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 sulfoarsenides) 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 $f\mathrm{S}_2$ and $f\mathrm{O}_2$ 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.

Апстракт. Полиметалично Pb-Zn-Cu-Ag-Bi-W лежиште Рудник највеће и најдетаљније истражено лежиште у шумадијској металогенетској области. Састоји се од система рудних тела, која су груписана у неколико већих рудних зона. Рудна тела су псеудо-стратификована и плочастих форми, са релативно високим садржајем корисних метала. Средњи садржај главних рудних елемената у оквиру целог лежишта варира у широким границама: Pb (0,94–5,66%), Zn (0,49–4,49%), Cu (0,08–2,18%), Ag (50–297 ppm), Bi (~100–150 ppm), Cd (~100–150 ppm). Генерално, одређена је сложена Pb-Zn-Cu-Ag-Bi-W полиметалична минерална асоцијација. Најчешће распрострањени сулфидни минерали су Fe-сулфиди, арсено-пирит, халкопирит, сфалерит, галенит и сулфосоли. Водећи минерали Bi и Ag су Bi-сулфосоли. Одређене су: галенобизмутит, козалит, Ag-ашамалмит, викингит, ширмерит и густавит. Локално је утврђена

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мања појава Sb-сулфосоли са Cu, Ag и Pb. Јављају се сложени Ni-минерали (сулфиди, арсениди и сулфоарсениди) са Fe, Co и Ag, као последица присутних серпентинских стена и њиховог утицаја на принос Ni, Co и Cr у рудним хидротермалним растворима. Из групе волфрамата, утврђено је приметно до значајно јављање шелитне минерализације у рудним зонама Нова Јама, Гушави Поток и Азна. Присуство Bi-сулфосоли указује на температуре деповање >350°C, док појава аргентопетландита указује на температуре <455°C. Наизменично смењивање коломорфних трака пирита, пиротина и сидерита у реликтним остацима коломорфних агрегата, потврђује честе промене fS_2 и fO_2 у хидротермалним растворима. Изотопски састав сумпора указује да је извор рудоносних раствора магматски. Обогаћивање Bi и Ag такође потврђује магматско порекло рудоносних раствора. Присуство Bi-минерала представља значајни генетски индикатор за откривање повећаних концентрација Ag у оквиру рудних минерализација. Минерале јаловине представљају кварц, силикати, карбонати, оксиди и различити окси-хидроксиди. Посебан осврт дат је парагенетским односима и генетском значају минералних асоцијација као индикаторима услова формирања руде.

Кључне речи: рудна минералогија, Pb-Zn-Cu-Bi-Ag-W полиметалична руда, сулфосоли, рудно поље Рудник, Србија.

Introduction

The Rudnik orefield (ROF) is one of the numerous Pb-Zn polymetallic deposits belonging to the Serbo-Macedonian Metallogenic Province (SMMP), located in the central part of the Balkan Peninsula (Southern Europe) (Janković, 1990). The mineralizations of Tertiary magmatism are related to hydrothermal activity. Lead-zinc polymetallic mineralizations are known from different metallogenic districts, e.g., Podrinje (Central Serbia and Bosnia & Herzegovina), Šumadija (Central Serbia), Rogozna (Central Serbia), Stari Trg (Serbia-Kosovo province), Zletovo-Kratovo (FYR of Macedonia), Lavrion (Greece), and many other (e.g., Smejkal & Rakić, 1957; Aleksandrov et al., 1990a,b; Dangić, 1993; Tošović, 1997, 2000; Serafimovski et al., 1990; Serafimovski & Aleksandrov, 1995; Serafimovski et al., 2006a,b; Serafimovski et al., 2013, 2015; Radosavljević-Mihajlović et al., 2007; Voudouris et al., 2008a-b; Kołodziejczyk et al., 2015, 2016, 2017; Radosavljević 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 (Radosavljević 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-
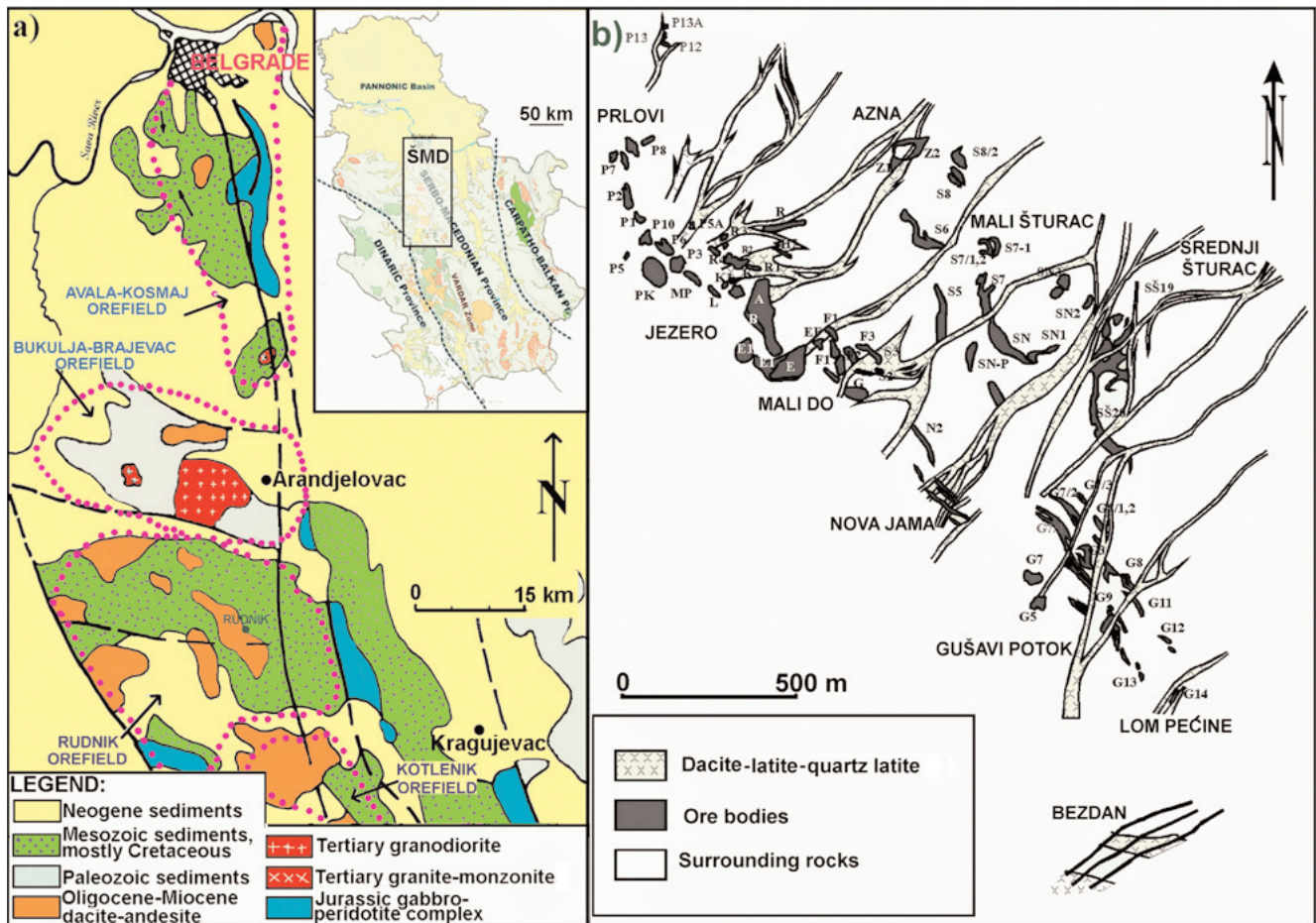

Fig. 1. **a)** Simplified geological map of the Šumadija Metallogenic District (ŠMD) showing the distribution of orefields (JANKOVIĆ 1990). Upper right corner shows exact location of ŠMD within Serbia (MONTHEL et al. 2002); **b)** Arrangement of ore zones within the ROF (according to TOŠOVIĆ 1997 and POPOVIĆ & UMELJIĆ 2015).

calkaline–shoshonitic and "slab-unrelated" alkaline magmas (CVETKOVIĆ et al., 2004; MARCHEV et al., 2005; AGOSTINI et al., 2010; NIMIS & OMENETTO 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 (PET-KOVIĆ, 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 (CVETKOVIĆ et al., 2004), and covers a relatively narrow area (up to 30 km in width) that extends from Belgrade to Kraljevo. The ŠMD is constituted of the

several small ore fields (JANKOVIĆ 1990): Avala-Kosmaj, Bukulja-Brajevac, Rudnik and Kotlenik (Fig. 1a).

The area of the ROF is of oval shape, elongated in NW–SE direction, and covers approximately 35 km² in areal extent (Fig. 1a). Sedimentary rocks are represented by sandstone, siltstone, limestone, Upper Cretaceous flysch, and marly limestone. The beginning of Oligocene dacite and quartz latite volcanic activity has an absolute age of 31.9–30.0 Ma (K–Ar on associated high-K volcanics – CVETKOVIĆ 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 (CVET-KOVIĆ 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 and disseminated mineralization types with extremely variable sizes. The thickness of ore bodies ranges up to 12 m, while length is up to 50 m along strike and depth. Mass of 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; Tomanec & 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 (BEI). The chemical compositions were determined using 1) a Link AN 1000 EDS microanalyser attached to a Jeol JSM-6460LV scanning electron microscope (SEM) at accelerating voltage 15 kV at counting time 250 using the ZAF-4/FLS software (Novi Sad); and 2) a Jeol JSM-6610LV SEM connected with an INCA energy-dispersion X-ray analysis unit at accelerating voltage20 kV for counting time 60 s (Belgrade). The following X-ray lines and standards (both natural (n) and synthetic (s)) were used 1) - $SK\alpha$ (n-$CuFeS_2$), $FeK\alpha$ (n-$CuFeS_2$), $PbM\alpha$ (n-PbS), $CuK\alpha$ (n-$CuFeS_2$), $AsK\alpha$, $L\alpha$ (n-FeAsS), $SbL\beta$ (n-Sb_2S_3), $ZnK\alpha$ (n-ZnS); pure metals for $AgL\alpha$, $BiL\alpha$, $CdL\alpha$, and $MnK\alpha$; 2) - $FeK\alpha$, $SK\alpha$ (FeS_2), $AsK\alpha$ (InAs), $SbL\alpha$ (InSb), $AgL\alpha$ (Ag_2Te), $PbM\alpha$ (PbS); pure metals for $NiK\alpha$, $CoK\alpha$, $CuK\alpha$ and $BiM\alpha$. EDX detection limits are $\sigma \sim 0.3$ wt%.

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

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

rials (Belgrade), the Institute of Mining and Metallurgy (Bor), and the Mine and flotation "Rudnik" Co. Ltd. (Rudnik).

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, WO_3= <0.02, Sb=0.01; Ag=29.3 ppm, Au=0.44 ppm (Radosavljević 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, WO_3=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.

	wt%					ppm	
	WO₃	Pb	Zn	Fe	Cu	Ag	Mo
1	1.06	0.27	0.06	1.86	0.01	9.0	160
2	0.44	0.02	0.01	1.72	<0.01	3.5	<50
3	0.03	0.02	0.02	1.77	<0.01	2.0	<50
4	0.99	0.74	1.08	2.92	0.04	14.0	75
5	4.48	0.27	0.05	2.89	<0.01	48.0	<50
6	0.78	0.27	0.06	2.19	<0.01	55.0	<50
7	0.35	0.39	0.09	0.37	0.03	5.0	130
Z-1	1.16	0.28	0.20	1.96	0.01	19.5	52
8	0.03	0.08	0.03	4.38	0.02	13.0	<50
9	0.03	0.68	0.16	5.12	0.02	47.0	<50
10	0.03	0.32	0.07	3.54	0.02	5.0	<50
Z-2	0.03	0.36	0.09	4.35	0.02	21.7	<50

Legend:
dacite
breccia
mineralized breccia
sandstone
mineralogical samples
chemical samples
zone 1 - stockwork scheelite-sulfide ore
zone 2 - disseminated scheelite-sulfide mineralization

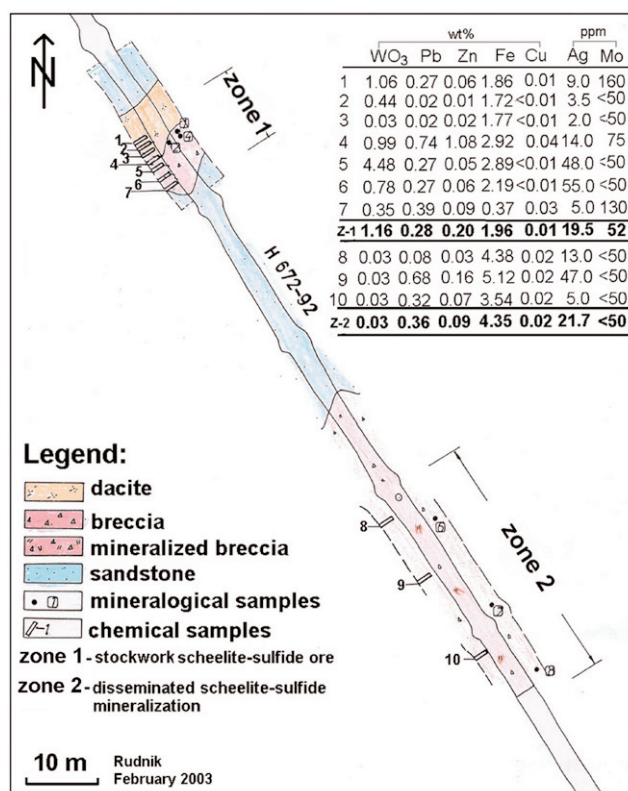10 m   Rudnik
February 2003

Fig. 2. Geological plan of the scheelite ore sampling from the gallery HI 672-92 (the Nova Jama ore zone; according to Radosavljević et al., 2003b).

Significant variations in contents of WO_3 have been determined in the scheelite ore (Z-1): 0.03-4.48 wt%, while in the mineralized zone (Z-2) WO_3 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, WO_3= 1.22 wt%; Ag= 20, Au= <0.5, Bi = 500, Mo= 200, Sn= 10 ppm.

According to the Pearson coefficient, a strong positive correlation has been determined between Bi and Ag (r = 0.947) and high between Pb and Ag (r = 0.624), while these are absent between all other metals within the Nova Jama ore zone. In the representative composite sample following trace elements were determined (MSA in ppm): Be 1, B 9, F 300, P 800, Cl 100, Ti 1000, Sc 70, V 20, Cr 200, Mn 400, Co 40, Ni 600, Ga 40, Se 20, Rb 1000, Sr 300, Y 5, Zr 300, Nb 100, Mo 60, Ag 40, Cd 10, In 0.8, Sn 10, Sb 20, Te 60, Cs 70, Ba 500, Rare Earths (La 8, Ce 20, Pr 3, Nd 20, Sm 5, Eu 1, Gd 10, Tb 1, Dy 5, Ho 0.3) Σ73.3, Hf 5, Ta 1, Tl 10, Th 2. Elements >1000: Na, Al, Si, S, K, 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 & Umeljić, 2015).

Ore mineralogy

Based on the microscopy study and EPMA, the following list of minerals was established: sulfides; sulfoarsenides and arsenides (pyrrhotite, pyrite, colloform pyrite, framboidal pyrite, marcasite, arsenopyrite, 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, willemite, 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
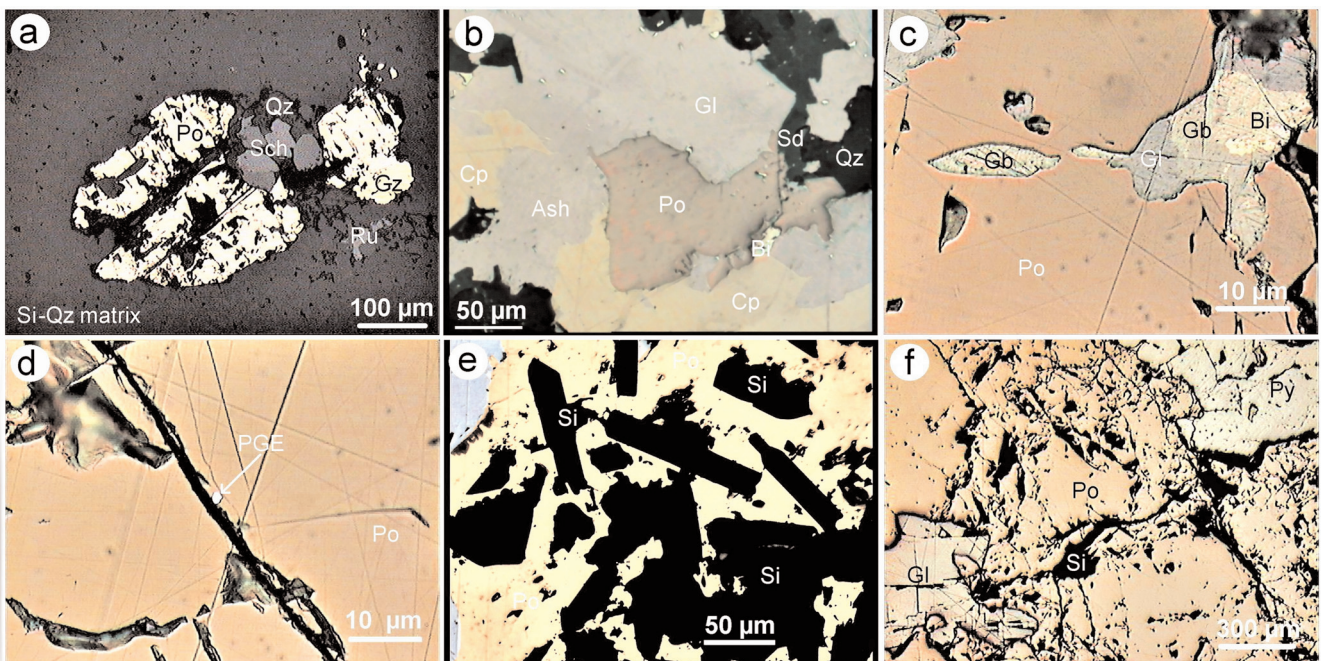

Fig. 3. Optical microscopy images showing the textural features of ore and gangue minerals of the ROF: **a)** tabular sections of pyrrhotite crystals (air, //N) – Nova Jama; **b)** pyrrhotite overgrown by Ag-bearing aschamalmite, galena and chalcopyrite (air, //N) – Azna; **c)** cracks and fractures of pyrrhotite cemented with native bismuth and Bi-sulfosalts (oil, //N) – Nova Jama; **d)** the inclusion of PGE-mineral embedded in pyrrhotite (oil, //N) – Nova Jama; **e)** newly formed hedenbergite penetrates through pyrrhotite (air, //N) – Azna; **f)** pyrrhotite overgrown by galena and pyrite (air, //N) – Azna. Abbreviations: Po – pyrrhotite, Py – pyrite, Cp – chalcopyrite, Sp – sphalerite, Gl – galena, – aschamalmite, Gb – galenobismutite, Bi – native bismuth, Sch – scheelite, Ru – rutile, Sd – siderite, Si – silicate, Qz – quartz (Rado-savljević & Stojanović (2003, 2006)).

silification manifested by appearance of quartz meta-crystals. The younger generation of pyrrhotite was formed in high-temperature hydrothermal mineralization phase in association with sphalerite, galena, chalcopyrite, 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; Radosavljević et al., 2006c, 2016). Although its presence is determined in the surrounding 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 transformation of pyrrhotite. It is related to the hypogenic transformation process of pyrrhotite established by Ramdohr (1980): pyrrhotite→ marcasite→ pyrite. Aggregates that have "bird's-eye" structure are less affected by alteration processes, which are similar to appearance of the colloform pyrite although they are compressed and oriented along of the pyrrhotite cleavage.

Pyrite appears in several generations in all ore zones. In the altered volcanic rocks, pyrite occurs in
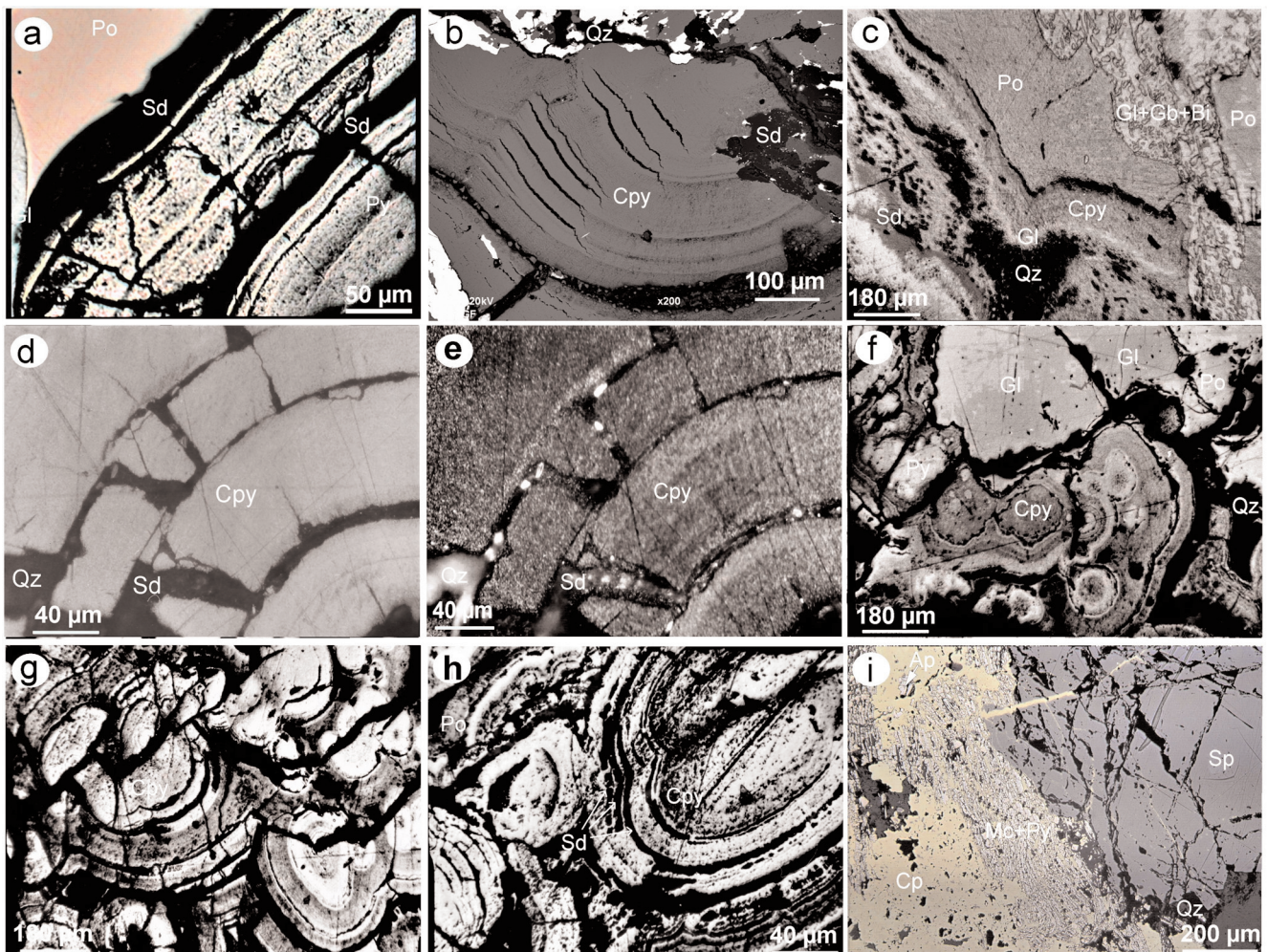

Fig. 4. Optical microscopy images in reflected light and BEI showing the textural features of ore and gangue minerals of the ROF: **a)** preserved forms of relic colloform pyrite, pyrrhotite and siderite cemented with galena (air, //N) – Azna; **b)** microscopic occurrence of a zonal colloform pyrite aggregate with various sulfides (light) (BEI) – Azna; **c)** a relic of colloform pyrite, pyrrhotite and siderite cemented with mixture of galena, native bismuth and Bi-sulfosalts (air, //N) – level 815; **d)** the annular forms of a colloforms pyrite relic (oil, //N) – level 815; **e)** anisotropic circular zone corresponds to the mix of marcasite-pyrite (oil, ×N) – level 815; **f)** a relic of colloform pyrite and siderite cemented with galena (air, //N) – Gušavi Potok; **g)** preserved forms of a colloform pyrite relic (air, //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, sphalerite 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 - Radosavljević & Stojanović (2006); Figures 4c-h - Zarić et al. (1992b); Figure 4i - this study).

euhedral crystal forms associated with pyrrhotite, 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–pyrrhotite and/or pyrite–pyrrhotite–siderite (Figs. 4b-h). Sometimes they form rhythmical zones cemented with siderite. Colloform pyrite is quite abundant mineral and is commonly cataclased and as relics embedded in younger sulfides in a form of "isolated islands".

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

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

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

Chalcopyrite displays diversity in its appearance within the Gušavi Potok and Nova Jama ore zones. The older generation is always associated with pyrrhotite, sphalerite, arsenopyrite, native bismuth and Bi-sulfosalts (Figs. 5b and 5d), while the younger mainly replaces all the other sulfides. Regularly, it contains skeletal portions of sphalerite, and commonly cemented cracks and fractures in pyrrhotite. Chalcopyrite occurs also as an exsolution oriented along the crystallographic directions in sphalerite (Fig. 5c). Chalcopyrite is the principal valuable mineral in the Azna ore zone. It either forms large masses or occurs as cement into 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_2S_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 pyrrhotite fissures, cataclased and fragmented pieces of older sulfides, and/or suppresses pyroxene along cleavage planes. Chalcopyrite, Bi-minerals and scheelite are characteristically concentrated in the lower parts of the Azna ore zone (level 720). Also, chalcopyrite appears with the same characteristics in the polymetallic ore from borehole No 197/12 (Fig. 5f). Cubanite also occurs in the form of thin lamellae in chalcopyrite and pyrrhotite, and represents exsolution from a more compositionally permissive chalcopyrite. EPMA showed that chalcopyrite has a typical stoichiometric chemical composition.
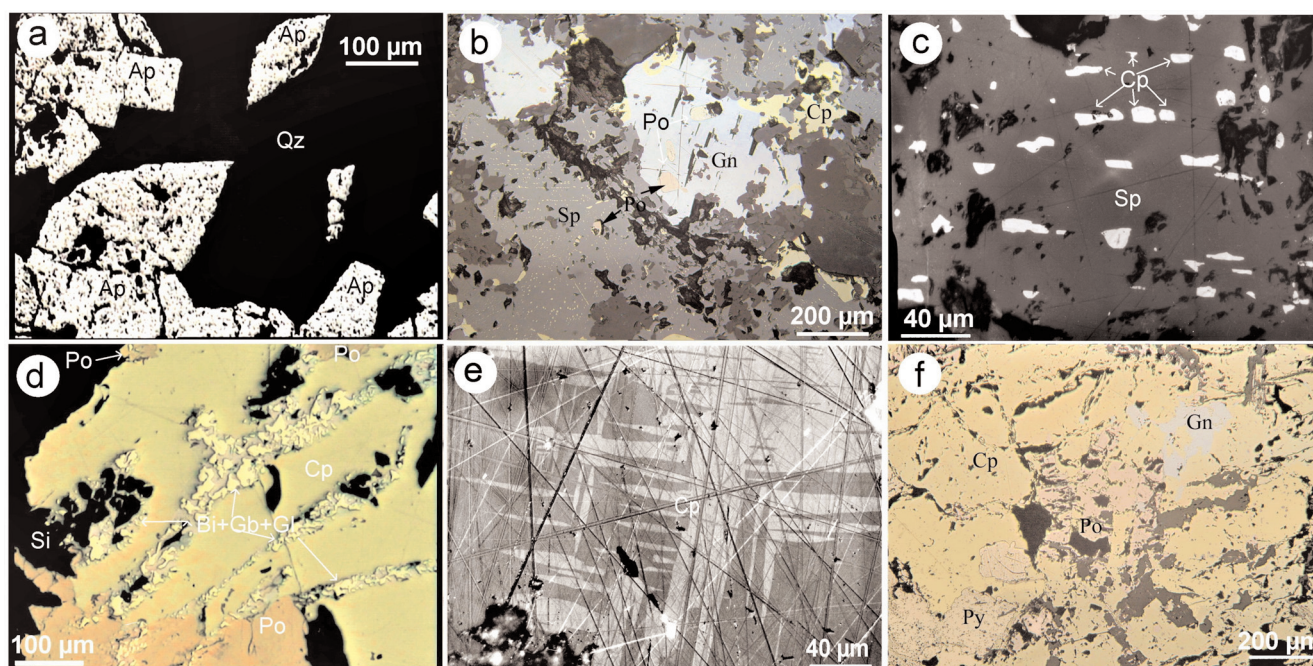
Fig. 5. Optical microscopy images in reflected light showing the textural features of ore and gangue minerals of the ROF: **a)** fractured and spongy arsenopyrite crystals in quartz matrix (air, //N) – Azna; **b)** a coarse-crystalline aggregate of sphalerite-chalcopyrite replaced by younger galena-siderite 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 - Radosavljević & Stojanović (2006); figures 5c, 5e - Zarić et al. (1992b); Figures 5b, 5f - this study).

Galena was formed in the high-temperature hydrothermal stage in the all ore zones. It occasionally replaces older pyrrhotite, but sometimes is replaced by younger pyrrhotite and chalcopyrite. The main characteristic of native bismuth is that it fills gaps between galena-pyrite contacts. It also forms free surfaces deposited in interspaces of pyrrhotite and silicates containing oriented inclusions of native silver and bismuth along crystallographic directions of galena. Galena is widespread in the Azna ore zone, but its relative abundance varies. It occurs as small "toothed" patches associated with pyrrhotite and silicates. To a lesser extent, galena is accompanied with pyrrhotite and chalcopyrite, and locally with native bismuth. Relics of spherulitic chalcopyrite and chalcopyrrhotite occur along sphalerite grain boundaries extensively overgrown by galena. Galena, embedded into chalcopyrite, is commonly replaced by Ag-bearing tetrahedrite and semseyite in the polymetallic ore from borehole No 197/12. (Figs. 6h-i). Galena sometimes has a fine mixture of exsolution of Ag-Pb-Bi sulfosalts with emulsions and droplets of native bismuth thus forming irregular "spongy" segments of up to 100 μm^2. AAS showed that galena commonly contains Ag between 0.10 and 1.70 wt% (argentiferous galena). Bismuth and Sb are below detection limits (< 0.01 wt%).

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

Cvetković (2001) described the occurrence of Ni-minerals (pentlandite, gersdorffite, and nickeline) in the footwall of the ROF (400 m beneath the surface). They are associated with the nickel-pyrrhotite mineral

paragenesis into serpentinite matrix. Moreover, gersdorffite has been microscopically discovered in the association with pyrrhotite, galena, Bi-sulfosalts, native bismuth, scheelite, Ti-minerals and quartz in the Nova Jama and Azna ore zones (Fig. 6a). Argentopentlandite, determined in the Azna ore zone, accompanied by native silver appears in a form of elongated crystals (90–115 μm in length), filling cracks and fissures in pyrrhotite (Fig. 7c). The chemical formula of argentopentlandite is as follows $Ag_{1.03}(Fe_{4.81}Ni_{3.14})_{\Sigma=7.95}S_{8.02}$ (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 $(Pb_{0.97}Cu_{0.05}Ag_{0.03})_{\Sigma=1.05}Bi_{1.97}S_{3.97}$ (Table 1). Galenobismutite contains noticeable Cu and Ag, and is also associated with chalcopyrite, Ag-bearing galena and native bismuth (STOJANOVIĆ et al. 2006). Lath-like to elongated aggregates composed of galena, galenobismutite, and native bismuth occur in chalcopyrite in the Azna ore zone (Fig. 5d).

Cosalite regularly appears in association with pyrrhotite, galena, chalcopyrite, native bismuth, arsenopyrite and pyrite (STOJANOVIĆ et al., 2006). Microscopically, the color of cosalite grains is light grayish-white to pale greenish. It is columnar to needle-like
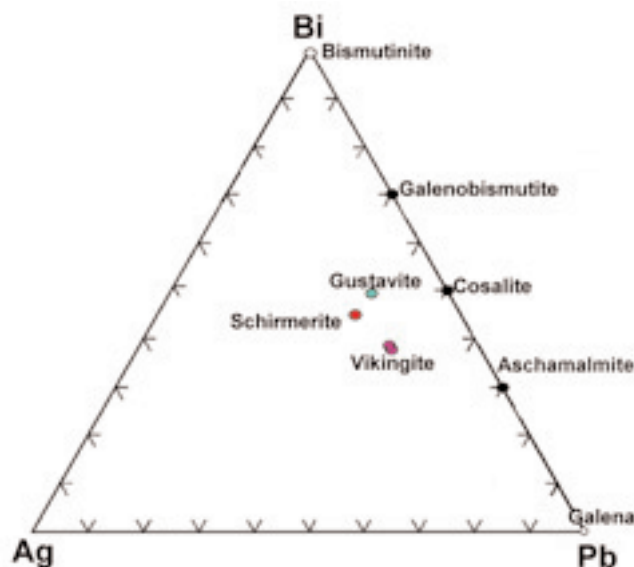

Fig. 6. Ternary Ag–Pb–Bi diagram of Bi-sulfosalts from the ROF showing intermediate kinds of lillianite–gustavite series, galenobismutite, cosalite and aschamalmite (atoms per formula unit).

Table 1. Representative average EPMA of **galenobismutite** (**1**), **cosalite** (**2**), **Ag-bearing aschamalmite** (**3**), vikingite (4-5), schirmerite (6) and gustavite (7) from different ore zones of the ROF (in wt%).

Element	1[a]	2[a]	3[b]	4[a]	5[c]	6[c]	7[c]
(n)	(6)	(4)	(6)	(2)	(1)	(1)	(1)
S	16.97	16.53	14.76	16.09	16.32	16.05	16.39
Se	-	-	0.04	-	-	-	-
Cu	0.46	0.53	-	-	-	-	-
Ag	0.44	0.52	1.12	8.01	9.30	8.90	7.88
Te	-	-	0.11	-	-	-	-
Pb	26.70	40.63	62.09	28.17	28.28	33.96	37.51
Bi	55.12	41.61	21.83	47.20	46.17	40.82	38.05
Total	99.69	99.82	99.94	99.47	100.07	99.73	99.83

Note: (n) number of analysis; - not detected (<0.3 wt%); [a]Nova Jama ore zone(STOJANOVIĆ 2005); [b]Azna ore zone(STOJANOVIĆ et al. 2016); [c]borehole No 197/12 (this study); 1–3 Pb(Ag)-Bi sulfosalts; 4–7 Ag-Pb-Bi sulfosalts; bolded minerals have been confimed by X-ray diffraction (XRD). General formulae of the sulfosalts were calculated according to MOËLO et al. (2008).

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 $(Pb_{1.91}Cu_{0.08}Ag_{0.05})_{\Sigma=2.04}Bi_{1.94}S_{5.02}$. Similar Ag and Cu contents to those from the ROF have been reported by several authors (TERZIĆ et al., 1974, 1975; RADOSAVLJEVIĆ-MIHAJLOVIĆ et al., 2007; VOUDOURIS 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 chalcopyrite. Microscopically, it occurs in a form of large irregular aggregates (>100 μm) cementing colloform Fe-sulfides, chalcopyrite, 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: $(Pb_{5.82}Ag_{0.20})_{\Sigma=6.02}Bi_{2.03}(S_{8.93}Te_{0.02}Se_{0.01})_{\Sigma=8.96}$ (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). It belongs to Bi-bearing vikingite and illustrates the coupled substitution of $Ag^{1+} + Bi^{3+} \leftrightarrow 2Pb^{2+}$ found in several Bi-sulfosalt (MAKOVICKY et al., 1992). From the borehole No 197/12, it always occurs in association with native bismuth as exsolution on the grain boundary of Ag-bearing galena (1.50 wt% Ag) (Fig. 7b). EPMA of a single grain gives following chemical formula: $Ag_{5.01}Pb_{8.03}Bi_{13.00}S_{29.95}$ (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 appears in mineral association with native bismuth as well as the exsolution in Ag-bearing galena. Microscopically, it is white with weak bireflectance and gray anisotropy (distinct to strong in oil). EPMA of a single grain gives chemical formula $Ag_{2.98}Pb_{5.91}B_{7.05}S_{18.06}$ (Table 1, Fig. 7d) and belongs to the last member of the solid solution $Ag_3Pb_3Bi_9S_{18}$ to $Ag_3Pb_6Bi_7S_{18}$. Due to the small grain size, it is not confirmed by using XRD. The identical sulfosalt

occurs within the polymetallic Pb(Ag)-Zn Veliki Majdan ore zone, Boranja ore field, West Serbia (RADOSAVLJEVIĆ et al., 2016c).

Microscopically, gustavite from the borehole No 197/12 is always associated with native bismuth as exsolution on the grain boundary of Ag-bearing galena (1.70 wt% Ag). It is white to grayish-white in tabular to chunky forms with white to greenish-gray bireflectance and moderate anisotropy (Fig. 7e). EPMA of a single grain gives following chemical formula: $Ag_{0.85}Pb_{1.30}Bi_{2.85}S_{6.00}$ (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 Stari Trg Pb(Ag)-Zn polymetallic deposit, Trepča ore field, Serbia (KOŁODZIEJCZYK et al., 2017).

Sb-sulfosalts

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

Microscopically, solid solution series $Cu_{10}(Fe,Zn)_2Sb_4S_{13}–Cu_{10}(Fe,Zn)_2As_4S_{13}$ within tetrahedrite-group have some optical distinctions in color, characterized by zonality with dominant tinge from coffee gray in central parts to greenish gray tint in peripheral parts (Fig. 7h). According to optical features, tetrahedrite minerals from the ROF belong to Ag-bearing varieties. They occur to a lesser extent in the form of small patches growing along boundaries of semseyite and galena, embedded in fissures of chalcopyrite. EPMA yielded two types of Ag-bearing tetrahedrite: I) Ag content of 31.10 wt%, and Ag/(Ag + Cu) atomic ratio of 0.55 (Table 2, Fig. 7i); and II) Ag content from 22.50 to 26.50 wt%, and Ag/(Ag + Cu) atomic ratio of 0.44 (Table 2, Fig. 7i). EPMA yielded following average chemical formula of Ag-bearing tetrahedrite: $(Ag_{5.47}Cu_{4.52})_{\Sigma=9.99}Fe_{2.01}Sb_{4.01}S_{12.99}$ (I), and $(Cu_{5.98}Ag_{4.11})_{\Sigma=10.08}Fe_{1.98}Sb_{3.95}S_{12.99}$ (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.

Semseyite belongs to a plagionite group together with fülöppite, plagionite and heteromorphite, forming homologous series. Semseyite, determined for the first time within the ROF, occurs in a form of isolated
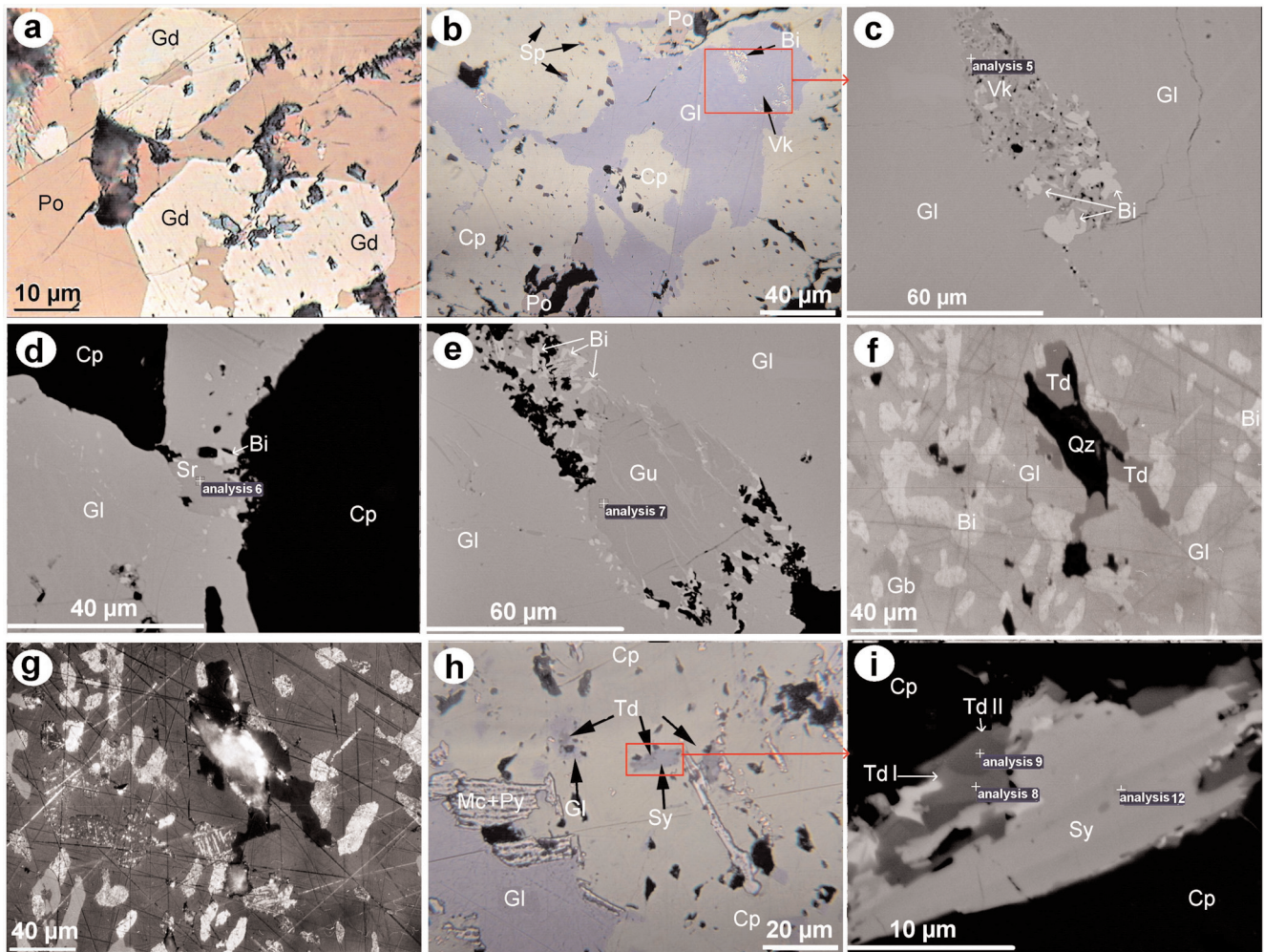
Fig. 7. Optical microscopy images in reflected light and BEI showing the textural features of ore and gangue minerals of the ROF: **a)** well-developed crystals of gersdorffite intergrown with pyrrhotite (oil, //N) – Nova Jama; **b)** chalcopyrite-galena-pyrrhotite mineral paragenesis with exsolution 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-arsenosulfides 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. 6h. 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. (1992в); Figures 7b-e and 7h-i - this study).

tabular crystals associated with galena and Ag-bearing tetrahedrite embedded in chalcopyrite matrix (Fig. 7h). EPMA yielded the following chemical formula: $Pb_{8.61}Sb_{8.28}S_{21.10}$ (Table 2, Fig. 7i). Due to the small grain size, it was not confirmed by XRD.

Native elements

Native bismuth, widespread into the ROF, occurs in several generations, and is commonly associated with Bi-sulfosalts, Ag-bearing galena and pyrrhotite (Figs. 3b-c, 5d). It occurs in a contact with pyrrhotite, rarely

silicates as veinlets (Fig. 8a), euhedral hexagonal and oval sections as inclusions in galena and scheelite (Fig. 8b), and as a product of the decomposition of the high temperature solid solution in Ag-bearing galena and Bi-sulfosalts (7b-d). EPMA yielded the following Ag contents: Nova Jama 0.67 wt%; Azna <0.3 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
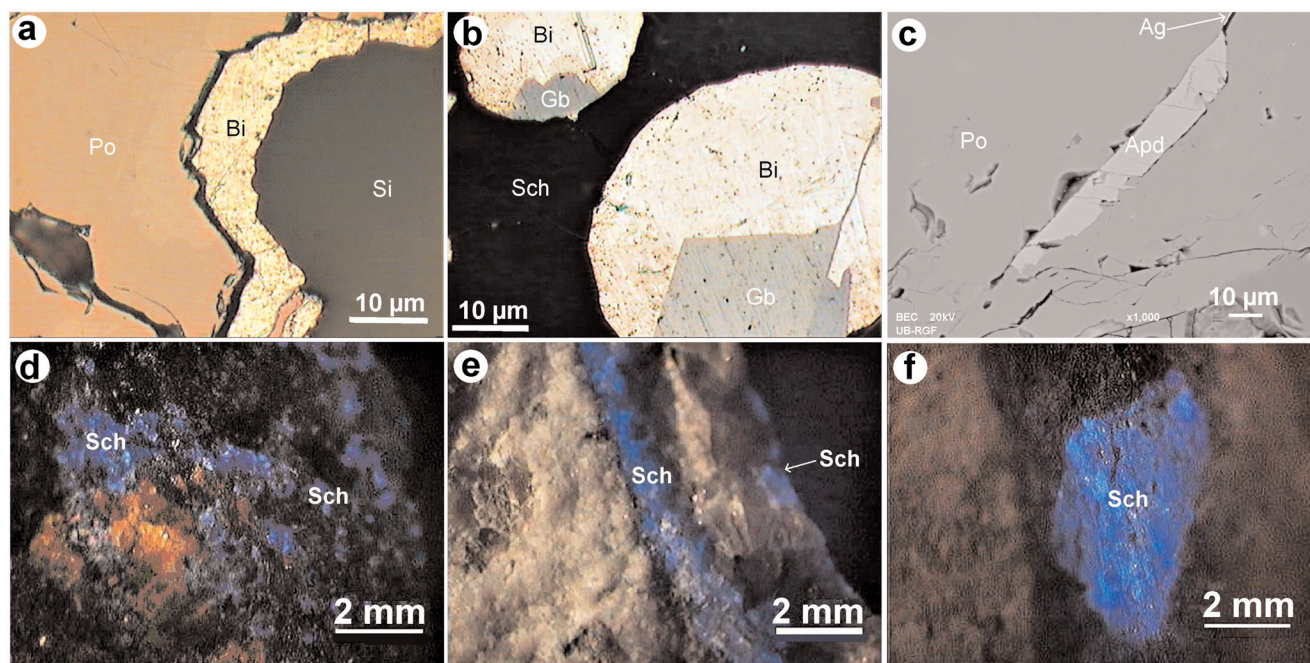
Fig. 8. Optical microscopy images in reflected light, BEI, and reflected UV-light (short wave) showing the textural features of ore and gangue minerals of the ROF: **a)** crust of native bismuth along the pyrrhotite-silicate contact (reflected light, oil, //N) – Nova Jama); **b)** galenobismutite embedded in spherulitic sections of native bismuth in the scheelite matrix (reflected light, oil, //N) – Nova Jama; **c)** argentopentlandite and native silver filling cracks and fissures in pyrrhotite (BEI) – Azna; **d)** scheelite crusts and coatings (fluorescent blue) – Nova Jama; **e)** scheelite veinless (fluorescent blue) – Nova Jama; **f)** scheelite single crystal embedded in the quartz-silicate matrix (fluorescent blue) – Nova Jama. Abbreviations: Po – pyrrhotite, Gb – galenobismutite, Apd – argentopentlandite, Ag – native silver, Bi – native bismuth, Sch – scheelite, Si – silicates, Qz – quartz. (All figures- Radosavljević & Stojanović 2003, 2006).

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

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

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

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, 2005; Stojanović et al., 2004, 2006a,b; Radulović et al., 2005, 2006; Milanović & Marković, 2009a,b; Magdali-

nović et al., 2010; Jonović et al., 2010; Radosavlje-vić, 2010; Sokić et al., 2014). 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 scheelite crystals from 0.02 to 40 mm (Fig. 8f) embedded in the quartz-silicate and/or quartz-sulfide matrix (the Azna ore zone; Radosavljević et al., 2003b, 2006; Stojanović, 2005; Stojanović et al., 2006).

Scheelite is grey-white to white, sometimes yellowish; with vitreous to diamond luster and white color of streak. Under the UV-short waves it is 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 majo-rity 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. granodiorite), 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: δS^{34}= +3.0 ‰ for pyrrhotite, +3.1 ±0.3 ‰ for sphalerite, +3.3 ±0.6 ‰ for chalcopyrite, +4.0 ±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 δS^{34} values, consistent with a source of sulfur from magmatic fluids (e.g. Shimazaki & Yamamoto, 1979, 1983; Shimazaki & Sakai, 1984). Minor fluctuations of δS^{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)	δS^{34} ‰
Pyrrhotite	Gušavi Potok (G-8)	689	+3.0
Sphalerite	Mali Do (S-7)	725	+3.5
Sphalerite	Gušavi Potok (G-9)	644	+3.0
Sphalerite	Srednji Šturac (SŠ-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	Prlovi (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–sphalerite–galena with Pb-Bi(Ag) sulfosalts); iv) micro-skarn (skarn silicates–sulfides–scheelite); v) high-temperature hydrothermal (colloform Fe-sulfides–arsenopyrite–siderite and chalcopyrite–sphalerite–galena with Ag-Pb-Bi-sulfosalts); vi) hypogene (pyrite–marcasite); vii) medium-temperature hydrothermal (sphalerite–chalcopyrite–Sb-sulfosalt 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 multi-stages skarn-replacement and high-temperature hydrothermal polymetallic mineral parageneses (Table 4).

The scheelite and pyrrhotite–sphalerite–galena with Pb-Bi(Ag)-sulfosalts paragenetic sequence are the most abundant within the ROF. The scheelite mineralization is commonly associated with mineralized silica breccias and/or potassic altered volcanic dykes. Mineral paragenetic analyses revealed at least several stages of skarn and ore formation. The first stage represents early prograde metasomatism, and is characterized by diopside-hedenbergite pyroxenes, and traces of andradite-grossular garnets. The second stage represents main-stage of prograde metasomatism and is characterized by axinite, hedenbergite, epidote, calcite, and quartz accompanied by rutile, anatase, 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-sphalerite-galena paragenetic sequence is represented by low-sulfidation state minerals deposited from low alkaline fluids (e.g. presence of pyrrhotite, Fe-bearing sphalerite, Ag-bearing tetrahedrite; according to EINAUDI et al., 2003). By changing of pH and temperature, the depo-

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

Stages	Paragenetic sequences
Pre-ore (Relict)	Sandstone – flysch – limestones – silicates – Ni-minerals – leucoxene – framboidal pyrite carbonic substances
Pyrometasomatic (skarnization 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 sanidine, adularia) – clay minerals Quartz I – molybdenite – scheelite I – magnetite I – rutile – anatase – monazite-(Ce)
High-temperature hydrothermal	Pyrrhotite I – sphalerite I– chalcopyrite I – chalcopyrrhotite – galena I – native silver – native bismuth I – bismuthinite – galenobismutite – cosalite – vikingite I – quartz II
Neocrystallization (Micro-skarn)	Diopside – hedenbergite – pigeonite – epidote II – scheelite II – pyrrhotite II – native PGE-minerals – argentopentlandite – gersdorffite – quartz II
High-temperature hydrothermal	Colloform Fe-sulfides – arsenopyrite – siderite I Sphalerite II – chalcopyrite II – native gold – cubanite – galena II – Ag-bearing aschamalmite – 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 – gustavite – Ag-bearing tetrahedrite – semseyite – quartz IV
Supergene	Covelline – mackinawite – marcasite III Anglesite – cerussite – smithsonite – willemite – hydrohetaerolite – zinc(II)metasilicate – goethite – lepidocrocite – hydrohematite – malachite – limonite tenorite – cuprite – massicot – scrutinyite – minium – zincite

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, Kopaonik, Trepča, Novo Brdo, Karavansalija, Blagodat, Crnac, and Kosmaj, Kotlenik, Koporić, Žuta Prlina, Ajvalija, Kižnica, Lece, Karamanica, 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 & Kullerud, 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 fO_2, pH field where H_2S and HS, were the prevailing sulfur aqueous species. Therefore, the most probable formation temperature ranges from 450° to 350°C.

Bi-sulfosalts can be valuable indicators of physico-chemical forming conditions due to their sensitivity to changings in temperature, Eh–pH, fS_2 and fO_2 (Cook & Ciobanu, 2004). According to Liu & Chang (1994), aschamalmite is not stable in PbS-PbSe-Bi_2S_3-Bi_2Se_3 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 Cu_2S–PbS–Bi_2S_3 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. Moëlo 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 inter-mediate phases of solid solution among lillianite homologues with high Ag content at the ROF, may suggest temperatures of 350–400°C, as it was pro-posed previously for Toroiaga deposit by Cook (1997) and the Stanos mineralization by Voudouris et al. (2013).

According to their mineral composition and MSA, transport of ore metals primarily took place in the form of acid halides (e.g. Zn, Fe, Cd) and basic poly-sulfide complex (e.g. Fe, Pb, Ag, Bi). However, the scheelite mineralization suggests that the later hy-drothermal fluids containing ore elements were large-ly complexed with halides (mainly Cl). According to MSA halide contents are as follows (ppm): F = 270 and Cl = 45 in pure pyrrhotite (Azna), F = <0.01 and Cl = 700 in pure scheelite (Nova Jama), Br and I not detected (<10 ppb) (Zarić et al., 1992b, Stojanović, 2005). However, the transport of ore elements was also possible with other anions (e.g. HS^-, H_3B^{2-}, H_3As^{2-}, $P_2O_7^{4-}$, KWO_4^-, HWO_4^-). Ways and direc-tions of movement of the hydrothermal fluids is not definitely known.

MSA showed the presence of all rare earth ele-ments (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–tourma-line–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 K_2O 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 (sanidine, "adularia"). High potassium content is a result of intensive K-metaso-matism 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 ŠMD. Pegmatites and greisens (Bukulja ore field – Sn-W), skarn-replacement, and high-temperature hy-drothermal 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 ŠMD, while the southern and northern parts of the ŠMD are typified by medium to low temperature hydrothermal mineral-izations (Avala ore field – Pb-Zn and Hg; Kotlenik ore field – Pb-Zn and Sb).

Conclusions

The present study consolidates all of the previous research conducted by Stojanović et al. (2006, 2016). The mineral associations of the ROF, composed of several mineral parageneses with characteristic poly-metallic compositions, propose a short interval of de-position (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, brecciat-ed, stockwork and/or disseminated ore bodies – pseu-dostratified and plate-like features with relatively high content of valuable metals, hosted in various sedimen-tary, 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, Molitve, and other loca-tions. Spatial distribution of mineral associations and metals has clear zonality manifested by deployment of FeS_2-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 poly-metallic mineralization dominate. Mineral parageneses, mineral chemistry, halide content and stable iso-tope 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-sul-fide 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 tipomorhic elements, such as Ag and Bi, are predom-inantly 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-bear-ing 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. Čumavići, Srebrenica, B&H – Radosavljević et al., 2016a; Veliki Majdan, Boranja, Serbia – Radosavljević et al., 1982; Lece, Medveđa, Serbia – Radosavljević et al., 2012; Crnac and Kaludjer, Rogozna, Serbia – Radosavljević et al., 2015; Trepča, Stari Trg, Kosovo, Serbia – Kołodziejczyk et al., 2016).

Besides the ROF, Bi-sulfosalt mineral parageneses have been identified in the Boranja ore field, Serbia (Dangić et al., 1984, Radosavljević-Mihajlović et al., 2007), in the Golija ore field, Serbia (Stajević & 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) sulfosalt mineral assemblages are very similar to those from the hydrothermal systems Larga in Romania (the Carpathian-Balkan Metallogenic Province – Cook & Ciobanu, 2004). In comparison to the other metallogenic districts within the SMMP, mineral associations of the ROF are distinguished by significant amounts and varieties of Ag-Pb-Bi sulfosalts and the unique occurrence of Ag-bearing aschamalmite.

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Резиме

Преглед полиметаличне Pb-Zn-Cu-Ag-Bi-W руде рудног поља Рудник, централна Србија

Српско-македонска металогенетска провинција (СММП), просторно захвата мањи део Источне Босне, веће делове Србије и Македоније, и наставља даље према Бугарској и Грчкој, садржи бројне и простране масе интрузив/вулканогених комплекса калко-алкалне магме. Површина њиховог развића у Србији износи око 30.000 km² и простире се преко три крупне геотектонске јединице: Унутрашњих Динарида, Вардарске тектонске зоне и Српско-македонске масе. У вези са овим магматским комплексима, директним или индиректним дејством, дошло је до стварања бројних лежишта и појава метала, у првом реду Pb-Zn, Sb, затим Cu, Mn, и у мањој мери Fe, Bi, Ag, Hg, U, Sn и W.

Шумадијска металогенетска област припада СММП. Мање металогенетске јединице издвојене су у оквиру рудних поља: Авала-Космај, Букуља-Брајковац, Рудник и Котленик (сл. 1а). Полиметалично рудно поље Рудник генетски је везано за олигоценски интрузив/вулканогени комплекс. Састоји се од неколико рудних сектора са високим садржајем Pb, Zn, Cu, и Ag; локално Bi, W и As. Скарнови су Са-типа, и формирани су дуж контаката кредних седимената и олигоценских дајкова и силова дацитског и кварц латитског састава. Одликује се са веома разноликим врстама рудних и нерудних минерала, где се јављају: сулфиди, сулфоарсениди и арсениди (пиротин, пирит, коломорфни пирит, бактероидни пирит, маркасит, арсенопирит, сфалерит, галенит, халкопирит, халкопиротин, кубанит, макинавит, бизмутинит, молибденит, пентландит, аргентопентландит, герздорфит, никелин), сулфосоли (галенобизмутит, козалит, Ag-ашамалмит, густавит, ширмерит, викингит, Ag-тетраедрит, семсеит), самородни метали (бизмут, сребро, злато, платинска група елемената – ПГЕ, родијум, паладијум, платина), оксиди (магнетит, хематит, рутил, анатас, тенорит, куприт, масикот, минијум, скрутинит, цинкит), волфрамати (шелит), нерудни минерали (кварц, санидин, адулар, андезинит, амфиболи, биотит, хлорити, клиноцоизит, хеденбергит, гранати, аксинит, епидот, минерали глина, апатит, циркон, монацит-(Се), сфен, леукоксен, сидерит, калцит, арагонит, церузит, смитсонит, англезит, барит, виљемит, хидрохетеролит, цинк(II) метасиликат, лимонит, гетит, лепидокрокит, хидрохематит, малахит).

Главни сулфидни минерали су Fe-сулфиди, сфалерит, галенит, халкопирит, арсенопирит и Ag-Pb-Bi сулфосоли. Коломорфни агрегати Fe-сулфида

карактеристични су за СЗ делове лежишта (Азна), и јављају се као жућкасто-црне до сивкасте „шагренасте" куглица (10–15 mm), које образују неправилне гроздасте до бубрежасте агрегате. Од стране појединих аутора они су погрешно дефинисани као „оолитни пирит" (седиментно порекло). Коломорфни Fe-сулфиди представљају типичне производе брзих и променљивих услова хидротермалног депоновања сулфидних минерала у оквиру високотемпературног стадијума (*f*S и *f*O, температура, притисак и др.). Такође, исти аутори погрешно су објаснили порекло „бактероидног пирита", који је генетски неоспорно везан за присутне старије седименте, и нема никакве генетске везе са млађим неогеним магматизмом.

Минерализације шелита значајне су и за сада су најперспективније у рудном сектору Нова Јама, где се јавља у виду штокверк-импрегнационих нагомилања. На основу урађених технолошких и металуршких експеримената из ове W-руде, комбинованим методама издвојен је сулфидно-шелитски концентрат, из којег су добијена једињење WO₃, као и чисти метали Bi и Ag.

Минералне 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-импрегнациона рудна тела – псеудостратификована и плочаста са релативно високим садржајем корисних метала, типична за рудне зоне Азну, Нову Јаму и остале, и б) жична рудна тела депонована у горње кредном флишу или кварц латитима, карактеристична за лежишта Бездан, Молитве, и на другим локацијама. У оквиру рудне области Рудник просторни распоред минералних асоцијација и метала има изражену зоналност, која се испољава размештајем жичних тела са FeS₂-Pb-Zn-Cu минерализацијама около централног дела лежишта, где доминирају плочаста и сложена скарн-метасоматска и хидротермално полиметалична Pb-Zn-Cu-Ag-Bi-W орудњења.

Рудномикроскопска 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 мери W и Cd. Сви они имају заједничко магматско порекло (гранодиорит?), које одговара минерализационом циклусу који се дешавао уз два одвојена догађаја. Магматско порекло сумпора потврђено је изотопским анализама сулфида на δS³⁴ са различитих рудних тела (табела 3).

Основна карактеристика у полиметаличној руди рудног поља Рудник је висок садржај типоморфних метала Ag и Bi. Они су највећим делом у виду високотемпературних „чврстих" раствора у галениту (среброносни галенит), а његовом декомпозицијом дуж ивица стварају се Ag-Pb-Bi сулфосоли (викингит, ширмерит и густавит) и самородни бизмут. Поред њих, и остале Bi-сулфосоли су среброносне, што потврђује константно високу активност Ag и Bi током целог минерализационог циклуса. Мањи део Ag се јавља у виду других минерала (Ag-тетраедрит, аргентопентландит, самородно сребро). Друга значајна геохемијска особина 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; Леце, Медвеђа; Црнац и Калуђер, Лепосавић; Трепча, Стари Трг).

Поред рудне области Рудника, сличне Bi-сулфосолне минералне парагенезе утврђене су и 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 такође део алпске металогенетске јединице и хидротермалним системима Ларга у Румунији (Карпато-Балканска металогенетска провинција). У поређењу са њима, минералне асоцијације и парагенезе рудног поља Рудника издвајају се значајним присуством и варијететима Ag-Pb-Bi сулфосоли и јединственом појавом среброносног ашамалмита.