



Low-temperature Ni-As-Sb-S mineralization of the Pb(Ag)-Zn deposits within the Rogozna ore field, Serbo-Macedonian Metallogenic Province: Ore mineralogy, crystal chemistry and paragenetic relationships



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ABSTRACT

The Rogozna ore field (ROF) belongs to the Serbo-Macedonian Metallogenic Province (SMMP), and covers a part of the western Dinarides rim and the Vardar ophiolite zone, situated within the Neogene volcanogenic-intrusive complex of calc-alkaline and shoshonitic rocks within the territories of Serbia and Kosovo. It is well-known for its Cu(Au, Pb, Zn) skarn mineralization and Pb(Ag)-Zn hydrothermal deposits and occurrences. Mineral associations, deposition order and genesis of the ROF were discussed in detail. Complex ore parageneses were determined in the Crnac, Plakaonica, and Kaludjer Pb(Ag)-Zn deposits and are composed of the following minerals: sulfides (pyrrhotite, chalcopyrrhotite, chalcopyrite, sphalerite, galena, pyrite, marcasite, millerite, bravoite), sulfosalts (arsenopolybasite, tetrahedrite, Ag-bearing tetrahedrite, Zn-bearing tetrahedrite, semseyite, heteromorphite, jamesonite, ferrokesterite), arsenides (nickeline), sulfarsenides and sulfantimonides (gersdorffite, Sb-bearing gersdorffite, Fe-bearing gersdorffite, As-bearing ullmannite, arsenopyrite), native metals (native Au, native Ag), oxides (Cr-spinel, rutile, anatase, leucoxene, magnetite, hematite) and gangue minerals (quartz, silicates, chalcedony, carbonates, monazite(Ce), barite, gypsum, anglesite, cerussite, smithsonite, zaratite, limonite). The high-, medium-, and low-temperature hydrothermal mineral assemblage occur throughout the Pb(Ag)-Zn deposits at Kaludjer-Crnac-Plakaonica ore system, in which the whole ore field as high- to medium-temperature hydrothermal formed at shallow to moderate depth. The following stages of ore mineral formation are recognized in the Pb-Zn mineral assemblage at the ROF: i) pre-ore; ii) high-temperature hydrothermal; iii) hypogene; iv) medium-temperature hydrothermal; v) low-temperature hydrothermal; and vi) supergene. Generally, there are two types of mineralization, brecciated ore veins with ribbon-like textures deposited in amphibolites or in contact with quartz latites, and impregnations within columnar ore bodies hosted in silicified and carbonated serpentinites (listwaenites). Ni-mineralization is represented by significant sulphide, arsenide, sulfarsenide, and sulfantimonide occurrences, but the most significant consists of gersdorffite-ullmannite series (GUS) minerals. It is the most developed in the Kaludjer deposit, much lesser at Plakaonica, whereas in the Crnac deposit it was not noted. The importance of the Ni mineralization is of scientific interest for now, as the attention has been directed only to the exploration of lead and zinc. However, it is believed that plans for the future will be focused on a detailed study of nickel.

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1. Introduction

The Serbo-Macedonian Metallogenic Province (SMMP) includes ore deposits formed within the collision zone of the Dinarides and the Carpatho-Balkanides during closing of the Tethys-Paratethys Ocean. It covers a small part of eastern Bosnia and Herzegovina (B&H), larger parts of Serbia and the Former Yugoslav Republic of Macedonia

(FYRM), and also extends towards Bulgaria and Greece (Fig. 1a). The SMMP contains numerous volcanic-intrusive complexes of calc-alkaline and shoshonitic affinity (Janković, 1990). The areal extent of the SMMP covers around 30,000 km² in the territory of Serbia and extends over the three major geotectonic units: the Vardar ophiolite zone, the Serbo-Macedonian massif, and the inner Dinarides (Anđelković, 1978; Cvetković et al., 2004; Grubić, 1974; Neubauer, 2002; Resimić-Šarić et al., 2009). These igneous complexes are directly associated with the development of numerous deposits and metal occurrences; primarily as Pb, Zn, Sb, then Cu and Mn, and to a lesser

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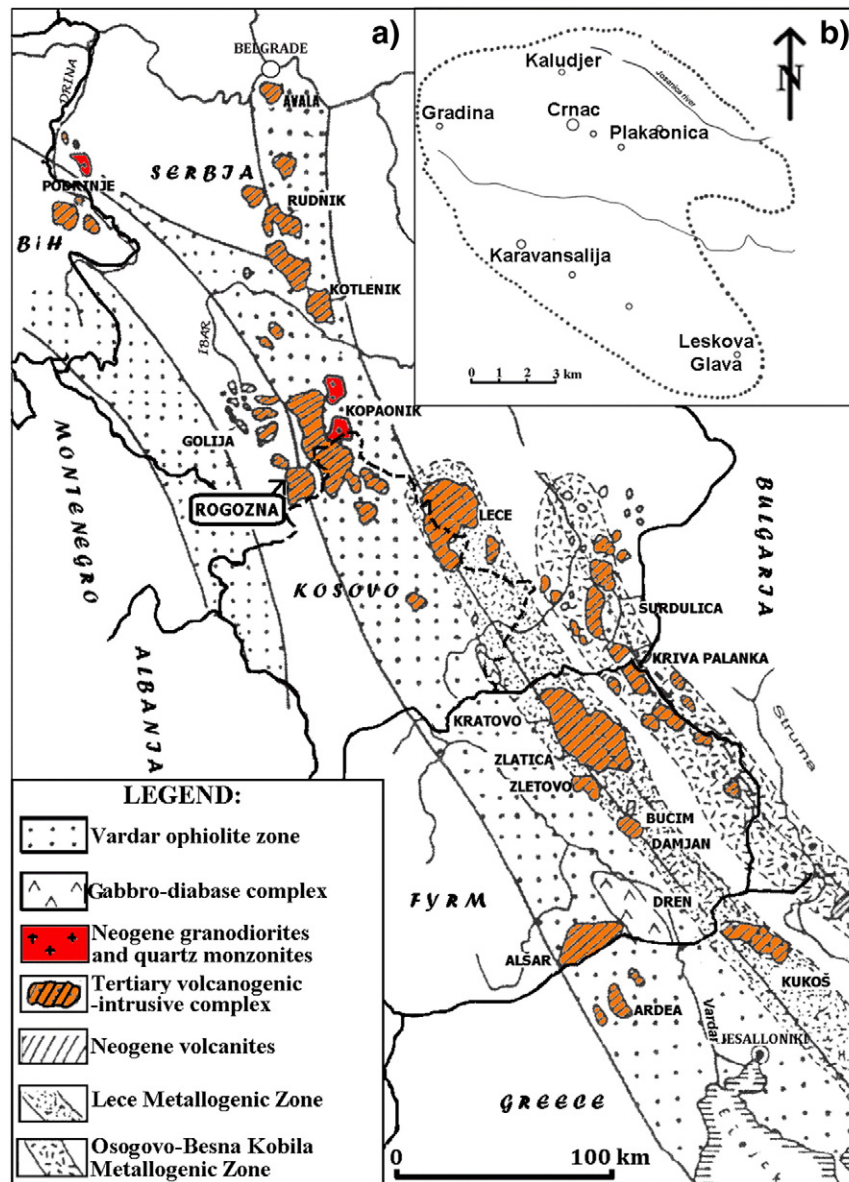


Fig. 1. a) Simplified geological map of the SMMP demonstrating distribution of ore fields (Janković, 1990), b) Location of ore deposits within the ROF.

extent Fe, Bi, Ag, Hg, U, Sn, and W. Ore deposits related to these Neogene igneous complexes of the SMMP are clustered into several metallogenic districts as shown in Fig. 1a: Fruška Gora, Podrinje (Cer, Boranja, Srebrenica), Šumadija (Avala, Kosmaj, Bukulja, Rudnik, Kotlenik), Kopaonik (Željina, Kremiči, Centralni Kopaonik, Kriva Reka, Raška, Belo Brdo, Krva Reka, Koporčić, Trepča, Ajvalija), Golija (Lisa-Crni Vrh, Radulovac, Kaldura, Asanovo selo i dr.), Rogozna, Merdare (Lece, Novo Brdo, Dražanj), Bujanovac, and Besna Kobila (Ruplje, Blagodat, Mačkatica, Karamanica, Radovnica) (Janković, 1990).

Nickel occurrences, associated with Pb-Zn mineralization, are mostly along contacts with the Vardar ophiolite zone. Besides Rogozna ore field (ROF), in the territory of Serbia within the SMMP these were found in several localities, including the Rajičeva Gora Pb-Zn-Sb polymetallic deposit, as well as the Central Kopaonik ore field (Janković and Zarić, 1980), Ni-Fe-Cu(Pb, Zn, Sb) sulfide polymetallic mineralization of the Asanovo Selo ore field (Stajević and Zarić, 1984), the Rudnik Pb-Zn-Cu(Bi, W, Ag) ore field (Cvetković, 2001), the Lece Pb-Zn-(Au) polymetallic deposit (Radosavljević et al., 2011) (Fig. 1a). These are mainly local occurrences represented by Ni-sulfides and Ni-sulfantimonides with rare Ni-arsenides. Elsewhere in Europe, similar

Ni-mineralization has been noted in Tunaberg, SE Bergslagen, Central Sweden (Dobbe, 1991), and Bottino, Apuane Alps, Italy (Benvenuti et al., 1989). Apart from the fact that these are Pb-Zn deposits like the ROF, a common feature is that the nickel originated from ultramafic rocks and precipitated from low-temperature hydrothermal solutions. Unlike the ROF and Bottino, Bergslagen is an occurrence of cobalt (a (Co,Ni)-Sb-S mineral association: ullmannite NiSbS, cobaltian ullmannite (Ni,Co)SbS, and willyamite (Co,Ni)SbS). In addition, within the SMMP in the territory of FYRM, Serafimovski et al. (2010) reported occurrences of Ni sulfides (bravoite and polydymite) in Cu-Au porphyry deposits of the Buchim-Damjan-Borov Dol Ore District.

Nickel mineralization in Pb(Ag)-Zn deposits of the ROF occurs in the Kaludjer deposit to a greater extent, lesser in the Plakaonica, whereas in the Crnac deposit it was not determined. On top of the Kaludjer deposit, which is an open pit mine, hostrocks and ore outcrops are typically manifested with green coatings of secondary Ni-minerals.

The aims of the present study are to evaluate the geological, mineralogical and chemical characteristics of the Pb(Ag)-Zn deposits of the ROF, to obtain information regarding the paragenetic ore sequence and to contribute to an understanding of the distribution of ore minerals

and associated mineralizations. Special emphasis is given on data obtained from optical microscopy and paragenetic research of Ni-Sb-As-S minerals and principal sulfides, which were used to define ore-forming conditions. The genesis of the Rogozna Pb(Ag)-Zn deposits and the spatial distribution of Ni-minerals and related ores were also compared with other metallogenetic districts and ore fields within the SMMP in the territory of Serbia and Kosovo.

2. Geology, structure and metallogenic characteristics of the Pb(Ag)-Zn deposits

The Pb(Ag)-Zn deposits at Crnac, Kaludjer, and Plakaonica form part of the ROF, which is located between Raška (Serbia), Novi Pazar (Serbia), and Mitrovica (Kosovo). The ROF is delineated by the Ibar River from the S and E, and by the Raška River from the NW. Crnac and Plakaonica were exploited during the Roman Empire, and during medieval time, and again in modern times for 50 years in the 20th century. Between the two World Wars, research in this area was carried out by the British. Crnac and Kaludjer are located within the territory of Serbia; Plakaonica is situated in Kosovo (Fig. 1b).

Volcanic/plutonic magmatism, initiated by one of the post-orogenic phases during the Palaeogene-Neogene with an age of 27–29 Ma (Borojević-Šošarić et al., 2013; Cvetković et al., 2004; Janković, 1995),

caused the formation of the granitoid complex of Rogozna (Pavlović and Todorović, 1961).

Palaeozoic schists, Triassic metamorphics, serpentinites, Jurassic shales, amphibolites, gabbros, and Neogene volcanic rocks are the main lithological units hosting the Rogozna Pb(Ag)-Zn deposits (Fig. 2a). Triassic metamorphics include a lower series of amphibolites and amphibole-pyroxene hornfels and an upper series consisting of plagioclase-andalusite gneisses and mica-cordierite hornfels. The serpentinites, an integral part of the Ibar peridotite massif belonging to the Vardar ophiolite zone, form the hanging wall of the Crnac deposit. Jurassic shales are poorly represented and are noted only in the western parts of the Crnac deposit. Gabbros, amphibolites, and gabbro-amphibolites appear beneath the serpentinites in the northern parts of the Crnac deposit (Miletić, 1995).

The Neogene volcanic rocks consist of andesite pyroclastics, and quartz latite dykes. The andesite pyroclastics overly the Triassic metamorphic rocks and the serpentinites in the southern parts of the Crnac deposit, while the quartz latite dykes are associated with contact zones of the amphibolites and the serpentinites (Miletić, 1995).

The listwaenites, considered to be formed after complete silicification and carbonatization of the serpentinites during hydrothermal processes are common hosts for mineralization elsewhere in the SMMP (e.g. Antonović and Vasković, 1992; Borojević-Šošarić et al., 2013; Dimou and Papastavrou, 1987; Miletić, 1995). In the Crnac deposit they

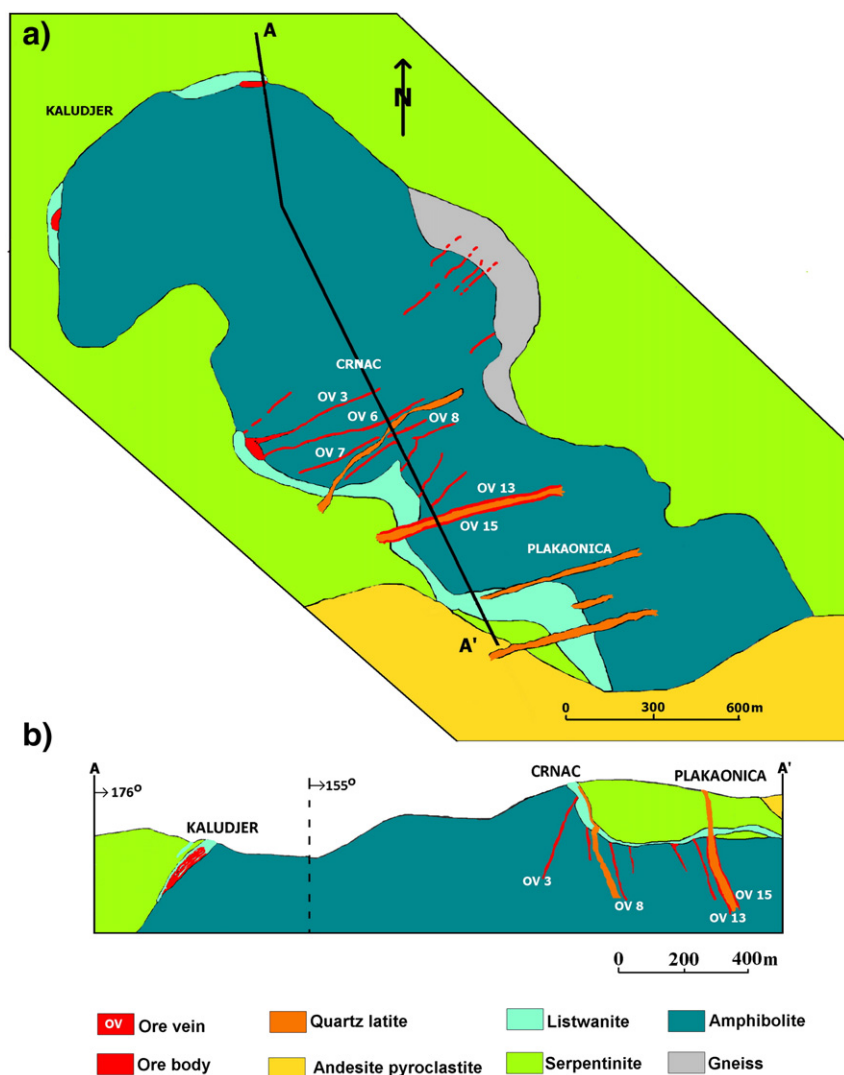


Fig. 2. a) Schematic geological plan view of the horizon IV of the Kaludjer-Crnac-Plakaonica ore system (Miletić, 1995); b) Schematic geological profile A-A' of the Kaludjer-Crnac-Plakaonica ore system (Miletić, 1995).

occur in a lesser extent in the footwall contacts of the serpentinites with amphibolites, and in the western parts of the ROF beneath the Neogene volcanic rocks (Fig. 2a).

The Rogozna Pb(Ag)-Zn deposits and occurrences (Crnac, Plakaonica, Kaludjer, Leskova Glava, etc.) are genetically connected to the calc-alkaline and shoshonitic volcanic-intrusive complex of Rogozna (Fig. 1b). There is also a genetic relation of the intrusive complex with the formation of a low grade Cu-Au-Mo-Pb-Zn polymetallic skarn mineralization in the Gradina – Karavansalija – Obradov potok (Fig. 1b). This mineralization style is uncommon for Neogene igneous complexes formed along the Vardar ophiolite zone and its rim. According to Janković (1995), Cu in the magma was probably sourced from the serpentinite basement and surroundings, and was mobilized during magma ascent through the metamorphic rocks. In spite of previous research, the volcanic-intrusive complex of Rogozna can not be considered fully delineated in terms of its mineral resource potential. Most likely, the reserves of mineral resources are far greater than those verified by previous exploration activities, particularly as regards the deeper parts of the terrain which may contain blind ore deposits (Carter, 2008).

In the eastern portions of the ROF, in a zone 15 km long and 1.2 km wide, from Kaludjer to the NW to Leskova Glava to the SE, amphibole-pyroxene hornfels were discovered beneath the serpentinites and Jurassic amphibolites (Fig. 2b).

The relationship between the serpentinites and Triassic metamorphic rocks is typically tectonic. According to Miletić (1995), during the initial phase of obduction of the serpentinites, it is likely that the contact between serpentinite and Triassic metamorphics was subhorizontal. As a result of continuing tectonic deformation in a NW direction, the serpentinite-Triassic metamorphics contact constitutes an anticlinal structure. After erosion of the anticline, remaining lateral limbs of the contact are manifest as faults, which control the ore bodies in the Crnac deposit, as well as numerous other occurrences in the SE of Crnac. The simultaneous effect of compressional forces perpendicular to the axes of the antiform contact resulted in formation of transverse faults filled with quartz latite dykes and ore veins (Miletić, 1995).

The Crnac Pb(Ag)-Zn deposit occurs along the contact between hanging wall serpentinites and footwall Triassic amphibolites. During pre-mineralization hydrothermal processes, intensive silicification of the serpentinites close to the contact with the amphibolites led to the formation of listwaenites, which along with the amphibolites are the host rocks for the mineralization (Fig. 2b). Besides vein-type mineralization in the amphibolites, impregnations and veinlet-type ore bodies are found in the listwaenites at the intersection axis of ore veins and the amphibolite-serpentinite contact. Closer to the amphibolite contact, ore veins are more massive. Towards the core of the antiform, amphibolite bodies are trending WSW-ESE, and less commonly in a SW-NE direction, from 200 to 500 m of depth before pinching out. In the northern and southern parts of the Crnac deposit they dip towards NW, and S, respectively (Miletić, 1995).

Lense-like ore veins are usually 0.2–2 m wide. High-grade ore zones of Crnac, up to 10 m wide, consist of subparallel arrays of ore veins (OV 7, Fig. 2a, Novović, 1978). In the southern part of the Plakaonica deposit, these same rupture structures control emplacement of both quartz latite dykes and ore veins. It is important to point out that faults trend in a NE-SW direction. Silicification (e.g. quartz-chalcedony) along the mineralized faults at Plakaonica accompanies metallic minerals in the form of veins, veinlets, and impregnations very similar to that present at the Crnac deposit.

The geological framework of Kaludjer is similar to the adjacent Crnac and Plakaonica. Amphibolites comprise the country rock, with the schists occurring on top of the amphibolites. The ore body (horizontal cross section area of 1100 m²) occurs at the contact between footwall serpentinites, and amphibolites, and irregular bodies of quartz latite at the hanging wall of the deposit (Fig. 2b). On the surface the ore body trends about 150 m in the ENE direction and dips 30–60° to the ESE.

Its thickness ranges from several meters to a maximum of 20 m. The ore body is a silicified and carbonatized listwaenite, created by the influence of hydrothermal solutions on serpentinites. Besides Kaludjer, other listwaenite-hosted ore deposits also occur at Plakaonica, in amphibolite-serpentinite contacts. These ore bodies, frequently associated with quartz latite dykes, are of elongated or isometric forms with impregnation mineralization (Jovičić, 1988).

The grade of Pb and Zn in the ore veins range from 1.70 (Kaludjer) to 8.55% (Crnac and Plakaonica), and from 3.45 (Kaludjer) to 3.82% (Crnac and Plakaonica), respectively. Pyrite, galena, and sphalerite are the principal ore minerals, while sulfides of Fe, Cu, and As, and sulfosalts of Pb, Ag, and Sb (Miletić, 1995).

3. Materials and analytical methods

Samples of Pb(Ag)-Zn ores were collected during 1988 from the Crnac and Plakaonica mine shafts (IV and V horizons, 3, 6, 7, 8, 10, 11, 13, 15 ore veins, a total of 42 polished sections); the Kaludjer open pit mine and the gallery 818 (8 polished sections); and the Plakaonica tailings dump (10 polished sections) (Fig. 2a, b). Polished sections were prepared for reflected-light microscopy and electron microprobe analyses (EPMA) after following standard preparation and polishing steps (Picot and Johan, 1982).

The polarizing microscope Carl-Zeiss, model “JENAPOL-U” equipped with a system for a photomicrography was used for ore microscope investigations. The reflectance measurements of nickeline, millerite and gersdorffite from the Kaludjer deposit were performed in air from 400 to 700 nm using a Vickers M-74 reflectance polarizing microscope equipped with an EMI 9592 B photomultiplier with S-10 response and a SiC-standard N° 154 supplied by Carl Zeiss, Oberkochen. Four values (470, 546, 589, 650 nm) supplied by the IMA/COM were obtained by interpolation. Microhardness measurements with a Durimet Leitz instrument were made on 10 grains (5 indentations) in which a load of 100 g of force was applied for 15 seconds.

EPMA were obtained at the Faculty of Mining and Geology, University of Belgrade, using a JEOL JSM-6610LV scanning electron microscope (SEM) connected with an INCA energy-dispersion X-ray analysis unit (EDX). An acceleration voltage of 20 kV was used. All analyzed samples were coated with carbon (15 nm thick layer, density 2.25 g/cm³). For quantitative analyses of sulfides, sulfarsenides, sulfantimonides and arsenides, the following standards were used: FeS₂ (FeK α , SK α), ZnS (ZnK α , SK α), Mn (MnK α), Ni (NiK α), Co (CoK α), Cu (CuK α), InAs (AsK α), InSb (SbK α), SnO₂ (SnL α), Ag₂Te (AgL α), CdS (CdL α), HgS (HgM α), PbS (PbM α) and Bi (BiM α).

For quantitative analyses of oxides, carbonates, and phosphates, the following standards were used: kyanite (AlK α , SiK α), apatite (PK α , CaK α), chromite (CrK α , AlK α , MgK α , FeK α), LaB₆ (LaL α), CeO₂ (CeL α), NdF₃ (NdL α), Nb (NbL α) and Ta (TaM α). EDX detection limits are 2 σ ~0.3 wt%, (counting time 60 s). Chemical formulae of sulfides, sulfarsenides, sulfantimonides, and arsenides were calculated according to Anthony et al. (1990), while oxides, carbonates and phosphates were calculated according to Ramdohr (1980).

Contents of cadmium and manganese extracted from selected sphalerite and galena grains were obtained by the atomic absorption spectroscopy method (AAS-Perkin Elmer AA-300).

4. Ore mineralogy

Two types of mineralization are recognized in the Pb(Ag)-Zn deposits of the ROF: i) ore veins in contacts of amphibolites with quartz latite dykes, typical for Crnac and Plakaonica, were deposited along brecciated fault zones. ii) columnar ore bodies in silicate-carbonate altered serpentinite-amphibolite (listwaenite) occurring above ore veins in amphibolites and are typical for the Kaludjer and Plakaonica deposits.

On the basis of ore microscopy, physical, and chemical analyses, the following minerals occur in ore bodies of the Crnac, Plakaonica and Kaludjer deposits: Sulfides (pyrrhotite, chalcopyrrhotite, chalcopyrite, sphalerite, galena, pyrite, marcasite, millerite, bravoite), sulfosalts (arsenopolybasite, tetrahedrite, Ag-bearing tetrahedrite, Zn-bearing tetrahedrite, heteromorphite, jamesonite, ferrokesterite, semseyite), arsenides (nickeline), sulfarsenides and sulfantimonides (gersdorffite, Sb-bearing gersdorffite, Fe-bearing gersdorffite, As-bearing ullmannite, arsenopyrite), native metals (native Au, native Ag), oxides (Cr-bearing spinel, rutile, anatase, leucoxene, magnetite, hematite), and gangue minerals (quartz, silicates, chalcedony, carbonates, Ce-bearing monazite and barite). Gypsum, anglesite, cerussite, smithsonite, zaratarite and limonite are supergene minerals.

4.1. Sulfides

Millerite is present in all parts of the Kaludjer deposit as a widespread nickel mineral, while in the Plakaonica deposit it is only noted in trace amounts. It occurs as euhedral spear-like crystals, embedded in recrystallized sphalerite or galena. Radial bundles of millerite are usually formed in sphalerite aggregates, while in galena it occurs in the form of subparallel elongated fine needles (0.05–0.40 mm), and rarely as isometric deltoid sections. Anisotropy of millerite is strong with high yellow, blue to violet reflectance and shows strong

bireflectance, ranging from light yellow to creamy yellow (Figs. 3a, 6). Measured reflectance curves intersect in blue spectra (470 nm), at Ro and Re values of 48.0%. Compared with published data (Beran and Mohsenzadeh, 1982), its optical values are somewhat higher, which is most probably a result of crystal orientation and mineral chemical composition. The microhardness, measured along basal and longitudinal sections, was determined to be 176–178, and 206–322 kg/mm², respectively, and is in good agreement with literature data (Chvilyova et al., 1988). EPMA of millerite from the Kaludjer deposit yielded Ni, S, Zn, and Co contents: 61.82–63.49, 35.27–35.38, 0.63–2.04, and 0.42–0.53 wt%, respectively, with a following average chemical composition of (Ni_{0.97}Zn_{0.02}Co_{0.01})_{Σ1.00}S_{1.00}. Fe, Cu, As, and Sb were not detected (Table 1).

Bravoite, identified only in the Kaludjer deposit, is extremely rare. It occurs in the central parts of crystals of Ni-sulfarsenides. EPMA yielded a very complex chemical composition with the following chemical formula: (Fe_{0.65}Ni_{0.24}Cu_{0.08}Ag_{0.03})_{Σ1.00}(S_{1.83}Sb_{0.10}As_{0.07})_{Σ2.00} (Table 1). Ag in Ni minerals is not very common; however, the Ag in Ni-bearing argentopentlandite is well-known in numerous localities in the world (e.g. Augsten et al., 1986; Barkov et al., 2002; Benvenuti, 1991; Groves and Hall, 1978; Maier et al., 2008; Némec and Scharmová, 1992).

Fe sulfides were determined in all three deposits and represent minerals that are quite common minerals in the ore. Pyrrhotite usually

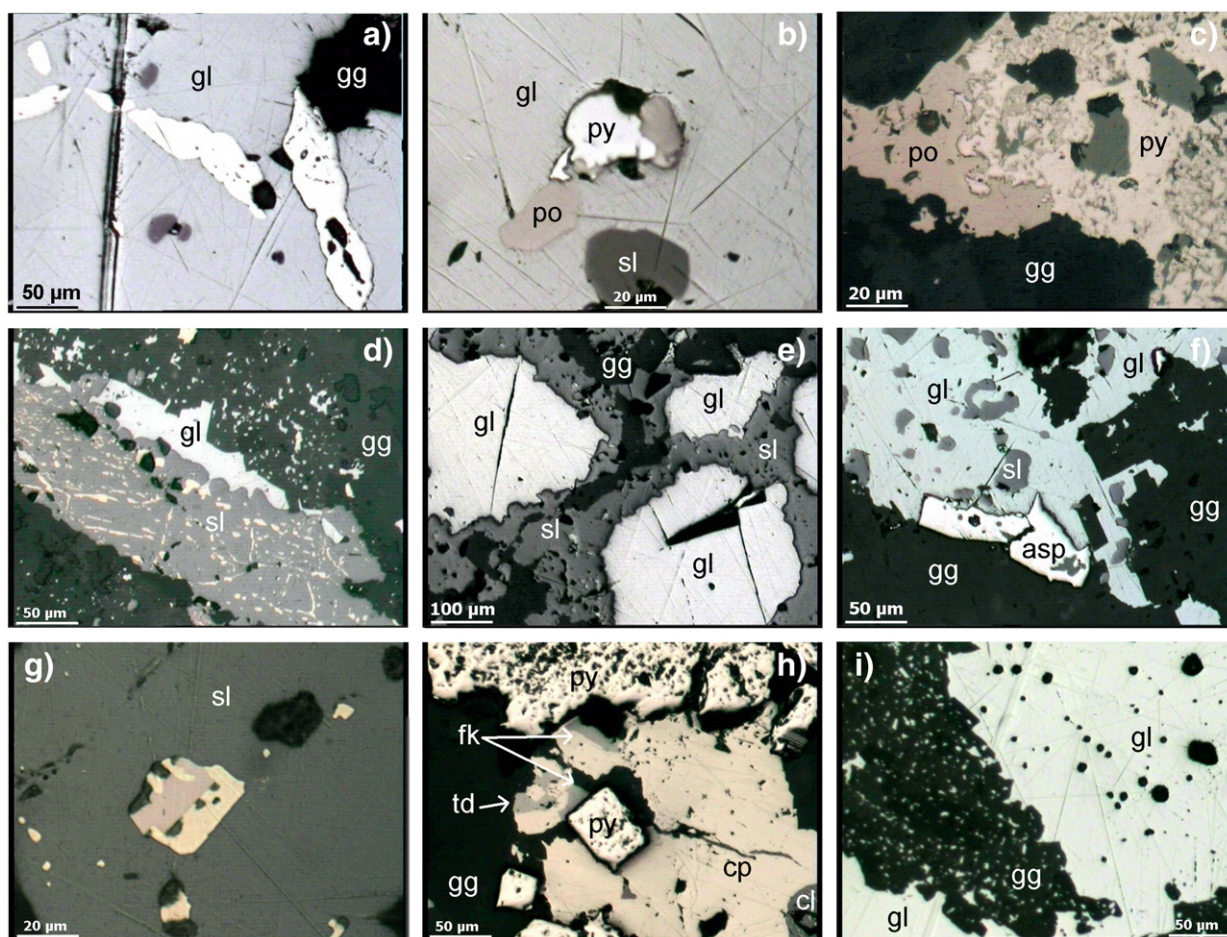


Fig. 3. Reflected light photomicrographs of sulfide minerals of the ROF: a) needle-like crystals of millerite (bright white) embedded in galena (white), Kaludjer (air, //N); b) pyrrhotite II (“neopyrrhotite”) (pale pink) partially transformed into pyrite (light yellow) embedded in galena (white), Plakaonica (air, //N); c) a pyrrhotite → pyrite hydrothermal transformation accompanied by magnetite (dark gray), Plakaonica (air, //N); d) thick and ribbon-like chalcopyrite disease (yellow) in sphalerite (light gray), Plakaonica (air, //N); e) a colloform texture of galena (white) and sphalerite (gray), Plakaonica (air, //N); f) a colloform texture of sphalerite (gray) in galena (white) with arsenopyrite (white), Plakaonica (air, //N); g) a chalcopyrite (pink-yellow) inclusion in sphalerite (gray), Plakaonica (air, //N); h) a pyrite assemblage (yellow) cemented with a chalcopyrite-tetrahedrite aggregate and quartz (black), Crnac (air, //N); i) gaseous or liquid blebs in galena (white), Plakaonica (air, //N); Mineral abbreviations: gn – galena, sl – sphalerite, cp – chalcopyrite, po – pyrrhotite, py – pyrite, asp – arsenopyrite, td – tetrahedrite, fk – ferrokesterite, ml – millerite, gg – gangue minerals.

Table 1
Representative average EMPA and atomic proportions of Ni-minerals from Kaludjer and Plakaonica (in wt%).

| Deposit | Mineral | (n) | S | Mn | Fe | Cu | Co | Ni | Zn | Ag | As | Sb | Total |
|------------|-----------------------------|------|-------|------|-------|------|------|-------|------|------|-------|-------|-------|
| Kaludjer | Nickeline | 5 | n.d. | n.d. | n.d. | n.a. | n.d. | 43.37 | n.d. | n.a. | 53.78 | 2.73 | 99.88 |
| | Millerite | 3 | 35.33 | n.d. | n.d. | n.a. | 0.49 | 62.71 | 1.37 | n.a. | n.d. | n.d. | 99.90 |
| | Gersdorffite | 6 | 19.07 | n.d. | 0.30 | n.a. | 0.45 | 31.47 | 2.43 | n.a. | 42.06 | 4.02 | 99.80 |
| | Sb-bearing gersdorffite | 8 | 17.75 | n.d. | 0.11 | n.a. | 0.04 | 31.14 | 0.91 | n.a. | 29.75 | 19.97 | 99.65 |
| | As-bearing ullmannite | 1 | 15.49 | n.d. | n.d. | n.a. | n.d. | 27.25 | 1.27 | n.a. | 6.28 | 49.53 | 99.81 |
| | Bravoite | 1 | 43.45 | n.d. | 26.74 | 3.91 | n.d. | 10.40 | n.d. | 2.06 | 4.06 | 8.98 | 99.59 |
| Plakaonica | Gersdorffite | 9 | 19.14 | 0.19 | 3.00 | n.a. | 0.36 | 30.40 | 1.60 | n.a. | 45.04 | n.d. | 99.74 |
| | As-bearing ullmannite | 1 | 16.10 | n.d. | n.d. | n.a. | n.d. | 30.03 | n.d. | n.a. | 11.46 | 42.33 | 99.92 |
| | Fe-bearing gersdorffite | 2 | 18.90 | n.d. | 12.69 | n.a. | 4.96 | 15.50 | 3.16 | n.a. | 44.52 | n.d. | 99.72 |
| Kaludjer | Atomic proportions Σ | | | | | | | | | | | | |
| | Nickeline | - | - | - | - | - | - | 1.00 | - | - | 0.97 | 0.03 | 2 |
| | Millerite | 1.00 | - | - | - | - | 0.01 | 0.97 | 0.02 | - | - | - | 2 |
| | Gersdorffite | 1.00 | - | 0.01 | - | 0.01 | 0.90 | 0.06 | - | 0.95 | 0.06 | 3 | |
| | Sb-bearing gersdorffite | 1.00 | - | 0.03 | - | - | 0.96 | 0.02 | - | 0.71 | 0.30 | 3 | |
| | As-bearing ullmannite | 0.99 | - | - | - | - | 0.96 | 0.04 | - | 0.17 | 0.84 | 3 | |
| Plakaonica | Bravoite | 1.83 | - | 0.65 | 0.08 | - | 0.24 | - | 0.03 | 0.07 | 0.10 | 3 | |
| | Gersdorffite | 0.99 | 0.01 | 0.09 | - | 0.01 | 0.86 | 0.04 | - | 1.00 | - | 3 | |
| | As-bearing ullmannite | 0.99 | - | - | - | - | 1.01 | - | - | 0.30 | 0.69 | 3 | |
| | Fe-bearing gersdorffite | 0.98 | - | 0.38 | - | 0.14 | 0.44 | 0.08 | - | 0.99 | - | 3 | |

Note: (n) number of analyses; n.d. not detected (< 0.03 wt%); n.a. not analyzed, n.a. not analyzed, Σ -number of atoms per formula unit.

occurs as intergrowths with sphalerite or as relics in hydrothermally altered pyrite and magnetite. Moreover, spherulitic pyrrhotite II (“neopyrrhotite”) in galena and quartz contain up to 1.41 wt% Ni, without the presence of Co and As (Fig. 3b). Pyrite is mainly a product of recrystallization via marcasite and hydrothermally transformed pyrrhotite (Fig. 3c). It is usually cataclased and cemented by younger sulfides or carbonates. Recrystallized pyrite aggregates are of typical stoichiometric composition, but they may contain up to 0.59 wt% As (without any presence of Ni and Co). Marcasite occurs throughout the ROF. Hydrothermal marcasite is the main mineral shown in OV 6, and is ubiquitous within the Plakaonica deposit. Younger generations of marcasite generally grow over older pyrite aggregates.

Sphalerite is widespread and occurs in several generations. The oldest is Fe-rich and belongs to the marmatite variety. It frequently contains irregular blebs of pyrrhotite, chalcopyrrhotite, and chalcopyrite (Fig. 3d). Fe-rich sphalerite mostly occurs at Crnac and Plakaonica, while in Kaludjer it was not found. The second generation is without chalcopyrite disease, but it sometimes contains Ag-bearing tetrahedrite that rims grain boundaries. This variety is characteristic as colloform spheres around galena (Fig. 3e, f). It is usually cataclased and cemented by silicates. The third generation belongs to sphalerite with low Fe content (cleophrane), which is widespread in the Kaludjer deposit. It frequently contains gaseous and liquid inclusions, and bundles of idiomorphic acicular millerite. The youngest sphalerite aggregates are often penetrated and overgrown along grain boundaries by younger sulfantimonides and sulfarsenides of nickel. EPMA showed that sphalerite contains from 0.5 to 20.2 mol% of FeS. The Fe-rich varieties are characterized by 16.2 to 20.2 mol% FeS and contain up to 1.9 wt% Mn, 0.55 wt% Cd, and 0.13 wt% of In, while Ni, Ge, Tl, and Sn are below detection limits. The Fe-poor sphalerite contain from 0.5 to 5.5 mol% FeS and up to 1.4 wt% Cd, 0.2 wt% Mn, and 0.2 wt% Ni, while Hg, Tl, Ge, and Sn are below detection limits.

Chalcopyrite is present in all three deposits; and is widespread in Plakaonica. The oldest generation of chalcopyrite occurs in the form of intergrowths in sphalerite I, accompanied with pyrite and chalcopyrrhotite (Fig. 3g). The contacts of sphalerite I with other ore minerals are often cemented by chalcopyrite. Moreover, chalcopyrite is usually accompanied with Zn-bearing tetrahedrite, tetrahedrite, and ferrokesterite (OV 3, Fig. 3h), although it also occurs to a lesser extent in the carbonate matrix and as relics in galena. The sphalerite-galena-chalcopyrite-sulfosal mineral assemblage was recognized in the Plakaonica deposit where it is present in the carbonate matrix along with Ag-bearing minerals (Ag-bearing tetrahedrite and arsenopolybasite)

along its grain boundaries. EPMA shows that chalcopyrite is of stoichiometric composition.

Galena occurs in several generations, but unlike sphalerite it is much less abundant. The first generation that is connected to the upper parts of the Crnac and Plakaonica ore bodies is characterized by “jagged” rim aggregates that commonly contain needles and relics of pyrrhotite II, and spherulitic chalcopyrite. The second generation, occurring only at Plakaonica, is associated with the chalcopyrite-tetrahedrite mineral paragenesis. However, the third and youngest generation, which is characteristic for its colloform forms with gaseous and liquid blebs, is the most widespread (Fig. 3i). The galena aggregates are partially recrystallized and contain large inclusions of spherulitic sphalerite, and to a lesser extent native Ag in square to rectangular forms. Moreover, these aggregates are usually overgrown along grain boundaries by skeleton-like crystals of gersdorffite and As-bearing ullmannite. Idiomorphic gersdorffite crystals can sometimes be included within galena. According to EPMA, third generation galena contains up to 0.51 wt% Sb, while Ag and Bi are below detection limits (< 0.3 wt%). Chemical analyses of monomineralic galena from Crnac and Plakaonica using AAS method yielded Ag content of 0.033 and 0.12 wt% respectively.

4.2. Ag-Cu-Sb, Cu-Fe-Sn and Pb-Sb sulfosalts

According to their respective optical features, tetrahedrite minerals from the ROF belong to Ag-rich varieties. However, there are some optical distinctions in color, characterized by zonality from a dominant tinge of greenish in their central portions to a bluish-gray tint in their peripheral parts (Fig. 4a). They occur in the form of small isometric grains embedded in younger sphalerite and galena, although sometimes they are overgrown by younger galena, and contain relics of chalcopyrite. EPMA from the Plakaonica deposit confirmed the existence of two varieties of Ag-bearing tetrahedrite: I) Fe-bearing having high Ag content up to 33.90 wt%, but low Bi and Cd content and an Ag/(Ag + Cu) atomic ratio of 0.6 (Table 2, Fig. 4b); II) Zn-Fe-bearing with Ag content up to 17.75 wt%, and with an Ag/(Ag + Cu) atomic ratio of 0.2 (Table 2). EPMA results also showed that Ag-bearing tetrahedrite from Kaludjer is highly ferrous, with low Bi content and Ag up to 29.17 wt%, and with an Ag/(Ag + Cu) atomic ratio of 0.4 (Table 2, Fig. 4c, d). Ag-bearing tetrahedrite, is rare in Crnac and is Zn-bearing with Ag up to 10.96 wt%, and an Ag/(Ag + Cu) atomic ratio of 0.2 (Table 2). Ag-bearing tetrahedrites from all Pb(Ag)-Zn deposits of the ROF are characterized by a complete absence of As, Hg, Cd, Ni, and Co.

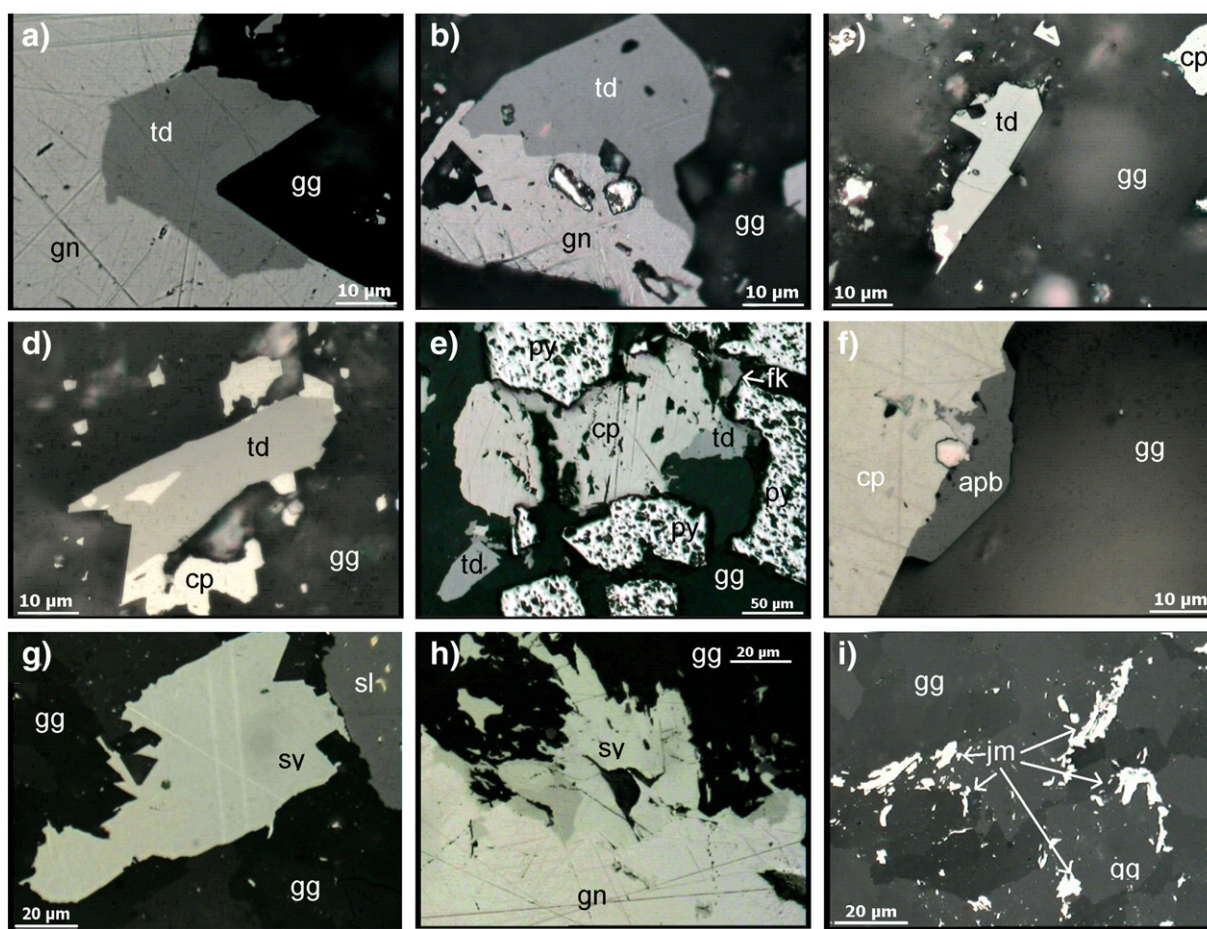


Fig. 4. Reflected light photomicrographs of Ag-Cu, Ag-Cu-Sb and Pb-Sb sulfosalts of the ROF: a) galena (white) overgrown by zoned Ag-bearing tetrahedrite (gray) in quartz (black), Plakaonica (oil, //N); b) Ag-bearing tetrahedrite (gray) intergrown with galena (white) Plakaonica (oil, //N); c) Ag-bearing tetrahedrite (gray) embedded in carbonate matrix, Kaludjer (oil, //N); d) Ag-bearing tetrahedrite (gray) accompanied with chalcopyrite (light) embedded in carbonate matrix, Kaludjer (oil, //N); e) chalcopyrite (yellow), tetrahedrite (gray blue), and ferrokesterite (olive gray) as cement to cataclased pyrite aggregates (yellow), Crnac (air, //N); f) arsenopolybasite (dark brown) intergrown with chalcopyrite (pale yellow), Plakaonica (oil, //N); g) a semseyite crystal embedded in carbonate matrix, Plakaonica (air, //N); h) a semseyite aggregate (pale greenish gray) intergrown with galena (white), Crnac (air, //N); i) lath-like crystals of jamesonite (light) embedded in carbonate matrix, Crnac (air, //N); Mineral abbreviations: gn – galena, sl – sphalerite, cp – chalcopyrite, py – pyrite, td – tetrahedrite, sy – semseyite, jm – jamesonite, fk – ferrokesterite, apb – arsenopolybasite, gg – gangue minerals.

Besides being Ag-bearing, tetrahedrites are widespread in the Crnac deposit. They are usually associated with chalcopyrite and ferrokesterite as cement to cataclastic pyrite aggregates (Fig. 4e). EPMA yielded two varieties, both Ag-poor (0.36–2.48 wt%): i) tetrahedrite with a Zn/Fe atomic ratio of 0.7, and having a low content of As and Ge; ii) Zn-bearing tetrahedrite with a Zn/Fe atomic ratio of 4.7, and containing a high content of As (Table 2). Besides Ag, small amounts of Te (up to 0.62 wt%), Mn (up to 0.25 wt%), and Bi (up to 1.59 wt%) were detected. Hg, Cd, Ni, and Co are below detection limits (Table 2).

Arsenopolybasite, present in small amounts, was found only in the Plakaonica deposit (OV 15). Optically, it is distinguished by its dominant brown-greenish tint, weak bireflectance and low reflectance (Fig. 4f). It occurs to a lesser extent in the form of small patches growing along boundaries of Ag-bearing tetrahedrite, chalcopyrite and galena. EPMA yielded the following crystal chemical composition: $(\text{Ag}_{13.42}, \text{Cu}_{2.57}, \text{Fe}_{0.18})_{\Sigma 16.18} (\text{Sb}_{1.27}, \text{As}_{0.66})_{\Sigma 1.92} \text{S}_{10.90}$ (Table 2).

Borojević-Šoštarčić et al. (2011) identified stephanite as an inclusion in galena (page 72). According to the optical features from their photomicrograph, this variety is most probably not stephanite but rather pyrrotite II (harder than galena, found in spherulitic sections), surrounded by younger galena. An identical microscopical and paragenetic motif is very widespread within the Plakaonica deposit (Fig. 3b). Stephanite, usually associated with Ag-bearing tetrahedrite or Cu-

minerals in low-temperature hydrothermal deposits (Radosavljević et al., 1986; Ramdohr, 1980), has not been observed during our research.

The presence of ferrokesterite is determined only in the Crnac deposit (OV 3). It belongs to the $\text{Cu}_2\text{FeSnS}_4\text{--Cu}_2\text{ZnSnS}_4$ mineral system (Bonazzi et al., 2003; Jovic et al., 2011; Kissin, 1989; Springer, 1972; Zarić et al., 2000). In reflected light ferrokesterite is very similar to stannite, however, its reflectance is somewhat lower and it has a greenish-olive tint (Fig. 4e). It is optically isotropic, its microhardness is moderate, but lower compared to tetrahedrite, with which it typically occurs along grain boundaries. EPMA yielded a dominant content of Fe compared to Zn and a complete absence of Ag, In, As, Sb, Bi, and Cd. Ferrokesterite was found to have a crystal chemical composition of $\text{Cu}_{1.97}(\text{Fe}_{0.74}, \text{Zn}_{0.25}, \text{Mn}_{0.01})_{1.00} \text{Sn}_{1.03} \text{S}_{3.99}$ (Table 3).

Pb-Sb sulfosalts are abundant, but in small amounts. Among them, semseyite is the major mineral, while jamesonite and heteromorphite are also present, but to a much lesser extent (Table 3). Semseyite usually occurs within the carbonate matrix in the form of independent tabular crystals (Fig. 4g). In addition, simple twinning, perfect cleavage along tabular aggregates and spiky to columnar individuals intergrown along galena boundaries are distinguishing characteristics (Fig. 4h). Heteromorphite is optically very similar to semseyite; the only difference is in its chemical composition (Table 3). Jamesonite is an important

Table 2
Representative average EPMA and atomic proportions of tetrahedrite, Ag-bearing tetrahedrite, Zn-bearing tetrahedrite, and arsenopolybasite from Pb(Ag)-Zn deposits of the ROF.

| wt% | Crnac | | | Plakaonica | | | Kaludjer |
|---------------------------|-----------------------------|------------------|-----------------------------|----------------------|--------------------------------|--------------------------------|-----------------------------|
| | Ag-bearing tetrahedrite (1) | tetrahedrite (5) | Zn-bearing tetrahedrite (6) | arsenopolybasite (3) | Ag-bearing tetrahedrite I (14) | Ag-bearing tetrahedrite II (8) | Ag-bearing tetrahedrite (3) |
| S | 23.82 | 24.73 | 25.34 | 16.07 | 21.55 | 23.57 | 22.10 |
| Mn | n.d. | 0.07 | 0.03 | n.d. | 0.05 | 0.19 | n.d. |
| Fe | 1.85 | 3.84 | 1.23 | 0.47 | 5.42 | 3.92 | 5.16 |
| Cu | 29.65 | 36.67 | 38.37 | 7.50 | 13.76 | 27.33 | 18.72 |
| Zn | 5.34 | 3.25 | 6.82 | n.d. | 0.10 | 2.48 | 1.50 |
| Ge | n.d. | 0.05 | n.d. | n.d. | n.d. | n.d. | n.d. |
| As | n.d. | 0.40 | 5.41 | 2.26 | n.d. | n.d. | n.d. |
| Ag | 10.96 | 1.22 | 0.85 | 66.56 | 32.51 | 14.58 | 25.25 |
| Cd | n.d. | n.d. | n.d. | n.d. | 0.91 | 0.07 | n.d. |
| Sb | 28.13 | 28.31 | 21.23 | 7.09 | 24.79 | 27.91 | 25.80 |
| Te | n.d. | 0.29 | 0.17 | n.d. | n.d. | n.d. | n.d. |
| Bi | n.d. | 0.88 | 0.28 | n.d. | 1.03 | n.d. | 1.26 |
| Total | 99.75 | 99.71 | 99.72 | 99.94 | 100.10 | 100.04 | 99.79 |
| <i>Atomic proportions</i> | | | | | | | |
| S | 13.00 | 12.97 | 12.89 | 10.90 | 12.94 | 12.98 | 12.89 |
| Mn | - | 0.02 | 0.01 | - | 0.02 | 0.06 | - |
| Fe | 0.58 | 1.16 | 0.36 | 0.18 | 1.87 | 1.24 | 1.73 |
| Cu | 8.17 | 9.70 | 9.85 | 2.57 | 4.17 | 7.60 | 5.50 |
| Zn | 1.43 | 0.84 | 1.70 | - | 0.03 | 0.67 | 0.43 |
| Ge | - | 0.01 | - | - | - | - | - |
| As | - | 0.09 | 1.18 | 0.66 | - | - | - |
| Ag | 1.78 | 0.19 | 0.13 | 13.42 | 5.80 | 2.39 | 4.39 |
| Sb | 4.04 | 3.91 | 2.84 | 1.27 | 3.92 | 4.05 | 3.96 |
| Te | - | 0.04 | 0.02 | - | - | - | - |
| Bi | - | 0.07 | 0.02 | - | 0.09 | - | 0.11 |
| Σ | 29 | 29 | 29 | 29 | 29 | 29 | 29 |

Note: (n) number of analyses; n.d. not detected (<0.3 wt%), Σ-number of atoms per formula unit.

mineral association at Crnac where it occurs in characteristic lath-like aggregates within the carbonate matrix (Fig. 4i). EPMA indicates Ag content of up to 0.20 wt% (Table 3).

4.3. Arsenides, sulfarsenides and sulfantimonides

Nickeline, the least abundant Ni mineral in the ROF, occur only in the lower parts of the Kaludjer deposit (gallery 818). Generally, it appears

as relics within the central portions of former aggregates that are replaced and overgrown along grain boundaries by sulfantimonides or sulfarsenides of Ni (Fig. 5a, b). Nickeline is characterized by moderately high reflectance (Fig. 6) and distinct, strongly-saturated, yellow-orange to yellow-pink bireflectance (Pe ~ 18 %). The color effects of anisotropy are very strong, having a gray to bluish tint. EPMA of nickeline from the Kaludjer deposit yielded a chemical composition of $Ni_{1.00}(As_{0.99}Sb_{0.01})_{\Sigma 1.00}$ (Table 1).

Table 3
Representative average EPMA and atomic proportions of Pb-Sb and Sn-Cu sulfosalts from Pb(Ag)-Zn deposits of the ROF.

| Deposit | Crnac | | | Plakaonica | Kaludjer | |
|---------------------------|--------------------|---------------|----------------|---------------|--------------------|---------------|
| | Ferrokesterite (2) | Semseyite (7) | Jamesonite (3) | Semseyite (2) | Heteromorphite (2) | Semseyite (3) |
| S | 29.4 | 19.48 | 21.93 | 19.11 | 20.09 | 19.24 |
| Mn | 0.17 | n.d. | n.d. | n.d. | n.d. | n.d. |
| Fe | 9.49 | n.d. | 2.75 | n.d. | n.d. | n.d. |
| Cu | 28.84 | n.d. | n.d. | n.d. | n.d. | n.d. |
| Zn | 3.76 | n.d. | n.d. | n.d. | n.d. | n.d. |
| Sn | 28.21 | n.a. | n.a. | n.a. | n.a. | n.a. |
| As | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ag | n.d. | n.d. | 0.13 | n.d. | n.d. | n.d. |
| Sb | n.d. | 27.26 | 35.55 | 27.79 | 32.14 | 27.90 |
| Pb | n.a. | 53.23 | 39.41 | 52.70 | 47.82 | 52.6 |
| Total | 99.87 | 99.97 | 99.77 | 99.59 | 100.05 | 99.74 |
| <i>Atomic proportions</i> | | | | | | |
| S | 3.99 | 21.21 | 14.05 | 21.00 | 19.00 | 21.05 |
| Mn | 0.01 | - | - | - | - | - |
| Fe | 0.74 | - | 1.01 | - | - | - |
| Cu | 1.97 | - | - | - | - | - |
| Zn | 0.25 | - | - | - | - | - |
| Sn | 1.03 | - | - | - | - | - |
| As | - | - | - | - | - | - |
| Ag | - | - | 0.02 | - | - | - |
| Sb | - | 7.82 | 6.00 | 8.04 | 8.00 | 8.04 |
| Pb | - | 8.97 | 3.91 | 8.96 | 7.00 | 8.91 |
| Σ | 8 | 38 | 25 | 38 | 34 | 38 |

Note: (n) number of analyses; n.d. not detected (<0.3 wt%); n.a. not analyzed, Σ-number of atoms per formula unit.

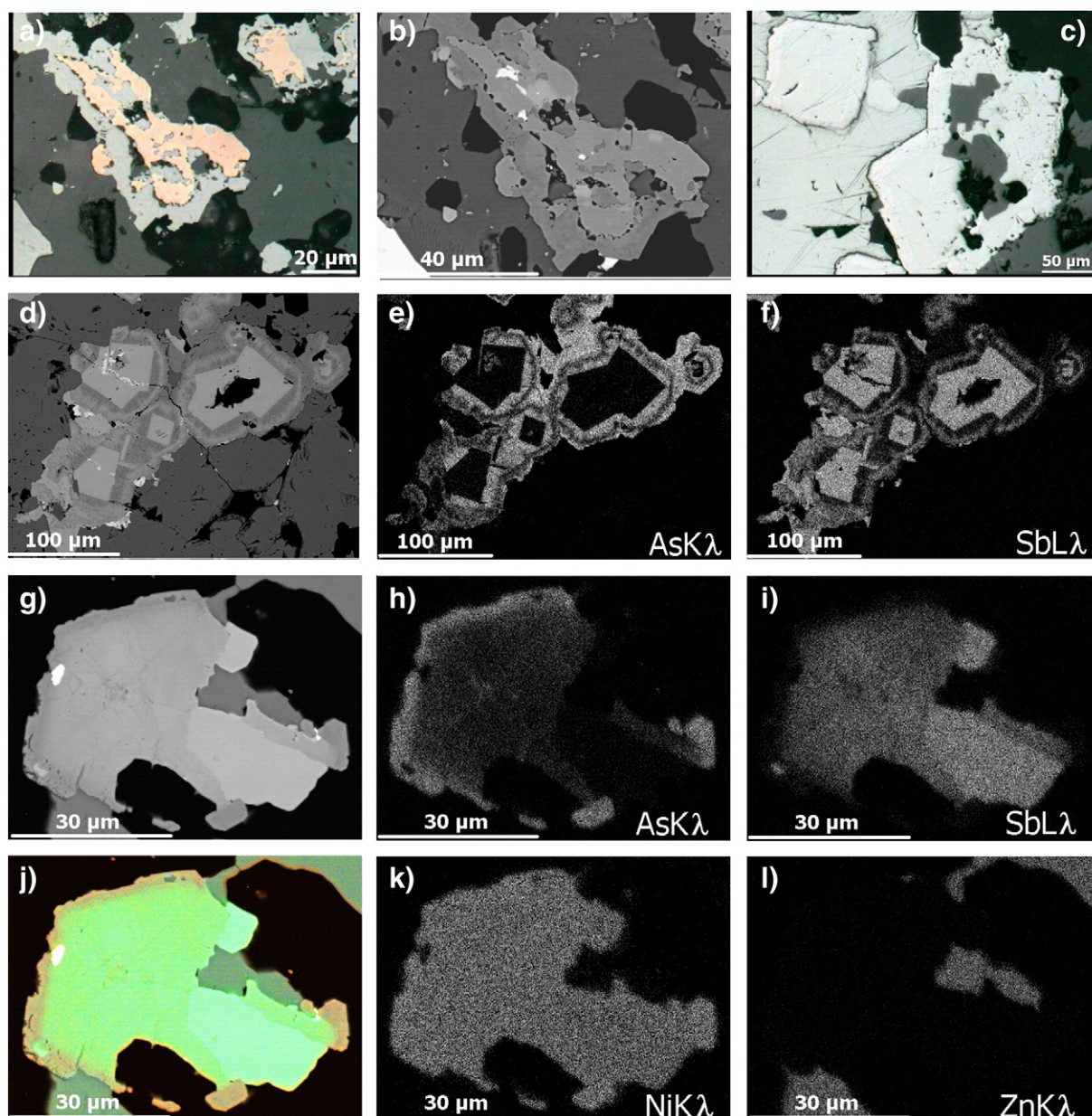


Fig. 5. Reflected light and SEM photomicrographs with X-ray elemental mapping of arsenides, sulfarsenides, sulfantimonides of Ni of the ROF: a) a nickeline aggregate (light pink) overgrown by the GUS (pale gray) embedded between sphalerite aggregates (dark gray), Kaludjer (air, //N); b) a SEM image of the Fig. 5a motif (BEI); c) overgrowth of galena (gray white) and sphalerite (gray) by GUS (white) Kaludjer (air, //N); d) a zoned crystal of the GUS, Kaludjer (BEI); e–f) an X-ray elemental mapping of the Fig. 5d; g) a zoned crystal of the GUS with intermediate member Sb-bearing gersdorffite, Kaludjer (BEI); h–i) an X-ray elemental mapping of the Fig. 5 g; j) composite image of an X-ray elemental mapping of AsK α and SbL α ; k–l) an X-ray elemental mapping of the Fig. 5 g.

Arsenopyrite is also rare, but is often cataclased and replaced into pyrite. It occurs only at Plakaonica in the form of idiomorphs mostly connected with Fe, Pb, and Zn sulfides (Fig. 3f). According to EPMA analyses, it contains a high S content with a chemical composition of $\text{Fe}_{0.96}\text{As}_{0.97}\text{S}_{1.07}$, with Sb (<0.3–0.37 wt%), but without Ni and Co as based upon two analyses.

A gersdorffite-ullmannite series (GUS), belonging to the pyrite subgroup (Bayliss, 1986; Dobbe, 1991; Parr and Chen, 1979; Yund, 1962), is recognized at both Kaludjer and Plakaonica. The GUS occurs as follows: i) intergrown with Ni minerals replacing nickeline; ii) in the form of euhedral square, hexagonal or octagonal crystals embedded within the carbonate matrix; and iii) in the form of skeletal crystals, rarely as hexagonal or square forms, replacing younger sphalerite and galena along grain boundaries (Fig. 5c). It is characterized by having moderately high reflectance with an extremely white to creamy or

yellowish tint (Fig. 6). Under SEM, some mixed crystals are zoned with clearly visible brown and white bands following the forms of crystal sections (Fig. 5d–f). Microhardness measurements yielded values from 473 to 519 kg/mm².

EPMA of the GUS from Kaludjer yielded two As- (gersdorffite and Sb-bearing gersdorffite), and one Sb-member (As-bearing ullmannite). The chemical composition of gersdorffite is $(\text{Ni}_{0.90}\text{Zn}_{0.06}\text{Fe}_{0.01}\text{Co}_{0.01})_{\Sigma 0.98}(\text{As}_{0.95}\text{Sb}_{0.06})_{\Sigma 1.01}\text{S}_{1.00}$ (Table 1). For an intermediate As-Sb member (Fig. 5g–l) EPMA yielded a composition of $(\text{Ni}_{0.96}\text{Zn}_{0.02}\text{Fe}_{0.03}\text{Co}_{0.02})_{\Sigma 1.01}(\text{As}_{0.71}\text{Sb}_{0.30})_{\Sigma 1.01}\text{S}_{1.00}$ (Table 1). This mineral composition corresponds to korynite, and according to the literature data published by Ramdohr (1980) and Chvilyova et al. (1988) it was defined as an intermediate member of the GUS having a Sb content of up to 25 wt%. However, Bayliss (1969) in his study determined korynite as Sb-bearing gersdorffite. For As-bearing ullmannite EPMA

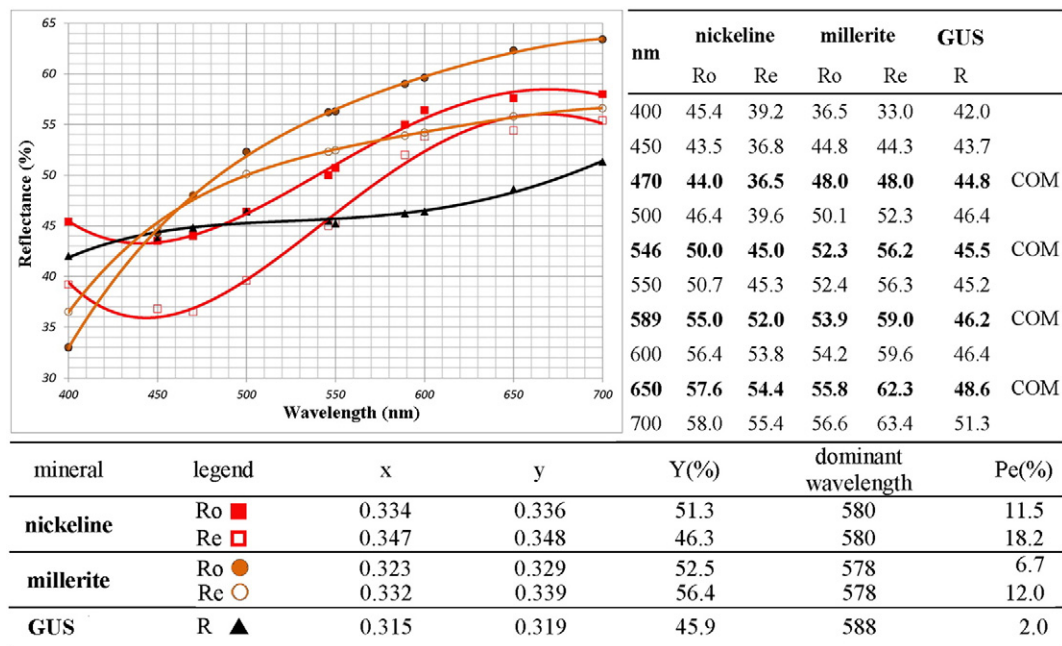


Fig. 6. Results of reflectance measurements and color values of nickeline, millerite and GUS from Kaludjer.

yielded a chemical composition of $(\text{Ni}_{0.92}, \text{Zn}_{0.07}, \text{Co}_{0.01})_{\Sigma 1.01}(\text{Sb}_{0.84}, \text{As}_{0.17})_{\Sigma 1.01}\text{S}_{0.99}$ (Table 1).

EPMA of the GUS from Plakaonica yielded two As- (gersdorffite and Fe-bearing gersdorffite), and one Sb-member (As-bearing ullmannite). The chemical composition of gersdorffite and Fe-bearing gersdorffite was determined to be $(\text{Ni}_{0.86}, \text{Fe}_{0.09}, \text{Zn}_{0.04}, \text{Co}_{0.01}, \text{Mn}_{0.01})_{\Sigma 1.01}\text{As}_{1.00}\text{S}_{0.99}$, and $(\text{Ni}_{0.44}, \text{Fe}_{0.38}, \text{Co}_{0.14}, \text{Zn}_{0.08})_{\Sigma 1.04}\text{As}_{0.99}\text{S}_{0.98}$, respectively (Table 1). Chemical composition of an As-member (As-bearing ullmannite) was found to be $\text{Ni}_{1.01}(\text{Sb}_{0.69}, \text{As}_{0.30})_{\Sigma 0.99}\text{S}_{0.99}$ (Table 1). By comparison, gersdorffite from the Lavrion carbonate-replacement deposit in Greece occurs as zoned idiomorphic crystals enclosed in galena, in which the As-content decreases and the Ni-content increases from crystal cores to rims. EPMA yielded gersdorffite with increased content of Fe, but without Sb and Co (Voudouris et al., 2008). A correlation analysis was carried out in order to obtain a ratio between macro and micro elements within the GUS in the ROF. According to the Pearson coefficient, no positive correlation was determined between the elements ($R < 0.6$, Table 1). The best negative correlations were obtained between the atomic ratios of As and Sb within the GUS (Kaludjer and Plakaonica, Fig. 7a) and between the atomic ratios of Ni and Fe in gersdorffite (Plakaonica, Fig. 7b). Good negative correlations were determined between the atomic ratios of Ni and Co, and Ni and Zn in the GUS (Kaludjer) and between Fe and Co, Ni and Co, and Zn and Co in gersdorffite (Plakaonica).

4.4. Native elements

Overall, native Au is rare, but it does occur as an electrum alloy as droplets, generally in arsenopyrite and within the silicate matrix. Native Ag also occurs as rare drop-like inclusions in galena.

4.5. Oxide, phosphate, carbonate and relic minerals

Magnetite, occurs at Crnac (OV 8) and Plakaonica (OV 15), is widespread. It is associated with pyrrhotite and its products of hydrothermal alteration (Fig. 3c). A crustification (carbonatization with comb structures) process is characteristic for coarse crystalline aggregates of magnetite. The boundaries of these net-like aggregates were filled with siderite, while ankerite filled interstices (Fig. 8a, b). The chemical

composition of magnetite was determined to be $\text{Fe}^{3+}_{2.00}(\text{Fe}^{2+}_{0.99}, \text{Mn}_{0.03})_{1.02}\text{O}_{3.98}$ from three analyses where the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio was obtained stoichiometrically. Titanium, Ca and Cr were not detected (< 0.3 wt%).

Spinel, present in small amounts, occurs only in the Kaludjer deposit in the form of isolated relics and irregular or corroded aggregates (Fig. 8c). It often contains cracks and fractures that are cemented with chalcedony accompanied by fragments of silicified serpentinites. Chemically it belongs to the Al-Cr spinel group with a chemical composition of $(\text{Mg}_{0.51}, \text{Fe}_{0.48}, \text{Zn}_{0.01})_{\Sigma 1.00}(\text{Al}_{1.47}, \text{Cr}_{0.51}, \text{Fe}_{0.03})_{\Sigma 2.01}\text{O}_{3.99}$ based upon two analyses. Atomic ratios of $\text{Mg}\# [\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]$ and $\text{Cr}\# [\text{Cr}/(\text{Cr} + \text{Al})]$ were found to be 0.50 and 0.26, respectively. Ubiquitous chromite was determined in the Vourinos ophiolite complex in northern Greece, with an increased Cr# $[\text{Cr}/(\text{Cr} + \text{Al})]$ ratio of 0.58–0.81 (Grammatikopoulos et al., 2011).

Rutile is present at both the Crnac and Plakaonica ore bodies. It is associated with the oldest generation of carbonatized and silicified pyrite (Fig. 8d). EPMA from three analyses show that rutile is stoichiometric with Fe impurities: $(\text{Ti}_{0.98}, \text{Fe}_{0.02})_{\Sigma 1.00}\text{O}_{2.00}$.

Anatase is only found at Crnac. It is associated with altered igneous rocks, which were intensely carbonatized (ankerite). It occurs in the form of small crystals with square to rectangular sections, which are often seen to be grouped into clusters located in carbonate matrix (Fig. 8e). EPMA yielded a chemical composition of $(\text{Ti}_{0.978}, \text{Sn}_{0.007}, \text{Si}_{0.005}, \text{Nb}_{0.004}, \text{Fe}_{0.004}, \text{Al}_{0.002}, \text{Ta}_{0.001})_{\Sigma 1.001}\text{O}_{1.999}$ from four analyses.

Monazite occurs only from Plakaonica (OV 15). It occurs as relics in the form of preserved, small, isometric crystals within completely altered igneous rocks (Fig. 8f). According to EPMA it belongs to the Ce-bearing monazite group with a chemical composition of $(\text{Ce}_{0.482}, \text{La}_{0.293}, \text{Nd}_{0.134}, \text{Pr}_{0.015}, \text{Sm}_{0.009}, \text{Gd}_{0.004}, \text{Eu}_{0.002}, \text{Ca}_{0.043})_{\Sigma 0.982}\text{P}_{1.011}\text{O}_{4.007}$ made from five analyses. Radioactive elements were not detected.

In the Kaludjer-Crnac-Plakaonica ore system the carbonates are mainly ankerite and in a lesser extent siderite. EPMA of ankerite yielded following minimum and maximum chemical composition: $\text{Ca}_{1.11-1.12}(\text{Mg}_{0.47-0.66}, \text{Mn}_{0.11-0.34}, \text{Fe}_{0.05-0.12})_{\Sigma 0.82-0.88}(\text{CO}_3)_{\Sigma 2.01-2.06}$ (4 analyses), Zn and Ni were not detected (< 0.3 wt%). The $\text{Mg}/(\text{Mg} + \text{Mn} + \text{Fe})$ atomic ratio in the Kaludjer-Crnac-Plakaonica ore system increases in the following order: Plakaonica (0.5) → Crnac (0.7) → Kaludjer (0.8).

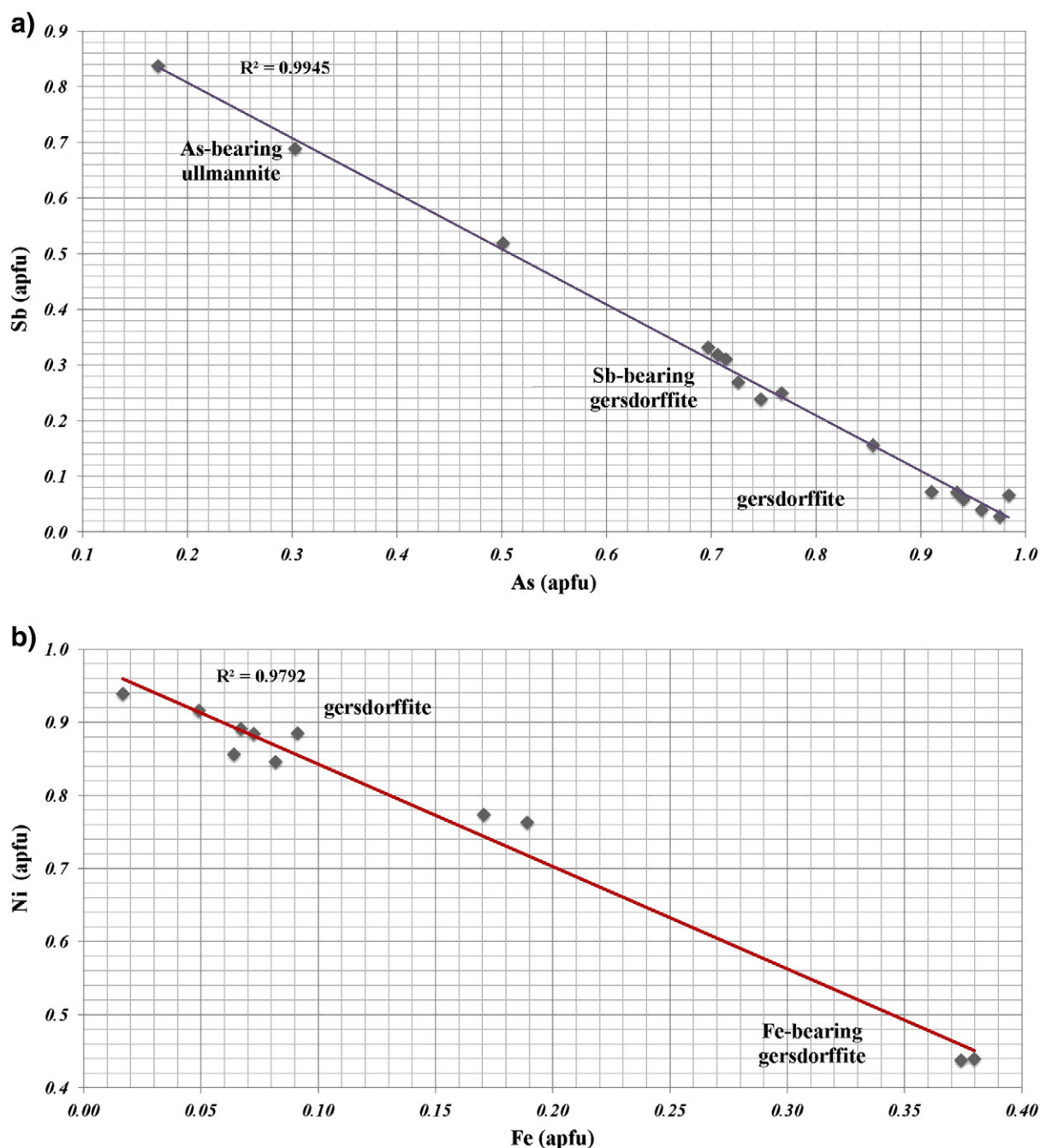


Fig. 7. Correlations between a) As vs. Sb of GUS from Kaludjer and Plakaonica; and b) Fe vs. Ni of GUS from Plakaonica (apfu: atoms per formula unit).

5. Paragenetic sequence

Ore microscopy studies confirmed the presence of the entire hydrothermal range (e.g. high- to low-temperature) in Pb(Ag)-Zn deposits of the ROF, however, in variable quantities (Table 4). Minerals were deposited in several successive stages and substages, all genetically related to the Neogene magmatism. The principal ore and typomorphic metals of the ROF are Fe, Pb, Zn, Ag and Sb, and to a lesser extent Cd, Sn, In. They probably all have a common magmatic (e.g. granodiorite) origin. The magmatic origin of sulfur from sulfides, sulfarsenides, and sulfosalts is indicated by isotopic analyses of δS^{34} from sphalerite and galena at Crnac, ranging from 0.3 to 5.9‰ (Borojević-Šoštarić et al., 2011). Minor fluctuations of δS^{34} are a function of the variation of their respective crystallization temperatures. According to their mineral

composition, transport of ore metals (e.g. Pb, Ag, Sb) primarily took place in the form of polysulfides, chlorides, and sulfides.

The following mineral parageneses were determined in Pb-Zn mineral associations at the ROF: i) *pre-ore*; ii) *high-temperature hydrothermal* (pyrrhotite I – magnetite – sphalerite I – galena I); iii) *hypogene* (pyrite I – marcasite I – sphalerite I); iv) *medium-temperature hydrothermal* (galena II – sphalerite II – chalcocopyrite II – sulfosalt with Ag); v) *low-temperature hydrothermal* (sphalerite III – galena III – Ni-As-Sb-sulfide – chalcocopyrite – carbonate); and vi) *supergene* (Table 4). Minerals of the high-temperature pyrrhotite I – magnetite – sphalerite I – galena I paragenesis are suggestive of low sulfidation fluid state (e.g. presence of pyrrhotite, Fe-rich sphalerite; according to Einaudi et al., 2003), and were deposited in a weak alkaline environment with variable Eh conditions (pyrrhotite I, magnetite I, sphalerite I, galena I). The change of pH

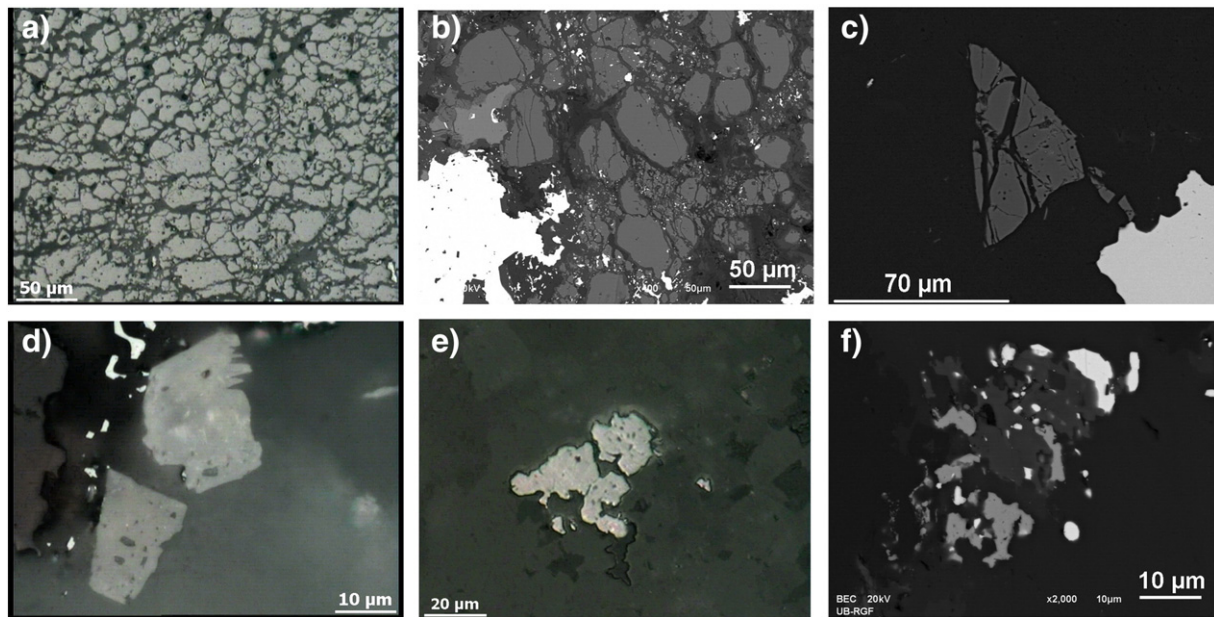


Fig. 8. Reflected light and SEM photomicrographs of oxides and phosphates of the ROF: a) crustification (carbonatization) of magnetite (light gray) embedded in carbonate matrix (dark), Plakaonica (air, //N); b) crustification (carbonatization) of magnetite (dark gray) embedded in carbonate matrix (dark), Plakaonica (BEI); c) a cataclased crystal of chromite (dark gray) embedded in serpentine matrix, Kaludjer (BEI); d) rutile crystals embedded in carbonate matrix, Plakaonica (oil, //N); e) anatase crystals embedded in carbonate matrix, Crnac (air, //N); f) a Ce-bearing monazite aggregate (gray) with carbonates (dark gray) and galena (white) in quartz (black), Plakaonica (BEI).

and Eh conditions, as well as the sulfidization of pre-existing sulfides led to hydrothermal paragenetic sequence of pyrrhotite → marcasite → pyrite (according to Ramdohr, 1980). Pyrite I – marcasite I – sphalerite I and galena II – sphalerite II – chalcocopyrite II – sulfosalt with Ag mineral parageneses seen as metasomatic-impregnation are widespread ore types and occur throughout the ROF. Change of pH and temperature when the depositional environment become more alkaline led to deposition of galena II – sphalerite II – chalcocopyrite II – sulfosalts with Ag, Cu, Pb, and Sn (Pb-Sn sulfosalts, ferrokesterite, tetrahedrite, Ag-bearing tetrahedrite, Mozgova et al., 1987). The final stage of mineralization is characterized by the deposition of the low-temperature Pb-Zn-bearing sulfides as overgrowths of older sulfides and the occurrence of the Ni-As-Sb-sulfide mineral assemblage embedded within the chalcedony-carbonate matrix. The sphalerite III – galena III – Ni-As-Sb-sulfide – chalcedony – carbonate mineral paragenesis is the most common in the Kaludjer deposit. It occurs to a lesser degree at Plakaonica, while at Crnac it was not recognized. It is characterized by the Ni-bearing minerals millerite, bravoite, nickeline, gersdorffite, Sb-bearing gersdorffite, Fe-bearing gersdorffite and As-bearing ullmannite, and form part of the

late-stage sphalerite III – galena III – Ni-As-Sb-sulfide – chalcedony – carbonate mineral paragenesis (Table 4).

The occurrence of nickeline at Kaludjer is very interesting when considering the origin of the sphalerite III – galena III – Ni-As-Sb-sulfide – chalcedony – carbonate mineral paragenesis. Nickeline was the first Ni-mineral deposited from medium-temperature hydrothermal solutions enriched in Ni and As. Nickeline crystallized before any sulfosalts from Sb-depleted and Ni- and As-enriched solutions at very low fS_2 . Similar observations regarding the origin of nickeline are described from the Crescencia Ni-(Co-U) deposit in the Pyrenees of Spain (Fanlo et al., 2006). According to the authors, three stages of mineral deposition can be distinguished: stage I: nickeline and parammelsbergite, stage II: gersdorffite, and stage III: uraninite.

According to Rakić (1962), the Pb-Zn deposits associated with Neogene magmatism within the SMMP (territories of B&H, Serbia, and FYRM), are of two main types characterized by distinct mineral assemblages: (a) contact-greisen-metasomatic mineralization (e.g. skarn- and carbonate-replacement-type), present in only a few deposits, and (b) medium- to low-temperature hydrothermal Pb-Zn mineralization

Table 4
Stages and paragenetic sequences of Pb(Ag)-Zn ores from the ROF.

| Stage | Paragenetic sequence | Deposits |
|---------------------------------|---|-----------------------------------|
| Pre-ore | Serpentinites – silicates – carbonates – ± Cr-bearing spinel – ± rutile – ± monazite-(Ce) – ± anatase – quartz I | Crnac*, Plakaonica*, Kaludjer** |
| High-temperature hydrothermal | Pyrrhotite I – magnetite – sphalerite I – chalcocopyrite – pyrrhotite II – chalcocopyrite I – galena I – ankerite I | Crnac***, Plakaonica** |
| Hypogene | Marcasite I – pyrite I – hematite – siderite | Crnac***, Plakaonica** |
| Medium-temperature hydrothermal | Quartz II – native gold – arsenopyrite – sphalerite II – chalcocopyrite II – pyrrhotite II | Crnac**, Plakaonica** |
| | Ankerite II – ± tetrahedrite – ± ferrokesterite – Ag-bearing tetrahedrite – galena II – native silver – ± arsenopolybasite – ± jamesonite – semseyite – ± heteromorphite – ± bravoite – ± nickeline | Crnac*, Plakaonica***, Kaludjer** |
| Low-temperature hydrothermal | Marcasite II – pyrite III – sphalerite III – galena III – millerite – As-bearing ullmannite – ± Sb-bearing gersdorffite – gersdorffite – ± Fe-bearing gersdorffite – chalcedony – barite – gypsum | Plakaonica**, Kaludjer*** |
| Supergene | Anglesite – cerussite – smithsonite – zaraitite – limonite | Kaludjer** |

Note: *** Main; ** Weak; * Trace.

(e.g. epithermal vein-type) of significant economic importance. The mineralization in both styles of deposits is genetically related the emplacement of plutonic and subvolcanic bodies.

The metallic mineral assemblages from the Neogene Pb–Zn deposits in Serbia are characterized by a regular presence of Cu, As, and Sb minerals, local occurrence of 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 metals are associated with specific mineralization types, and to 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- and carbonate-replacement-type, and epithermal vein-type mineralizations: Avala, Rudnik, Podrinje, Kopaonik, Trepča, Novo Brdo, Karavansalija, Blagodat and Crnac, and Kosmaj, Kotlenik, Koporić, Žuta Prlina, Ajvalija, Kižnica, Lece and Karamanica, respectively.

6. Conditions of ore formation

The chemical composition of sphalerite provides important information on metallogenic features and conditions of mineral formation in hydrothermal ore deposits (Ramdohr, 1980). The crystal structure of sphalerite is capable of incorporating a large number of elements and part of the Zn is isomorphously substituted by Fe, and sometimes In, Cu, Co in Fe-rich, and Cd, Ge, Tl in Fe-poor sphalerite as a general rule of low-temperature hydrothermal stages (Cook et al., 2009). Based on FeS content and unit-cell parameter shifting of sphalerite, mineral deposition at Crnac occurred in a wide temperature interval ranging from 500 to 220 °C (Nikolić et al., 1978). The above authors concluded that the first generation of sphalerite deposited in the range of 500 to 330 °C and that younger sphalerite crystallized from 330 to 220 °C. These results are in good agreement with fluid inclusion data obtained from Pb–Zn mineral parageneses at Crnac, and elsewhere within the ROF (Borojević-Šoštarić et al., 2011, 2013). Besides temperature, Fe-content of sphalerite is also a function of sulfur fugacity of the fluids (Scott and Barnes, 1971).

According to Arsenijević (1998), the following trace elements were identified by AAS from single sphalerite crystals (in ppm): In (10–350), Ga (1–20), Ge (0–35), Sn (10–2000), Ni (<10–3000), Co (8–27), As (0–78), Se (1–6) and Te (1–3). The ratio of Ga/In (0.03–1.84) suggests that crystallization of sphalerite occurred in all three generations, due to a fact that In tends to concentrate in high-temperature Fe-rich sphalerites, and its concentration decreases with temperature.

Deposition temperatures of sphalerite and galena were determined according to the ratio of cadmium and manganese contained in both minerals. Coefficients of distribution of cadmium and manganese were calculated using following equations:

$$K_{Cd} = Cd^{sph} / Cd^{gal}$$

$$K_{Mn} = Mn^{sph} / Mn^{gal}$$

Deposition temperatures of Pb–Zn mineral associations were calculated by the following equations:

$$T_{(K)} = \frac{1663}{(\log K_{Cd} + 0.702)}$$

$$T_{(K)} = \frac{1299}{(\log K_{Mn} - 0.099)}$$

at a pressure of 1000 bars (Chelety et al., 1979).

Deposition temperatures of Pb–Zn minerals from the high-temperature stage at Crnac and Plakaonica were calculated by their contents of Cd and Mn found in sphalerite I and galena I (high-

temperature hydrothermal stage), as well as their respective coefficients of distribution K_{Cd} and K_{Mn} (see equations above). The obtained depositional temperatures indicate that associated sphalerite + galena were deposited during high-temperature hydrothermal stages, in the range of 350–430 °C (Table 5). It should be pointed out the fact that Cd- and Mn-based estimates are very similar for each sample and in good argument in favor of equilibrium. Distribution of cadmium and manganese, fractionation of sulfur isotopes between coexisting galena and sphalerite, and filling temperatures in sphalerite have also been studied by Bortnikov et al. (1995). The formation temperatures of a large number of sphalerite-galena pairs, estimated on the basis of the Cd distribution, range from 320–370 °C, while the results of geothermometry based on manganese distribution between galena and sphalerite are not useful. The cadmium galena-sphalerite geothermometer gives reliable temperatures for high-temperature associations (>250 °C). However, applicability for low-temperature hydrothermal stages is doubtful (Bortnikov et al., 1995). The results obtained by Bortnikov et al. (1995) are slightly higher, but still in a good agreement with the present data. However, according to Borojević-Šoštarić et al. (2011), the crystallization temperature of sphalerite + galena pairs (δS^{34} isotopic analyses) is in a range from 230 to 310 °C. Comparison of these results with average values obtained in this study can be explained that the authors analyzed samples from Plakaonica, which are of slightly lower deposition temperatures (Table 5). Sphalerite and galena δS^{34} values decrease due to rapid deposition of the youngest sulfides generally having colloform textures. Post-mineralization temperatures were less than 190 °C (Borojević-Šoštarić et al., 2011).

The most significant Ni mineralization consists of GUS minerals, that characterize the Pb(Ag)-Zn mineral associations from the Kaludjer and Plakaonica deposits. As-bearing ullmannite, exceptionally rare in the Kaludjer and Plakaonica ore bodies, crystallized first and was followed by Sb-bearing gersdorffite (Fig. 5g-l). Over time, with inflow of new hydrothermal solutions, As concentration increased, while Sb content decreased. Further increase of As favored crystallization of skeletal aggregates of As minerals over previously deposited Sb-bearing gersdorffite (Fig. 5a). Rhythmical zoning can sometimes be noted indicating occasional interruption and changing chemistry of the ore-bearing solutions (Fig. 5e, f). The termination of Ni mineral crystallization in both deposits began with millerite that occurs in the form of acicular to idiomorphic crystals encapsulated within the youngest generation of sphalerite and galena.

The origin of Ni within the Pb(Ag)-Zn associations of the ROF is most probably from the Vardar ophiolite zone (Dimou and Papastavrou, 1987). However in the Lavrion deposit Greece (e.g. Clemence mine) the gersdorffite-gold-bismuthinite assemblage is interpreted to be of magmatic origin, related to dikes of both acid and basic composition (Voudouris et al., 2008). Large sedimentary deposits of Fe with Ni, Co, and Cr of Cretaceous age have been discovered in Serbia (Janković, 1990). The Ni-Fe sedimentary ore zone in the Mokra Gora-Rzav basin is situated on the paleorelief of the Zlatibor serpentinous peridotite

Table 5

Contents of Cd and Mn in sphalerite and galena and temperatures of deposition of Pb–Zn minerals in Crnac and Plakaonica.

| Deposit | sphalerite (wt%) | | galena (wt%) | | temperature °C | |
|------------------------------|------------------|------|--------------|-------|----------------|-------|
| | Cd | Mn | Cd | Mn | by Cd | by Mn |
| Crnac (level V, ov 8) | 0.55 | 0.93 | 0.009 | 0.008 | 395 | 388 |
| Crnac (level V, ov 8) | 0.14 | 0.99 | 0.003 | 0.011 | 428 | 427 |
| Average | | | | | 411 | 407 |
| Plakaonica (level IV, ov 15) | 0.34 | 0.53 | 0.008 | 0.006 | 441 | 430 |
| Plakaonica (level IV, ov 15) | 0.30 | 0.20 | 0.002 | 0.001 | 305 | 317 |
| Plakaonica (level IV, ov 15) | 0.58 | 0.21 | 0.005 | 0.001 | 328 | 311 |
| Average | | | | | 358 | 353 |

Note: ov – ore vein.

massif and represents a basal series of the Upper Cretaceous. The average thickness of the ore horizon is 24.4 m and the average metal content amounts to: 21.2 of Fe and 0.7 wt% of Ni. On the basis of present results, it can be concluded that a mineral inventory of the whole basin contains over one billion tons of potential ore. Nickel occurs as the sulfides millerite and bravoite and is hosted in carbonate cement of conglomerates and sandstones (Fotić, 1964).

Within the SMMP, Pb(Ag)-Zn associations of the ROF are very similar to those found in the Srebrenica ore field that is situated within the Podrinje Metallogenic District (PMD) (Fig. 1a). The similarities are reflected in mineralogical composition (marcasite-galena-sphalerite-siderite-Ag-Sn-bearing sulfosalts), structural relationships (vertical ore veins in dacites), textures (brecciated and ribbon-like textures) and genetical features (greisen and high-temperature hydrothermal mineralizations) (Radosavljević and Dimitrijević, 2001; Radosavljević et al., 1986).

7. Conclusions

The present study expands on previous work conducted by Radosavljević et al. (1990) in order to define Pb(Ag)-Zn mineral associations and parageneses of the Kaludjer-Crnac-Plakaonica ore system. Pb(Ag)-Zn mineral associations of the ROF are composed of a large number of mineral parageneses with characteristic polymetallic compositions reflecting a long interval of deposition. Generally, there are two types of mineralization: i) brecciated ore veins with ribbon-like textures hosted in amphibolites and along contacts with quartz latite dykes, typical for Crnac and Plakaonica, that were deposited along fault zones, ii) stockwork within columnar ore bodies hosted in listwaenites that, lay above ore veins in amphibolites and are characteristic for Kaludjer and Plakaonica. Serpentinites are mostly metasomatically altered under formation of small occurrences of listwaenite. This relationship with listwaenites may possibly prove that these rocks are indicators of mineralization, for it is clear that hydrothermal solutions have passed through them. Most probably, listwaenites only served as pathways for magmatic-hydrothermal fluids and hostrocks for Oligocene mineralization.

Unlike other deposits (e.g. Lavrion in Greece, Voudouris et al., 2008, and Bou Azzer, Morocco, Ahmed et al., 2009) where the Ni-Co association is related to Au-Ag mineralization the only connection between Ni mineralizations and a precious metal distribution in the studied deposits is the small amounts of Ag in bravoite from Kaludjer (2.06 wt%, Table 1). Since nickel is the youngest in mineral associations, hydrothermal solutions enriched in Ni probably dissolved a certain amount of Ag-bearing tetrahedrites, and later during the crystallization small quantities of Ag entered the structure of bravoite.

According to Dimou and Papastavrou (1987) Ni-minerals in listwaenites are sourced from the original constituents of the ultramafic rocks. Arsenic may possibly have a two-fold origin, as a primary component of the ultramafic rocks as well as having been transported by hydrothermal solutions. The last hypothesis is supported by the fact that Ni mineralizations contain considerable amounts of As in several different forms.

Textural and structural relationships indicate that ore metals were rapidly precipitated and later recrystallized from gels (sphalerite colloform spheres surrounded by galena and vice versa). Moreover, the presence of Zn in most Ni-minerals (sulfides, sulfarsenides, and sulfantimonides); Sb in arsenides and sulfarsenides; As in sulfantimonides; Mn and Fe in ankerite and sulfarsenides; and Ni in low-temperature sphalerite favors the above-mentioned hypothesis. High- and medium-temperature hydrothermal associations are widespread in the Crnac and Plakaonica deposits, while at Kaludjer a low-temperature hydrothermal association is prevalent. Accordingly, by way of deposition of mineral associations, the ROF as a whole is high- to medium-temperature hydrothermal ore system formed at shallow to moderate depths.

So far, the importance of the Ni-mineralization in the systems herein discussed is of scientific interest only. It is distinct in rare genetic and paragenetic relations of mineral parageneses present. Namely, the complete GUS (gersdorffite → Sb-bearing gersdorffite → As-bearing ullmannite) occurs only in the ROF within the SMMP (territories of B&H, Serbia, and FYRM). Since these are completely new studies dealing with the Ni-mineralization, economic importance is questionable since Ni contents in the ore are still unknown. The main reason why it is so is that the ROF was recognized only as a source of lead and zinc. The management of the mines has not been paying enough attention on any other valuable metal including nickel, but it is believed that plans for the future will be focused on a detailed study of the Ni-mineralization.

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