Conclusions

The present study consolidates all of the previous research conducted by STOJANOVIĆ et al. (2006, 2016). The mineral associations of the ROF, composed of several mineral parageneses with characteristic polymetallic compositions, propose a short interval of deposition (occurrence of relic gel aggregates). They are generally caused by metasomatic processes and replacement of various sedimentary, metamorphic and/or igneous lithological types and a small part is the result of precipitation from hydrothermal solutions in the open spaces (veins, vugs and fissures). There are two types of mineralization: i) massive, brecciated, stockwork and/or disseminated ore bodies – pseudostratified and plate-like features with relatively high content of valuable metals, hosted in various sedimentary, metamorphic and magmatic lithologies, typical for Azna, Nova Jama, and other ore zones, and ii) ore veins hosted in the Upper Cretaceous flysch or quartz latite, typical for Bezdan, Motlve, and other locations. Spatial distribution of mineral associations and metals has clear zonality manifested by deployment of FeS2-Pb-Zn-Cu vein ore bodies around central part of the deposit, where plate-like and complex skarn-metasomatic and hydrothermal Pb-Zn-Cu-Ag-Bi-W polymetallic mineralization dominate. Mineral parageneses, mineral chemistry, halide content and stable isotope studies are consistent with the hypothesis that the Rudnik deposit is a distal skarn (MEINERT et al., 2005, VEZZONI et al., 2016).

The scheelite mineralization determine two types of mineral parageneses different in their features, but spatially associated: i) scheelite with quartz-silicates±carbonate matrix; and ii) scheelite with quartz-sulfide matrix (pyrrhotite, native bismuth, Bi-sulfosalts, etc.).

Lead, Zn, Cu, and Ag, locally Bi and W are the most valuable metals of the ROF. High content of tipomorphic elements, such as Ag and Bi, are predominantly in a form of high-temperature solid solutions associated with Ag-bearing galena, when Ag-Pb-Bi sulfosalts (vikingite, schirmerite, and gustavite) and native bismuth were formed by their decomposition along the edges (WERNICK, 1960; CHANG et al., 1988). Beside them, in all other Bi-sulfosalts there are also Ag-bearing minerals confirming consistently high activity of Ag and Bi during the whole mineralization cycle. A small part of Ag is incorporated in Ag-bearing tetrahedrite, argentopentlandite and native silver.

This ore mineralogy, and especially the close relation-
ship of Ag and Bi in the ore, is strong evidence of magmatic-hydrothermal inputs in the system. Wu & Petersen (1977) noticed that silver content in tetrachalcoprite is increasing with distance from the center of volcanic activity in complex hydrothermal systems. However, the second geochemical distinguishing feature is occurring of Ag in both mineralization types within the ROF, and is typical for almost all of the Pb-Zn polymetallic deposits within SMMP (e.g. Cumativeči, Srebrenica, B&H – Radiosavljevic et al., 2016a; Veliki Majdan, Boranja, Serbia – Radiosavljevic et al., 1982; Lece, Medveda, Serbia – Radiosavljevic et al., 2012; Crnac and Kaludjer, Rogozna, Serbia – Radiosavljevic et al., 2015; Trepča, Stari Trg, Kosovo, Serbia – Kolodzijevsky et al., 2016).

Besides the ROF, Bi-sulfosalts mineral parageneses have been identified in the Boranja ore field, Serbia (Dangic et al., 1984, Radiosavljevic-Mihajlovic et al., 2007), in the Golija ore field, Serbia (Stajevic & Zaric, 1984) and in the Trepča, Stari Trg, Kosovo, Serbia (Kolodzijevsky et al., 2015, 2017). According to the mineral compositions, they are close to the Stanos shear-zone related deposit, Chalkidiki, northern Greece (Vooudous et al., 2013). Moreover, the Pb-Bi(Ag) sulfosalts mineral assemblages are very similar to those from the hydrothermal system Larga in Romania (the Carpathian-Balkan Metallogenic Province – Cook & Ciobanu, 2004). In comparison to other metallogenic districts within the SMMP, mineral associations of the ROF are distinguished by significant amounts and varieties of Ag-Pb-Bi sulfosalts and the unique occurrence of Ag-bearing aschamalmite.

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Prilog polimetalične Pb-Zn-Cu-Ag-Bi-W rudne rudnog poja Rudnik, centralna Srbija

Srpsko-makedonska metalogennetska prostorija (CMMPP), prostorno zahvata manji deo Istočne Bosne, veće delove Srbije i Makedonije, i na-stavljaju da je prema Bugariskoj i Grčkoj, sadržaju brojnije i i prostorne masce intruziv/vulkanogenih kompleksa kalko-alkalne magme. Površina njihovog raviča u Srbiji iznosi oko 30.000 km² i prostire se preko tri ključne geotektonске jedinice: Unutrašnjih Dinarida, Vardarske tektonske zone i Srpsko-makedonske masse. U vezi sa ovim magmatikom kompleksima, direktnim ili indirektnim dejstvom, došlo je do stvaranja brojnih lежишta i pojava metala, u prvom redu Pb-Zn, Sb, znatim Cu, Mn, i u manjoj meri Fe, Bi, Ag, Hg, U, Sn i W.

Шумадијска металогенетска област припада CMMPP. Мање металогенетске јединице издвојене су у оквиру rudnih поља: Авал-Космај, Букулд-брајковат, Рудник и Котленик (сл. 1а). Полимета-лно рудно пољо Рудник генетски је везано за олигоценски интрузив/вулканоген комплекс. Стоји се од неколико рудних сектора са високим sadržajem Pb, Zn, Cu, i Ag; локално Bi, i W. СКарнови су Ca-типа, и формирану су дуж конт-катакрних седимената и олигоценских дакова i silova daцитског и кварц латитског састава. Од-ликуje се са веома разноликим врстама rudnih i nerudnih minerala, где се јављају: сулфиди, сул-фоарсениди и арсениди (пирит, коло-морфни пирит, бактериондни пирит, маркасит, арсенопирит, сфалерит, галенит, халкопирит, хал-копирит, кубанит, макинавит, бизмутин, мо-либденит, пентландит, аргентопентландит, гер-дарфит, никелен), сулфосоли (галенопирит, козалит, Ag-ашамаллит, галенобизмутит, сул-фоарсениде и арсениде (пирит, пирит, коло-
карактеристични су за СЗ делове лежишта (Азна), и јављају се као жућкасто-црне до сивкасте "шагренасте" куглице (10–15 mm), које образују неправилне гроздасте до бубрежасте агрегате. Од стране појединих аутора они су погрешно дефинисани као "оолитни пирит" (седиментно пореκло). Коломорфни Fe-сулфиди представљају типисне производе брзих и променљивих услова хидротермалног депоновања у оквиру високотемпературног стадијума (\(f_S\) и \(f_O\), температура, притисак и др.). Такође, исти аутори погрешно су објаснили порекло "бактероидног пирита", који је генетски неоспорно везан за присутне старије седименте, и нема никакве генетске везе са млађим неогеним магматизмом.

Минералохије шелита значајне су и за сада су најперспективније у рудном сектору Нова Јама, где се јавља у виду цистерни и у степени нанасања на металургиско експерименталне слојеве (из W-руде, комбинованим методама издобијен је сулфидно-шелитски концентрат, из којег су добијена висококалорична ваза како и чисти метал Bi и Ag.

Минералне асоцијације изграђене су из неколико минералних парагенеза са карактеристичним полиметаличким саставом, које одражавају брз интервал таложења (појава гелских агрегата). Оне су углавном настале процесима метасоматског замењивања различитих седиментних, метаморфних и/или магматских литолошких чланова, а мањи део је резултат депоновања хидротермалних раствора у отвореним просторима (гири, шупљине и пукотине). Генерално, постоје две врсте орудњења: а) масивна, бречаста и/или штокверк-импрегнационе рудне тела — псеудостратификована и плочаста са високим садржајем корисних метала, типична за рудне зоне Азну, Нову Јаму и остале, и б) жична рудна тела депонована у горње кредном флишу или кварц латитима, карактеристична за лежишта Бездан, Молитве, и на другим локацијама. У оквиру рудног поља Рудника просторни распоред минералних асоцијација и метала има изражену зоналност, која се исплаћује размештајем жичних тела са \(\text{FeS}_2\)-\(\text{Pb-Zn-Cu}\) минерализацијама око централног дела лежишта, где доминирају плочаста и сложена скарн-метасоматска и хидротермално полиметалична \(\text{Pb-Zn-Cu-Ag-Bi-W} \) орудњења.