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

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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 sulfoselenides) with Fe, Co and Ag were formed under to 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 argentopentlandite 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 \( f_{\text{S}_2} \) and \( f_{\text{O}_2} \) 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.
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 et al., 2006a,b; SERAFIMOVSKI et al., 2013, 2015; RADOVELJUĆ-MIHAILOVIĆ et al., 2007; VOU SOURIS et al., 2008a-b; KOLODZIEJCZYK et al., 2015, 2016, 2017; RADOVELJUĆ et al., 2014a,b, 2015, 2016a).

The ROF belongs to the Šumadija Metallogenic District (ŠMD), and is located on Rudnik Mt., Serbia. It consists of the several ore zones associated with the metallogeny of Tertiary magmatism (Fig. 1b). The area has complex geological structure, as the sedimentary rocks are more abundant than the igneous rocks (Fig. 1a). Besides the sedimentary and igneous rocks, contact-metamorphic rocks schist, hornfels and skarns were also found (MILIĆ, 1972). The ore deposits are associated with skarn of hydrothermal origin belonging to the Oligocene-Miocene magmatic complex of intrusive volcanic series (DELALOYE et al., 1989; CVETKOVIĆ et al., 2000; NEUBAUER 2002). The ore has complex mineral composition representing a source of many metals such as Pb, Zn, Cu, Ag, Bi, Cd, etc., but scheelite was determined only in the Rudnik deposit so far (RADOVELJUĆ et al., 2003b, 2006a, 2016b).

According to the archaeological remains found, mining activities in this region date from the Neolithic Period, over the Roman Empire, the Kingdom of Serbia (medieval), and the Ottoman Empire, to the present day. Intensive examinations have begun in the middle of 20th century when mining-geological, mineralogical, petrological, geochemical and other surveying started. That led to extensive discovering of new minerals and rocks (e.g., RAKIĆ, 1952, 1958; MILIĆ, 1972; TERZIĆ & TERZIĆ, 1972; TOŠOVIĆ, 1997, 2000; CVETKOVIĆ et al., 2004; STOJANOVIĆ, 2005). Several newly discovered minerals (ZARIĆ et al., 1992a; CVETKOVIĆ, 2001; STOJANOVIĆ et al. 2006, 2016) complete the extensive list of mineral species found in the ROF (RAKIĆ 1958). The results were summarized and reported in previous studies (ZARIĆ et al., 1992b 1; TOŠOVIĆ, 1997, 2000; STOJANOVIĆ, 2005).

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 & Omelotto 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 (Petrović, 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 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 impacted 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 metaclastites, carbonate sediments, olistolith limestones, breccia-filled volcanic pipes formed by gaseous explosions and volcanics of quartz latite and latite composition (Popović & Umeljić, 2015). The ore bodies are oriented NNW–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 Prlovi (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 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 ore bodies range from 20,000 to 900,000 tons, with the average amount of about 70,000 tons. Contacts between ore bodies and the surrounding rocks are not commonly visible.

Ore bodies of the Prlovi ore zone characterize high contents of Pb and Zn fractured by post-ore tectonic processes, which led to a high oxidation of sulfide minerals. Three types of mineral associations can be recognized in the Prlovi-2: (i) secondary oxide ore (near the surface); (ii) mixed sulfide-oxide ore (beneath the oxide zone); and (iii) primary sulfide ores. Ore bodies belong to the complex morphogenetic types and have earthy, kidney-like, brecciated, coarse grained and disseminated textures. (Radosavljević et al., 2002, 2003a; Tomasević & Lazić, 2012).

The Azna ore zone (levels 815 and 720) is characterized with high Cu, Ag, Bi contents, found in three major ore bodies (Z, Z1, Z2) having massive, brecciated, banded, and disseminated textures. The mineralogical and geochemical data obtained in 1991 (Zarić et al., 1992b) and in the period from 2006 to 2010 are shown in this study.

The Nova Jama ore zone consists of several ore bodies of pseudostratified and plate-like features. Except the group “N” ore bodies, all the others are excavated (Popović & Umeljić, 2015). The geological, mineralogical (ore-microscopic) and geochemical data obtained between 2003 and 2006 on the gallery HI-672-92 are also presented in this study (Stojanović et al. 2004).

The ore bodies of the Gušavi Potok ore zone have inclination of 45° to the North. They are characterized with a relatively high content of valuable metals. The mineralogical (ore-microscopic) and geochemical data obtained in 1991 on the “G-16” ore body are discussed in study by Zarić et al. (1992b).

**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 & Johan 1982). A Carl Zeiss polarizing microscope, model Jenapol-U, equipped with 10×, 20×, 50×, air medium, 100×, immersion medium (cedar oil), objectives and a system for photomicrography (AxioCam 105 color camera equipped with Carl Zeiss AxioVision 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 (AxioCam 105 color camera equipped with Carl Zeiss AxioVision 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 microanalysers 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), FeKa (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), AgLa (Ag2Te), 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 Mater-
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 (RADOSSAVLJEVIĆ 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: B, Na, Al, Si, S, K, Ca, Ti, Mn, Ni, Cu, Zn, Pb and W. Following metals were 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.

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) Σ 73.3, Hf 5, Ta 1, Tl 10, Th 2. Elements >1000: Na, Al, Si, S, K, Ca, Cu, Zn, Pb, Bi and W. Qualitatively detected: Li, Mg, Er.
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 & UMELIĆ, 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, chalcopyrrhotite, chalcopyrite, cubanite, mackinawite, sphalerite, galena, bismuthinite, molybdenite, pentlandite, argentopentlandite, gersdorffite, and nickeline); sulfosalts (galenobismutite, cosalite, Ag-bearing aschamalmite, gustavite, schirmerite, vikingite, Ag-bearing tetrahedrites, and semseyite); 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, clinozoisite, hedenbergite, garnets, axinite, epidote, clay minerals, apatite, zircon, monazite-(Ce), sphene, leucoxene, calcite, siderite, aragonite, anglesite, cerussite, smithsonite, willemitte, hydrohetaerolite, 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](image-url)
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; RADOŠAVLJEVIĆ 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-
ance 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) – Gušavi Potok; 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
cemented with galena (air, //N) – Gušavi Potok; g) preserved forms of a colloform pyrite relic (oil, //N) – level 720; h) preserved forms
of a colloform pyrite relic (oil, //N) – level 720; i) a complex mineral paragenesis of Fe-sulfides and arsenopyrite with chalcopyrite, spha-
lerite and galena (air, //N) – borehole No 197/12. Abbreviations: Po – pyrrhotite, Py – pyrite, Cpy – colloforms pyrite, Mc – marcasite,
Ap – arsenopyrite, Cp – chalcopyrite, Sp – sphalerite, Gl – galena, Gb – galenobismutite, Bi – native bismuth, Sd – siderite, Qz – quartz.
(Figures 4a-b - RADOŠAVLJEVIĆ & STOJANOVIĆ (2006); Figures 4c-h - ZARIĆ et al. (1992b); Figure 4i - this study).
euhehed crystal forms associated with pyrhotite, sphalerite, galena, quartz and other ore minerals.

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–pyrhothotite and/or pyrite–pyrhothotite–siderite (Figs. 4b-h). Sometimes they form rhythmic zones cemented with siderite. Colloform pyrite is quite abundant mineral and is commonly cataclased and as relics embedded in younger sulfides in a form of “isolated islands”.

TOMANEC & LAZIĆ (2012) and POPOVIĆ & UMELIĆ (2015) unintentionally wrongly named these sections of colloform pyrites as “oolites relics 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 frambooidal 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 frambooidal pyrite from the ROF is genetically related to the metallogeny of Neogene magmatism as stated in literature data (POPOVIĆ & UMELIĆ, 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 euhehedral crystals or/and complex rosettes in quartz and galena matrix accompanied with younger chalcopyrite. Arsenopyrite is commonly related to the arszenization 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-twinneu, euhehedral 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 anhehdal 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 pyrhotite, 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 pyrhotite. 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 cataclased Fe-sulfides and arsenopyrite. It occasionally forms complex intergrowths with galena overgrowing the siderite matrix. Galena, galenobismutite and native bismuth of acicular mix-aggregates as products decomposition of solid solution Bi$_2$S$_3$-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 pyrhotite fissures, cataclasised 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 pyrhotlite, 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 tetra- hedrite 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. Oriented sphalerite “stars” in chalcopyrite are characteristic for the younger generations of the hydrothermal stage (Fig. 5c). Oriented sphalerite “stars” in chalcopyrite are characteristic for the younger generations of the 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

Fig. 5. Optical microscopy images in reflected light showing the textural features of ore and gangue minerals of the ROF: a) fractured and spongy arsenopyrite crystals in quartz matrix (air, //N) – Azna; b) a coarse-crystalline aggregate of sphalerite-chalcopyrite replaced by younger galena-siderite mix (air, //N) – borehole No 197/12; c) chalcopyrite exsolution oriented parallel to the crystallographic directions of sphalerite (oil, //N) – Gušavi Potok; d) exsolution acicular mix-aggregates of galena-galenobismutite-native bismuth in the chalcopyrite matrix (air, //N) - Azna; e) anisotropic effects in high-temperature chalcopyrite (“parquet-like twinning”) (oil, ×N) – level 720; f) coarse-crystalline aggregates of pyrrhotite and sphalerite suppressed by younger chalcopyrite-galena-siderite mix (air, //N) – borehole No 197/12. Abbreviations: Po – pyrrhotite, Ap – arsenopyrite, Cp – chalcopyrite, Sp – sphalerite, Gl – galena, Gb – galenobismutite, Bi – native bismuth, Si – contact silicate, Qz – quartz. (Figures 5a-b - RADOŠAVLJEVIĆ & STOJANOVIĆ (2006); figures 5c, 5e - ZARIĆ et al. (1992b); Figures 5b, 5f - this study).
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 \( \text{Ag}_{1.03}(\text{Fe}_{4.81}\text{Ni}_{3.14})_{\Sigma=7.95}\text{S}_{8.02} \) (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 \( \text{Pb}_{1.91}\text{Cu}_{0.08}\text{Ag}_{0.05}\Sigma=2.04\text{Bi}_{1.97}\text{S}_{5.02} \) (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 \( \text{Pb}_{1.91}\text{Cu}_{0.08}\text{Ag}_{0.05}\Sigma=2.04\text{Bi}_{1.97}\text{S}_{5.02} \). 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; VOUĐOURIS et al., 2013; KOŁODZIEJCZYK et al., 2017).
Sulfosalts of lillianite homologous series, namely Ag-bearing aschamalmite, gustavite, schirmerite 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.

Aschamalmite was mistakenly described as heyrovskyite in the study by Dimitrijević et al., (1992). Aschamalmite from the Azna 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 chloropyrite. Microscopically, it occurs in a form of large irregular aggregates (>100 µm) cementing colloform Fe-sulfides, chloropyrite, galena, and arsenopyrite (Fig. 3b). Aschamalmite 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 aschamalmite (6 analyses) amounts to: 

\[
(Pb^{5.88}_{9}Ag_{0.20})^{2+}Bi_{2.03}(S^{8.93}_{8}Te_{0.02}Se_{0.01})^{2-}_{8.96}\]  

(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 aschamalmite (Stojanović 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 (Stojanović, 2005). EPMA of a single grain gives following chemical formula:

\[
Ag_{4.43}Pb_{8.12}Bi_{13.49}S_{29.96}\]  

(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 aschamalmite (Stojanović et al., 2016).

Microscopically, vikingite and 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. 7c). EPMA of a single grain gives following chemical formula:

\[
Ag_{0.83}Pb_{1.30}Bi_{2.85}S_{6.00}\]  

(Table 1). Similarly to schirmerite, it is not confirmed by XRD due to the small grain size. The lillianite–gustavite series with intermediate phases occur within the Sturi Trg Pb(Ag)-Zn polymetallic deposit, Trepača ore field, Serbia (Koldziejczyk et al., 2017).

Sb-sulfosalts

Sb-sulfosalts from the SE part of the ROF, associated with Fe-sulfides, arsenopyrite, chloropyrite, 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. Srebenica ore field – Rakić et al., 1978, Radosavljević & Dimitrijević, 2001, Radosavljević et al., 2016a; Boranja ore field – Radosavljević et al., 2016c; Kopaonik ore zone – Zaric et al., 1984; Rogozna ore field – Radosavljević et al., 2014b, 2015).

Microscopically, solid solution series

\[
Cu_{10}(Fe,Zn)_{5}Sb_{3}S_{13} - Cu_{10}(Fe,Zn)_{2}As_{3}S_{13}\]  

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 chloropyrite. 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:

\[
Ag_{5.01}Pb_{8.03}Bi_{13.00}S_{29.95}\]  

(Table 1, Fig. 7c). Due to the very small grain size, it is not confirmed by XRD.

Schirmerite from the borehole No 197/12 always occurs in mineral 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:

\[
Ag_{5.47}Cu_{4.52}Sb_{3.9}S_{12.99}\]  

(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 heteromorphite, forming homologous series. Semsyeite, determined for the first time within the ROF, occurs in a form of isolated

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tabular crystals associated with galena and Ag-bearing tetrahedrite embedded in chalcopyrite matrix (Fig. 7h). EPMA yielded the following chemical formula: Pb\textsubscript{8.61}Sb\textsubscript{8.28}S\textsubscript{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 wt% with oxygen content from 0.5 to 0.7 wt%; and borehole No 197/12 <0.3 wt%. Tellurium, Pb and Sb were below detection limits (<0.3 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

Fig. 7. Optical microscopy images in reflected light and BEI showing the textural features of ore and gangue minerals of the ROF: a) well-developed crystals of gersdorffite intergrown with pyrrhotite (oil, //N) – Nova Jama; b) chalcopyrite-galena-pyrrhotite mineral paragenesis with exsolution of the Bi-minerals in galena (air, //N) – borehole No 197/12; c) exsolution of vikingite and native bismuth in galena (BEI) – detail of Fig. 6b; d) schirmerite and native bismuth exsolution in Ag-bearing galena (BEI) – detail of Fig. 6b; e) gustavite and native bismuth exsolution in Ag-bearing galena (BEI) – detail of Fig. 6b; f) Pb-Bi-S high temperature solid solution (native bismuth, galenobismutite and Ag-bearing tetrahedrite) (oil, //N) – level 815; g) strong anisotropy of native bismuth with appearance of polysynthetic twining (oil, ×N) – the same motif from the Fig. 6g; h) chalcopyrite-galena-Fe-arsenousulfides mineral paragenesis and common replacement of galena and chalcopyrite with younger Ag-bearing tetrahedrite and semseyite (oil, //N) – borehole No 197/12; i) replacement of galena with a younger Ag-bearing tetrahedrite I, Ag-bearing tetrahedrite II and semseyite (BEI) – detail of Fig. 6b. Abbreviations: Po – pyrrhotite, Py – pyrite, Mc – marcasite, Ap – arsenopyrite, Gd – gersdorffite, Cp – chalcopyrite, Sp – sphalerite, Gl – galena, Gu – gustavite, Vk – vikingite, Sr – schirmerite, Td – tetrahedrite, Sy – semseyite, Bi – native bismuth, Qz – quartz. (Figure 7a - RADOSAVLJEVIĆ & STOJANOVIĆ (2003); figures 7f-g - ZARIĆ et al. (1992b); Figures 7b-e and 7h-i - this study).
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; RADOSAVLJEVIĆ et al., 2003b, 2006; STOJANOVIĆ et al., 2004, 2006a,b; RADULOVIĆ et al., 2005, 2006; MILANOVIĆ & MARKOVIĆ, 2009a,b; MAGDALI-
The latest data have been shown by Popović & Umeljić (2015), describing the scheelite mineralization from the level 815 and Srednji Šturac ore zone (Fig. 1b). These mineralizations have also been tested to obtain a scheelite concentrate, however the results were not satisfactory, due to very low WO$_3$ content in technological samples (WO$_3$ <0.30 wt%). Quartz veins, in which scheelite is commonly embedded, increase the luminescence effects (very strong under the UV-short waves), thus creating wrong impression of rich scheelite ore.

The scheelite mineralizations appear in three morphological types: i) stockwork swarms in the Nova Jama ore zone (Fig. 8e) consisting of numerous veinlets, coatings and scum of scheelite associated with 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 lonely euhedral crystals accompanied by sulfide-silicate-carbonate small coatings of agglomerated isometric scheelite matrix (the Azna ore zone; Radosa Vljević et al., 2010; Sokić et al., 2014).

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 intensive 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 majority of ore mineralizations have been formed during several distinct periods of time, the complete description of the paragenesis of the deposit involves establishing the order in which the constituent minerals have been formed and the sequence of resorptions and replacements that have occurred. Variations in the pressure and temperature and in the chemical constituents of hydrothermal solutions will result in precipitation of various minerals at different times within the same ore deposit. The general sequence of deposition are gangue minerals (silicates and carbonates) first; oxide minerals next, with sulfides and arsenides of iron, nickel, and cobalt, closely following wolframites, molybdates, and the Pb-Zn-Cu sulfides, and finally native metals and tellurides followed by As-Sb-Hg sulfides. Mineral parageneses at any particular location may be complicated if the ore deposit has been formed by more than one period of hydrothermal activity (Ramdohr, 1980).

The ore microscopy studies confirmed the presence of the entire skarn-replacement and hydrothermal range in the Pb-Zn-Cu-Ag-Bi-W polymetallic ores of the ROF. Minerals were deposited in several successive stages and paragenetic sequences, all genetically related to the Neogene magmatism. The principal ore and typomorphic elements of the ROF are Fe, Pb, Zn, Cu, Ag and Bi, and in a lesser extent W, Cd. They probably all have a common magmatic origin (e.g. grandoiritie), which together correspond to a multi-stage cycle of mineralizations. The magmatic origin of sulfur, indicated by isotopic analyses from sulfides and sulfoarsenides of different ore bodies (Table 3), is fairly uniform: $\delta S^{34} = +3.0 \%$ for pyrrhotite, $+3.1 \pm 0.3 \%$ for sphalerite, $+3.3 \pm 0.6 \%$ for chalcopyrite, $+4.0 \pm 0.6 \%$ for arsenopyrite (Tošović, 2000). Sulfur stable isotope studies on a variety of sulfide minerals from skarn-replacement hydrothermal deposits indicate a very narrow range of $\delta S^{34}$ values, consistent with a source of sulfur from magmatic fluids (e.g. Shimazaki & Yamamoto, 1979, 1983; Shimazaki & Sakai, 1984). Minor fluctuations of $\delta S^{34}$ are a function of the variation of their respective crystallization temperatures.

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

| Mineral | Ore zone (ore body) | Level (m) | $\delta S^{34} \%$ |
|---------|---------------------|-----------|-------------------|
| Pyrrhotite | Gušči Potok (G-8) | 689 | +3.0 |
| Sphalerite | Mali Do (S-7) | 725 | +3.5 |
| Sphalerite | Gušči Potok (G-9) | 644 | +3.0 |
| Sphalerite | Srednji Šturac (SS-20) | 715 | +2.9 |
| Chalcopyrite | Azna (Z-1) | 725 | +3.8 |
| Chalcopyrite | Azna (Z-2) | 725 | +2.9 |
| Arsenopyrite | Bezdan | 600 | +3.4 |
| Arsenopyrite | Azna (Z-1) | 725 | +4.6 |
| Arsenopyrite | Prlovci (P-12) | 720 | +3.9 |
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–spalerite–galena with Pb-Bi(Ag) sulfosalts); iv) micro-skarn (skarn silicates–sulfides–scheelite); v) high-temperature hydrothermal (colloform Fe-sulfides–arsenopyrite–siderite and chalcopyrite–spalerite–galena with Ag–Pb–Bi–sulfosalts); vi) hypogene (pyrite–marcasite); vii) medium-temperature hydrothermal (spalerite–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 late-stage skarn 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 multistage skarn-replacement and high-temperature hydrothermal polymetallic mineral parageneses (Table 4).

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

| Stages                           | Paragenetic sequences                                                                 |
|----------------------------------|---------------------------------------------------------------------------------------|
| Pre-ore (Relict)                 | Sandstone – flysch – limestones – silicates – Ni-minerals – leucoxene – framoidal pyrite carbonic substances |
| Pyrometasomatic (skarization of sandstone, flysch, and limestones) and pneumatolytic (breccia-filled volcanic pipes) | Calcite I – garnet (andradite-grossular) – pyroxenes – clinozoisite (Fe,Mn)-axinite – epidote I – chlorites – sericite –feldspars (needle-like sandine, adularia) – clay minerals Quartz I – molybdenite – scheelite I – magnetite I – rutile – anatase – monazite(Ce) |
| High-temperature hydrothermal   | Pyrrhotite I – spalerite I– chalcopyrite I – chalcopyrrhotite – galena I – native silver – native bismuth I – bismuthinite I – galenobismuthite I – cosalite – vikingite I – quartz II |
| Neocrystallization (Micro-skarn) | Diopside – hedenbergie – pigeonite – epidote II – scheelite II – pyrrhotite I – native PGE-minerals – argentopentlandite – gersdorffite – quartz II |
| High-temperature hydrothermal   | Colloform Fe-sulfides – arsenopyrite – siderite I – Spalerite II – chalcopyrite II – native gold – cubanite – galena II – Ag-bearing aschamalinite – native bismuth II – quartz III |
| Hypogene                        | Marcasite I – pyrite I – hematite – aragonite                                         |
| Medium-temperature hydrothermal | Chalcopyrite III – galena III – native bismuth III – vikingite II – schirmerite – gusnate I – Ag-bearing tetrahedrite – semevite – quartz IV |
| Supergene                        | Covellite – mackinawite – marcasite III – Anglesite – cermisite – smithsonite – willenite – hydrothoriteolite – zinc(II)metasilicate – goethite – lepidocrocite – hydrohematite – malachite – limonite |
sitional 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 occur in the SE parts of the ROF (borehole 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, Kopanik, Trešća, Novo Brdo, Karavanalija, Blagodat, Crnac, and Kosmaj, Kotelnik, 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 physicochemical forming conditions due to their sensitivity to changings in temperature, Eh–pH, /S2 and /O2 (COOK & CIOBANU, 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 (BORODAEV 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 Cu3S–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. MOELO 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 Toroiga deposit by COOK (1997) and the Stanos mineralization by VOUĐOURIS 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, ŠTOJANOVIĆ, 2005). However, the transport of ore elements was also possible with other anions (e.g. HS⁻, H₃B₂⁻, H₃As₂⁻, 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 (RADOSAVLJEVIĆ et al., 2011) and in the listwaenites from the Rogozna ore field, Serbia (RADOSAVLJEVIĆ 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 RADOSAVLJEVIĆ 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-feldspars (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 ŠTOJANOVIĆ 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 – pseuodotriated 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, Motlave, 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-meta somatic 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 determinate 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 tetrahedrite 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. Čumavica, Serbia – RADOSAVLJEVIĆ et al., 2015; D&M, Rudnik, Serbia – KOŁODZIEJCZYK et al., 2012; Crnac and Kaludjer, Rogoзна, Serbia – RADOSAVLJEVIĆ et al., 2015; Trepča, Stari Trg, Kosovo, Serbia – KOŁODZIEJCZYK et al., 2016).

Besides the ROF, Bi-sulfosalts mineral parageneses have been identified in the Boranja ore field, Serbia (DANGIĆ et al., 1984, RADOSAVLJEVIĆ-MIHAILOVIĆ et al., 2007), in the Golija ore field, Serbia (STAJIĆ & ZARIĆ, 1984) and in the Trepča, Stari Trg, Kosovo, Serbia (KOŁODZIEJCZYK et al., 2015, 2017). According to the mineral compositions, they are close to the Stanos shear-zone related deposit, Chalkidiki, northern Greece (VOUDOURIS et al., 2013). Moreover, the Pb-Bi(Ag) sulfosalts of Ag-bearing aschamalmite.

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References

ADAMOVIC, M., RADOSAVLJEVIĆ, S. & MARINKO, M. 2000. Increase of Copper Recovery from Polymetallic Ores. Journal of Mining and Metallurgy, 36 (1–2) A: 1–12.

AGOSTINI, S., DOGLIONI, C., INNOCENTI, F., MANETTI, P. & TONARINI, S. 2010. On the geodynamics of the Aegean rift. Tectonophysics, 488: 7–21.

ALEKSANDROV, M., MANKOV, S. & SERAFIMOVSKI, T. 1990a. Silver minerals from the Pb – Zn deposit Sasa – East Macedonia. Proceedings of the 12th Congress of Geologists of Yugoslavia, Ohrid, 86–102, (in Macedonian).

ALEKSANDROV, M., MANKOV, S. & SERAFIMOVSKI, T. 1990b. The new type of Bi mineralization from the Sasa deposit – East Macedonia. Proceedings of the 12th Congress of Geologists of Yugoslavia, Ohrid, 103–115, (in Macedonian).

ALEKSANDROV, M., SERAFIMOVSKI, T. & MANKOV, S. 1999. Silver-bearing contents and mode of occurrence of silver in the Sasa Pb-Zn deposit, eastern Macedonia. Geologica Macedonica, 12: 23–36.

BARTULOVIĆ, Z., RADOSAVLJEVIĆ, S., IVOSHEVIĆ, B. & ZILDŽOVIĆ, S. 2008. Laboratory investigation of valuable minerals concentration from polymetallic W-Pb-Bi-Ag Nova Jima mining sector, the mine and flotation, Rudnik Company Ltd. Proceedings of 21th International Serbian Symposium on Mineral Processing, November 4th-6th, Bor, Serbia, 101–107.

BORODAEV, Y.S., GARAVELLI, A., GARBARINO, C., GRILLO, S.M., MOZGOVA, N.N., PAAR, W.H., TOPA, D., & VURRO, F. 2003. Rare sulfosalts from Vulcano, Aeolian Islands, Italy. V. selenian heyrovskyite. Canadian Mineralogist, 41: 429–440.

CHANG, T.L.Y. & HODA, S.N. 1977. Phase relations in the system PbS–Cu3S–Bi2S3 and the stability of galenobismutite. American Mineralogist, 62: 346–350.

CHANG L.L.Y., WU D. & KNOWLES C.R. 1988. Phase relations in the system Ag2S-Cu3S-PbS-Bi2S3. Economic Geology, 83: 405–418.

COOK, N.J. 1997. Bismuth and bismuth–antimony sulfosalts from Neogene vein mineralization, Baia Borşa area, Maramureş, Romania. Mineralogical Magazine 61: 387–409.

COOK, N.J. & CIOBANU, C.L., 2004. Bismuth tellurides and tellurites of Yugoslavia. Economic Geology, 68: 301–321.

CRAIG, J.R., & KULLERUD, G. 1969. Phase relations in the Cu-Fe-Ni-S system and their application to magmatic ore deposits. Economic Geology, 4: 344–358.

Cvetković, LJ. 2001. Ni-Fe mineralization products from the area floor seam deposits of lead and zinc Rudnik mine. Annual of the Yugoslav Association of Mineralogy, Belgrade, 3: 135–138. (in Serbian with English abstract)

Cvetković, V., Knežević, V. & Peckray, Z. 2000. Tertiary igneous formations of the Dinarides, Vardar zone and adjacent regions: from recognition to petrogenetic implications. In: Karamata, S. & Janković, S. (eds), Geology and Metallogeny of the Dinarides and the Vardar Zone, Banja Luka-Sarajevo, 245–253.

Cvetković, V., Prelević, D., Downes, H., Jovanović, M., Vaselli, O. & Peckray, Z. 2004. Origin and geodynamical significance of Tertiary postcollisional basaltic mag-
Dangić, A., Rakić, S., Radosavljević, S. & Dobosi, G. 1984. Bismuth minerals in the Veliki Majdan lead-zinc ore area, Yugoslavia. Geološki anali Balkanskoga poluostrova, 48: 231–237. (In Serbian with English abstract)

Dangić, A. 1993. Tertiary lead-zinc ore deposits and calco-alcaline magmatism of the Serbo-Macedonian Province: metallogenic and geochemical characteristics, hydrothermal systems and their evolution. Geološki anali Balkanskoga poluostrova, 57 (1): 257–285.

Delaloye, M., Lovrić, A. & Karamata, S. 1989. Age of Tertiary granite rocks of Dinarides and Vardar zone. In: Extended Abstracts, 14th Congress CBGA, Sofia, 1186–1189.

Dimitrijević, R., Radosavljević, S. & Cvetković, L.J. 1992. Mineralogy and crystallographic characteristics of heyrovskite from the polymetallic Rudnik deposits. Extended abstracts of the 1 Conference of the Serbian Crystallographic Society, Belgrade, 36–37. (In Serbian and English)

Einaudi, M.T., Hedeenquist, J.W. & Inan, E.E. 2003. Sulfidation state of hydrothermal fluids: the porphyry-epithermal transition and beyond. In: Simmons, S.F., Graham, I.J. (Eds.), Volcanic, Geothermal Ore-Forming Fluids: Rulers and Witnesses of Processes within the Earth. Society of Economic Geologists Special Publication, 10: 285–313.

Gao, S., Huang, F., Wang Y. & Gao W. 2016. A Review of Research Progress in the Genesis of Colloform Pyrite and Its Environmental Indications. Acta Geologica Sinca (English Edition), Geological Society of China, 1353–1369.

Janković, S. 1990. The ore deposits of Serbia: Regional metallogenic settings, environments of deposition, and types. Faculty of Mining and Geology, Belgrade, 760 pp. (In Serbian with English summary)

Jelenković, R., Kostić, A., Živođić, D. & Ercegovac, M. 2008. Mineral resources of Serbia. Geologica carpathica 59 (4): 345–361.

Jonović, R., Avramović, Lj. & Marković, S. 2010. Silver Leaching from Sulfide Concentrate from the „Rudnik“ Mine. Mining engineering (Rudarski radovi), 1: 81–88. (In Serbian and English)

Kolaržičkzyk, J., Pršek, J., Voudouris, P.C. & Melfos, V. 2017. Bi-sulphotellurides associated with Pb–Bi–(Sb ±Ag, Cu, Fe) sulphasalts: an example from the Stari Trg deposit in Kosovo. Geologica Carpathica, 68 (4): 366–381.

Liu, H., & Chang, L.L.Y. 1994. Lead and bismuth chalcogenide system. American Mineralogist, 79: 1159–1166.

Magdalinić, R.S., Jonović, R.R., Avramović, R.J. & Milanović, B.D. 2010. Tungsten Oxide Obtaining from Polymetal Ore. Copper, 35 (1): 63–70. (In Serbian with English summary).

Makovicky, E., Mumme, W.G., & Hoskins, B.F. 1991. The crystal structure of heyrovskite. Canadian Mineralogist, 29: 553–559.

Makovicky, E., Mumme, W.G., & Madsen, I.C. 1992. The crystal structure of vikingite. New Jahrbuch für Mineralogie - Monatshefte, 10: 454–468.

Mandziuk, Z.L., & Scott, S.D. 1977. Synthesis, stability, and phase relations of argentian pentlandite in the system Ag-Fe-Ni-S. Canadian Mineralogist, 15: 349–364.

Marchev, P., Kaiser-Roehrmeier, M., Heinrich, C.A., Ovtcharova, M., von Quadt, A., & Raicheva, R. 2005. Hydrothermal ore deposits related to post-orogenic extensional magmatism and core complex formation: the Rhodope massif of Bulgaria and Greece. Ore Geology Reviews, 27: 53–89.

Meinert, D.L., Dipple, M.G. & Nicolescu, S. 2005. World Skarn Deposits. Society of Economic Geologists, Inc. Economic Geology 100th Anniversary Volume, 299–336.

Meihrr, H., 2007. Diffusion in Solids, Fundamentals, Methods, Materials, Diffusion-Controlled Processes. Springer-Verlag Berlin Heidelberg, pp. 654.

Milanović, B.M. & Marković, S.Z. 2009a. Zeta-potential and flotability of the scheelite mineral in different type of water. Part 1. Zeta-potential. Hemijska industrija (Chemical Industry), 63 (5): 369–376. (in Serbian with English summary)

Milanović, B.M. & Marković, S.Z. 2009b. Zeta-potential and flotability of the scheelite mineral in different type of water. Part 2. Flotability. Hemijska industrija (Chemical Industry). 63 (5): 377–385. (in Serbian with English summary)

Milic, Č.R. 1972. Metalliferous structure factors control the mineralization area in the polymetallic Rudnik deposit. Proceedings of the 7th Congress of Geologists of Yugoslavia, SFRJ, Zagreb, 3: 111–117. (in Serbian with English summary)

Moëlo, Y., Marcoux, E., Makovicky, E., Karup-Moller, S. & Legendre, O. 1987. Homologues de la lillianite (gustavite, vikingite, heyrovskyite riche en Ag et Bi...) de l’indice W-As-(Pb, Bi, Ag) de La roche-Balue (Loire-Atlantique, France). Bulletin de Minéralogie, 110: 43–64.

Moëlo, Y., Makovicky, E.G., Mozgova, N.N., Jambor, L.J., Cook, N., Pring, A., Paar, W., Nickell, H.E., Graeser, S., Karup-Moller, S., Balić-Zunic, T., Mumme, W.G., Vurro, F., Topa, D., Bendi L., Bente, K., & Shimizu, M. 2008. Sulfoalum systematics: A review

Geol. an. Balk. poluos., 2018, 79 (1), 47–69.
report of the sulfosalt sub-committee of the IMA/COM. 

*European Journal of Mineralogy*, 20: 7–46.

**Monthel, J., Vadala, P., Leistel, J.M. & Cottard, F., with the collaboration of Ilič, M., Strumberger, A., Tosovic, R. & Stepanović, A. 2002.** *Mineral deposits and orefields of Serbia.* Compilation map and GIS databases. BRGM/RC-51448-FR, 67 p., 26 Fig., 1 Table, 1 Plate, 2 App., 1 CD-rom.

**Neubauer, F. 2002.** Contrasting Late Cretaceous with Neogene ore provinces in the Alpine–Balkan–Carpathian–Dinaric collision belt. In: Blundell, D.J. Neubauer, F. & Quadt, A. (eds.), *The Timing and Location of Major Ore Deposits in an Evolving Orogen*, Geological Society, London, Special Publications, 204: 81–102.

**Nimis, P. & Omenetto, P. 2015.** Does subduction polarity control metallogeny? The Mediterranean case. *Terra Nova*, 27 (2): 139–146.

**Peković, M. 1997.** On magmatic complexes and metallogenic affinity (an example from the Tethys Sea). *Proceedings of Symposium “Ore Deposits Exploration”*. Faculty of Mining and Geology, Belgrade, Serbia, 5–16.

**Pepović, R. & Umelić, G. 2015.** *Metallogeny of the Rudnik Mt. (place in the time and space).* Special Publications, “Rudnik i flogacija” Rudnik Co.Ltd. Belgrade, Serbia, pp. 224. (In Serbian)

**Radosavljević-Mihajlović, A., Stojanović, J., Dimitrijević, R. & Radosavljević, S. 2007.** Rare Pb-Bi sulfosalt mineralization from the Boranja ore field (Podrinje district, Serbia). *Neues Jahrbuch für Mineralogie - Abhandlungen*, 184 (2): 217–224.

**Radosavljević, S., Živković, S. & Šešić, M. 1982.** The distribution of silver in the ore of lead and zinc in Veliki Majdan mine. *Proceedings of the 10th Anniversary of the Congress of Geologists of Yugoslavia*, Budva, Montenegro, 2: 299–303. (In Serbian, English abstract)

**Radosavljević, S. & Dimitrijević, R. 2001.** Mineralogical data and paragenetic association for semenite from Srebrenica ore field, Bosnia and Herzegovina. *Neues Jahrbuch für Mineralogie - Monatshefte* 4: 146–156.

**Radosavljević, S., Radosavljević-Mihajlović, A., Kašić, V. & Adamović, M. 2002.** The mineral composition of oxidic ore from the Prlovci-2 deposit at the Rudnik mine. *Proceedings of the 18th Yugoslav Symposium on the Mineral Processing*, Banja Vrujci, 173–176. (In Serbian with English summary)

**Radosavljević, S., Stojanović, J., Zarić, P. & Marjanović, M. 2003b.** The scheelite ore from the “Rudnik” polymetallic deposits, near Gornji Milanovac. *Annual of the Yugoslav Association of Mineralogy*, Belgrade, 4: 125–130. (In Serbian with English summary)

**Radosavljević, S., Stojanović, J., Kašić, V. & Tešmanović Lj. 2006b.** Mineralogical Characteristics of the heavy minerals of a polymetallic ore from Rudnik orefield. *Proceedings 38th IOC on Mining and Metallurgy*, Donji Milanovac, Serbia, 91–95.

**Radosavljević, S., Stojanović, J. & Kašić, V. 2006c.** *Mineralogy of the Polymetallic Ore from Rudnik Mine. Proceedings of 20th International Serbian Symposium on Mineral Processing*, Sokobanja, Serbia, 8–12.

**Radosavljević, S., Đorđević, D., Stojanović, J., & Kašić V. 2011.** Srebrenica orefield, Podrinje Metallogenic District, east Bosnia: Greisenization and mineralization of tin, titanium and REE. *Proceedings of 4th Conference of Geologists of Bosnia and Herzegovina*, 117–126. (In Serbian with English summary)

**Radosavljević, S., Stojanović, J., Pačevski, A., Kašić, V. & Vuković, N. 2012.** Mineralogical and chemical study of silver in polymetallic ore of the Lece mine-Medveda. *Proceedings of 44th IOC on Mining and Metallurgy*, Bor, Serbia, 21–26.

**Radosavljević, S., Stojanović, J., Radosavljević-Mihajlović, A. & Vuković, N. 2014a.** Rujevac Sb-Pb-Zn-As polymetallic deposit, Boranja orefield, western Serbia: Native arsenic and arsenic mineralization. *Mineralogy and Petrology*, 108 (1): 111–122.

**Radosavljević, S., Stojanović, J., Vuković, N., Radosavljević-Mihajlović, A. & Kašić, V. 2014b.** Pb(Ag)-Zn deposits within the Rogozna orefield, Serbia: Ore mineralogy and paragenetic settings. *Proceedings of IOC 46th on Mining and Metallurgy*, Bor Lake, Serbia, 453–456.

**Radosavljević, S., Stojanović, J., Vuković, N., Radosavljević-Mihajlović, A. & Kašić, V. 2015.** Low-temperature Ni-As-Sb-S mineralization of the Pb(Ag)-Zn deposits within the Rogozna orefield, Serbia: Ore mineralogy, crystal chemistry and paragenetic relationships. *Ore Geology Reviews*, 65: 213–227.

**Radosavljević, S., Stojanović, J., Radosavljević-Mihajlović, A., & Vuković, N. 2016a.** (Pb-Sb)-bearing sphalerite from the Čumavići polymetallic ore deposit, Podrinje Metallogenic District, East Bosnia and Herzegovina. *Ore Geology Reviews*, 72: 253–268.

**Radosavljević, S., Stojanović, J., Radosavljević-Mihajlović, A., Pačevski, A. & Stojanović, V. 2016b.** Mineralogical and chemical analyses of the polymetallic ore zone Azna from the Rudnik mine, Serbia. *Proceedings of IOC 45th on Mining and Metallurgy*, Bor Lake, Serbia, 281–284.

**Radosavljević, S., Stojanović, J., Radosavljević-Mihajlović, A., Pačevski, A. & Kašić, V. 2016c.** A review of Pb-Sb(As)-S, Cu(AG)-Fe(Zn)-Sb(As)-S, Ag(Pb)-Bi(Sb)-S and Pb-Bi(S-Te) sulfosalt systems from the Boranja orefield, west Serbia. *Geološki anali Balkanskoga poluostrova*, 77: 1–12.

**Radulović, D., Jovanović, V. & Ivošević, B. 2005.** Obtainment of Scheelite-Sulfide Preconcentration from Polymetallic Ore from Rudnik Mine. *Proceedings of the 37th IOC on Mining and Metallurgy*, Borsko jezero, Serbia, 206–213.

**Radulović, D., Jovanović, V., Ivošević, B. & Tešmanović, Lj. 2006.** Preconcentration of scheelite ore from the Rudnik Mine. *Proceedings of the 23th International Mineral Processing Congress*, Istanbul, Turkey, 3: 2012–2017.
RAKIĆ, S. 1952. Notes on the types of mineralization on the Rudnik mine in the Šumadija (Serbia). Bulletin of the Natural History Museum, Series A: 195–203. (in Serbian with German summary)

RAKIĆ, S. 1958. A new contribution to the knowledge of mineral assemblages of the Rudnik Pb-Zn mine in the Šumadija. Geologocal and Geophysical Bureau bulletin of the People’s Republic of Serbia, 16: 233–242. (in Serbian with German summary)

RAKIĆ, S. 1962. Classification of genetic types of Pb–Zn deposits related to Tertiary magmatism in the Dinarides on the basis of characteristics mineral assemblages. Proceedings of the Presentations V Counseling, Geological Association of Companies F.N.R. Yugoslavia, Belgrade, part II Mineralogy–Petrology–Ore Deposits: 189–195. (in Serbian and German).

RAKIĆ, S., DIMITRIJEVIĆ, R., & RADOŠA VLJEVIĆ, S. 1978. Sulfosalts of Srebrenica: boulangerite–sensseyite–jasmonite. Proceedings of the 9th Congress of Geologists of Yugoslavia, Sarajevo, Bosnia and Herzegovina, 386–390. (in Serbian with English summary)

RAMDOHR, P. 1980. The Ore Minerals and their Intergrowths. Pergamon Press, 1205 pp.

SERAFIMOVSKI, T., MANKOV, S. & CEFILGANEC, V. 1990. Bi-Se mineralization from the Cu deposit Bučim-Radoviš. Proceedings of the 12th Congress of Geologists of Yugoslavia, Ohrid, 73–85, (in Macedonian).

SERAFIMOVSKI, T. & ALEKSANDROV, M. 1995. Lead-zinc deposits and occurrences in the Republic of Macedonia. Special Issue 4: 387 pp. Faculty of Mining and Geology, Štip, (in Macedonian).

SERAFIMOVSKI, T., TASEV, G. & LAZAROV, P. 2006a. Au-Ag-Te-Bi-Se minerals associated with porphyry copper mineralization in the Buchim copper mine, Republic of Macedonia. Aurora-Ag-Te-Se deposits IGCP Project 486. Field Workshop, Izmir, Turkey: 154–158.

SERAFIMOVSKI, T., DONEC, T., TASEV, G. 2006b. New data concerning the major ore minerals and sulfosalts from the Pb-Zn Zletovo Mine, Macedonia. RMZ – Materials and Geoenvironment, 52 (3): 535–548.

SERAFIMOVSKI, T., TASEV, G. & STEFANOVA, V. 2013. Rare mineral phases related with major sulphide minerals in the Bučim porphyry copper deposit, R. Macedonia. Geologica Macedonica, 27 (1): 43–54.

SERAFIMOVSKI, T., TASEV, G. & STEFANOVA, V. 2015. Mineral assemblages group of major and associated mineral phases in the Kadiča porphyry copper deposit, Eastern Macedonia. Geologica Macedonica, 29 (2): 183–196.

SHIMAZAKI, H. & YAMAMOTO, M. 1979. Sulfur isotope ratios of some Japanese skarn deposits. Geochemical Journal, 13: 261–268.

SHIMAZAKI, H. & YAMAMOTO, M. 1983. Sulfur isotope ratios of the Akatami, Iide and Waga-Sennin skarn deposits, and their bearing on mineralizations in the “Green Tuff” region, Japan. Geochemical Journal, 17: 197–207.

SHIMAZAKI, H. & SAKAI, H. 1984. Regional variation of sulfur isotope composition of skarn deposits in the western most part of the Inner zone of Southwest Japan. Mining Geology, 34: 419–424.

SMEJKAL, S. & RAKIĆ, S. 1957. Mineral assemblages the lead-zinc ore deposits of Ajvalija, Prline and Kišnica. Vesnik ZGGI, 14: 7–28 (in Serbian with Germany summary).

STAJEVIĆ, B. & ZARIĆ, P. 1984. General characteristics of the ore paragenetic associations of the Golija Mt. Proceedings of the 2nd Symposium of the Yugoslav Association of Mineralogy, Kopaonik, 251–260. (in Serbian)

STOJOVIĆ, J., RADOŠAVLJEWIĆ, S., KAŠIĆ, V., BRANKOVIĆ, A., MARIJANOVIĆ, M. & MILOŠAVLJEVIĆ, B. 2004. The scheelite ore from the Rudnik orefield, near Gornji Milanovac. Proceedings of the 36th IOC on Mining and Metallurgy: Borsko jezero, Serbia, 26–30.

STOJOVIĆ, J. 2005. Mineralne paragenese rudne zone „Nova jama“ polimetalničnog ležišta Rudnik [Mineral parageneses of the “Nova Jama” ore zone from the Rudnik polymetallic deposit – in Serbian, with an English Abstract]. Unpubl. MSc Thesis. Faculty of Mining and Geology, University of Belgrade, 80 pp.

STOJOVIĆ, J., RADOŠAVLJEWIĆ, S., KARANOVIĆ, L. & CVETKOVIC, L. 2006a. Mineralogy of W-Pb-Bi ores from Rudnik Mt., Serbia. Neues Jahrbuch für Mineralogie - Abhandlungen, 182 (3): 299–306.

STOJOVIĆ, J., RADOŠAVLJEWIĆ, S. & KAŠIĆ, V. 2006b. Mineralogical and chemical analyses of the scheelite ore from Rudnik Mine, Serbia. Proceedings of the 23rd International Mineral Processing Congress, Istanbul, Turkey, 1: 215–217.

STOJOVIĆ, J., RADOŠAVLJEWIĆ-MIHALJOVIĆ, A., RADOŠAVLJEWIĆ, S., VUKOVIĆ, N. & PAČEVSKI, A. 2016. Mineralogy and genetic characteristics of the Rudnik Pb-Zn/Cu,Ag,Bi,W polymetallic deposit (Central Serbia) – New occurrence of Pb(Ag)Bi sulfosalt. Periodico di Mineralogia, 85 (2): 121–135.

SOKIĆ, M., RADOŠAVLJEWIĆ, S., MARKOVIĆ, B., MATKOVIĆ, V., STRBAC, N., KAMBEROVIĆ, Ž. & ŽIVKOVIĆ, D. 2014. Influence of Chalcopyrite Structure on Their Leaching by Sodium Nitrate in Sulphuric Acid. Metallurgical and Materials Engineering AMES, 20 (1): 53–60.

SUGAKI, A., KITKOE, A. & KOLMA, S. 1987. Bulk compositions of intimate intergrowths of chalcopyrite and sphalerite and their genetic implications. Mineralium Deposita, 22: 26–32.

TAKAGI, J. & TAKEUCHI, Y. 1972. The crystal structure of lilianite. Acta Crystallographica, B28: 649–651.

TERIŽ, M. & TERIŽ, S. 1972. Ignimbrite wider area of the Rudnik Mt. Proceedings of 7th Congress of Geologists, SFRJ, Zagreb, 2: 359–369. (in Serbian with English summary)

TERIŽ S.B., SOMMERAUER J. & HARNIK A.B. 1974. Macroseopic cosalite crystals from the Pb-Zn Ore Deposit Trepča (Yugoslavia). Schweizerische Mineralogische and Petrographische Mitteilungen, 54: 209–211.

TERIŽ S.B., SOMMERAUER J. & HARNIK A.B. 1975. Needle galena and cosalite from the Stari Trg-Trepča. Bulletin...
du Museum d'histoire naturelle, Serie A, 30: 5–12. (in Serbian with English summary)

TOMANEC, R. & LAZIĆ, P. 2012. Mineral composition of sulphide-oxide Pb-Zn ore from Rudnik mine. Underground mining engineering, 21: 15–159.

TOSOVIĆ, R. 1997. Morfogenetski tipovi oruđnjenja i paragenetske asocijacije u polimetaličnom ležištu Rudnik [Morphogenetic types of the ore mineralization and paragenetic association on the Rudnik polymetallic deposit – in Serbian, with an English Abstract]. Unpubl. MSc Thesis. Faculty of Mining and Geology, University of Belgrade, 109 pp.

TOSOVIĆ, R. 2000. Genetsko i geološko-ekonomsko modeliranje polimetaličnog ležišta Rudnik [A genetical and geology-economical modeling of the Rudnik polymetallic deposit – in Serbian, with an English Abstract]. Unpubl. PhD Thesis. Faculty of Mining and Geology, University of Belgrade, 259 pp.

VEZZONI, S., DINI, A. & ROCCH, R. 2016. Reverse telescoping in a distal skarn system (Campiglia Marittima, Italy). Ore Geology Reviews 77: 176–193.

VOUDOURIS, P., MELFOS, V., SPRY, P. G., BONSALL, T., TARKIAN, M. & ECONOMOU-ELIOPOULOS, M. 2008a. Mineralogical and fluid inclusion constraints on the evolution of the Plaka intrusion-related ore system, Lavrion, Greece. Mineralogy and Petrology 93: 79–110.

VOUDOURIS, P., MELFOS, V., SPRY, P. G., BONSALL, T.A., TARKIAN, M. & SOLOMON, C.H. 2008b. Carbonate-replacement Pb-Zn-Ag±Au mineralization in the Kama-riza area, Lavrion, Greece: Mineralogy and thermochemical conditions of formation. Mineralogy and Petrology 94: 85–106.

WERNICK, J.H. 1960. Constitutions of the AgSbS2-PbS, AgSbS2-AgBiSe, systems. American Mineralogist, 45: 591–611.

WU, L. & PETERSEN, U. 1977. Geochemistry of tetrahedrite and mineral zoning at Casapalca, Peru. Economic Geology, 72: 993–1016.

ZARIC, P., BORODADEF, Y.S., ARSENIJEVIĆ, M. & VUKASOVIĆ, M. 1984. Semseyite and native arsenic from Žuta Prla Pb-Zn deposit. Annual of the Yugoslav Association of Mineralogy, Kopaonik, Serbia, Abstracts 2: 22. (in Serbian)

ZARIC, P., RADOSAVLJEVIĆ, S. & JEKNIC, M. 1992a. The preliminary results on the presence of PGE-minerals in the Rudnik polymetallic deposit. Proceedings of the 24th IOC on Mining and Metallurgy, Donji Milanovac, Serbia, 76–78. (in Serbian with English summary).

Geol. an. Balk. poluos., 2018, 79 (1), 47–69.

**Résumé**

Prégléd polimetalične Pb-Zn-Cu-Ag-Bi-W rude rudnog pola Rudio, centralna Srbija

Srpsko-makedonska metalogenetska provenicija (CMMIP), prostorno zahteva mađi deo Istochne Bosne, veća deležne Srbiije i Makedonije, i na-stavila dale prema Bugarskoj i Grčkoj, sdržeci bojne i prostrene masse intruziv/vulkanogenih kompleksa kalko-alkalične magme. Površina njihovog ravinja iznosi oko 30.000 km² i prostire se preko tri krune geotehonske jedinice: Unutrašnjih Dinaresha, Vardarské tecton- ske zone and Srpsko-makedonske masse. U vezi sa ovim magmatickim kompleksima, direktnim ili indirek- nijem dejstvom, došlo je do stvaranja bojnih ležišta on pojava meta, u prvom redu Pb-Zn, Sb, zatim Cu, Mn, i u mažoj mjeri Fe, Bi, Ag, Hg, U, Sn i W.

Shumadijaska metalogenetska oblast predipada CMMIP. Maše metalogenetske jedinice izdvojene su u okviru rudnih pola: Avala-Kosmaj, Bukulja-Brajkovac, Rudnik i Kotležen (sl. 1a). Polimetalmaticko rudno pole Rudnik genetski je vezano za olokoenoski intruziv/vulkanogen kompleks. Sastoje se od nekoliko rudnih sektora sa visokim sadržajem Pb, Zn, Cu, i Ag; lokalno Bi, W i As. Skarnovni su Sr-tipa, i formirani su džun konta-kata krednih sedimenata i olokoenских dažaka i silova dažetskog i varac latiškog saставa. Odi- likuje se sa veoma raznolikim vrtstama rudnih i nerudnih minerala, gde se javljaju: sulfidi, sul- foarsenidi i arsenidi (pirot, pir, kolomorfini pir, bakteriodini pir, markasit, arsenopirin, sfaleritel, galelin, halkopirin, hal- koiropirin, kaban, makina, bitumin, mob- liđen, nicaland, argetopentland, gerd- sdrif, nikleriin), sulfosolici (gabonobismut, kozalit, Ag-ashamalmit, gavrat, širmerel, vi- kinit, Ag-tetraedrit, semcet), samorodni me- taši (bismut, srebro, zlato, plata), plata, grčke grupa elemenata – PGE, rodij, poladij, plata, oksidi (magnet, heman, rutil, anata, tenor, kupr, masik, minij, skrutin, cink), vorfamati (velji, nerudni minerali (kvarc, sani, adular, anaborni, fobi, klor, klorou, klinocin, sklenber, grani, ak- sim, epiot, minerali glina, anati, koron, mona-(Ce), sfe, leukosen, sendat, kalic, aragonit, ceruzit, smitson, anglez, bart, vitel, pla- xoditerolit, cink(Z) metallicak, limonit, gavrat, plenidokrokit, hlorohemati, malahit).

Glavni sulfidni minerali su Fe-sulfide, sfal- derel, galelin, halkopirin, arsenopirin i Ag-Pb- Bi sulfosolici. Kolomorfini agregati Fe-sulfida
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 порео). Коломорфни Fe-сулфиди представљају ти-пичне производе брзих и променљивих услова хидротермалног депоновања сулфидних минерала у оквиру високотемпературног стадијума (fS и fO, 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 магматизmom.

Минерални асоцијације изграђене су из неколико минералних парагенеза са карактеристичним полиметаличним саставом, које одражавају релативно бржи 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 из хидротермалних раствора у отвореним просторима (жице, шупљине и пукотине). Генерално, постоје две врсте орудњења: а) масивна, бречаста и/или штокверк-импрегнациони рудни тела – псевдостратификована и плочаста са релативно високим садржајем корисних метала, типична за рудне зоне Рудник, где доминирају плочаста и сложена скарн-метасоматска и хидротермално полиметалична Pb-Zn-Cu-Ag-Bi-W орудњења. Руднострукспонска испитивања потврдила су присуство скарн-метасоматског и хидротермалног стадијума (високо- до средње-температурног) у рудном пољу Рудника (табела 4), међутим, они су заступљени у променљивим односима. Минерали су депоновани у неколико узастопних стадијума и подстадијума, који су генетски везани за неогени магматизам. Главни рудни и типоморфни метали рудне области Рудник су Fe, Pb, Zn, Cu, Ag и Bi, и у мањој мерi W и Cd. Сви они имају заједничко високотемпературно депоновање (гранодиорит?), које одговара минерализационом циклусу који се дешавао уз два одвојена догађаја. Магматско порекло суморе депоновање изграђено је изотопским анализама сулфида на δ34S са различитих рудних тела (табела 3).

Основна карактеристика у полиметаличној руди рудништа Рудник је висок садржај типоморфних минерала Ag и Bi. Они су највећим делом у виду графит-импрегнационих раствора у галениту (реброносни галенит), а његовом декомпозицијом дуж ивица стварају сулфосоли Ag-Pb-Bi (викингит, ширмерит и густавит) и самородни бизмут. Поред њих, и остали Bi-сулфосоли су среброносне, што потврђује константно високу активност Ag и Bi током целог минерализационог циклуса. Мали део Ag се јавља у виду других минерала (Ag-тетраедрит, аргентопентландит, сабородно сребро). Друга важна геохемијска осиба је повећана концентрација сребра у оба типа орудњења, а то је типоморфно и за највећи део полиметаличних Pb-Zn лежишта СММП (на пример: Чумавићи, Сребреница; Велики Мајдан, Љубовија; Лече, Медвеђа; Ћирио и Калуђер, Лепосавић; Трепча, Стари Трг). У поређењу са њима, малих концентрација сребра у оба типа орудњења изграђено је изотопским анализама сулфида.

Минерални асоцијације и парагенезе утврђене су у рудним пољима Рудника, СММП (Борања, Голија, Стари Трг, Злетово-Кратово и др.). Према минералном саставу, оне су веома сличне минерализацијама Станоса (Халкидики, Северна Грчка), која су као срцеброносне нарушења и хидротермални системи Ларга у Румунији (Карпато-Балканска металогенетска провинција). У поређењу са њима, минералне асоцијације и парагенезе утврђене су у другим рудним пољима СММП (Борања, Голија, Стари Трг, Злетово-Кратово и др.). Према минералном саставу, оне су веома сличне минерализацијама Станоса (Халкидики, Северна Грчка), која су као срцеброносне нарушења и хидротермални системи Ларга у Румунији (Карпато-Балканска металогенетска провинција). У поређењу са њима, минералне асоцијације и парагенезе утврђене су у другим рудним пољима СММП (Борања, Голија, Стари Трг, Злетово-Кратово и др.). Према минералном саставу, оне су веома сличне минерализацијама Станоса (Халкидики, Северна Грчка), која су као срцеброносне нарушења и хидротермални системи Ларга у Румунији (Карпато-Балканска металогенетска провинција).