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Geochemical characteristics and genesis of Mačje Jame and Vranjski Potok As-Cu-bearing iron occurrences west and southwest of the town of Busovača, Mid-Bosnian Schist Mountains (MBSM)

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ABSTRACT

In this study two small, but genetically related iron carbonate deposits Mačje Jame and Vranjski Potok, south west of Busovača (MBSM), located in the pre-Devonian metamorphic complex were investigated in detail. Analyses of the main chemical components, trace elements, REE, isotope composition of C, O, S, $^{87}Sr/^{86}Sr$ ratio of rhyolite, plot of REE normalized to CI chondrites and a microscopic study of thin and polished sections were performed. Three mineralization phases were identified: the oldest is the main phase (90-95 wt %) with Fe (Ca, Mg, Mn) carbonates (siderite, ankerite, Fe-dolomite) as the predominant minerals, whereas magnetite, haematite, albite, allanite, pyrite I, quartz I represent subordinate minerals. The second phase is the pneumatolytic-kata-thermal phase (5-10 wt %) characterized by pyrrhotite relicts, pyrite II, quartz II, arsenopyrite and some supposed accessory minerals such as cassiterite, wolframite, gersdorffite, and columbite. The youngest is the kata-meso-epithermal-hydatogene phase (<1 wt %) which gave quartz III-chalcedony as gangue mineral and marmatite, chalcopyrite, boulangerite, gel-pyrite-marcasite, sphalerite, enargite, tetrahedrite, galena, cosalite, bismuth and sternbergite as ore minerals. An almost identical paragenesis has been observed in the oldest ore deposit of the Gemericum Palaeozoic metamorphic complex (RADVANEC and BARTALSKY, 1987).

The first and second mineralization phase of both ore deposits formed in the Carboniferous from metamorphogeno-hydrothermal fluids generated from S-granitoid magmatic rocks and their protoliths. This claim is strongly supported by very similar REE and their interior disposition between these deposits and metarhyolites as well as by the obtained strontium ratios. The third, youngest phase is the product of a very weak overprint of hydrothermal activity in the Late Variscan (290-260 Ma) and in the Upper Permian-Lower Triassic (260-240 Ma).

Keywords: iron deposits, Mačje Jame, Vranjski Potok, Hercynian metallogeny, Mid-Bosnian Schist Mts.

1. INTRODUCTION

The Busovača region with the Mačje Jame and Vranjski Potok ore deposits is situated in the north-eastern part of the Mid-Bosnian Schist Mountains (MBSMts) (Fig. 1). It is the oldest part of MBSMts. The Palaeozoic complex area (3000 km^2) is delimited by the deep first order Busovača Fault on the north-eastern side, by the Kozica river on the south-eastern and southern sides, by the Krušćica river on the south-western side and by the Lašva river on the north side.

The Mačje Jame deposit is located in the spring zone of the Kozica river in the Živčička Mt. Similar paragenetic but smaller ore occurrences were observed at the **Rudno**

mountain ridge (+843 m) locality, SW of the village of Tisovac and at the locality of **Gornje Brizove Stijene**, 6.5 km SE to the town of Busovača. These small ore occurrences are characterized by siderite and ankerite as the main minerals, with subordinate magnetite, haematite, albite, pyrite, quartz and Fe, As, Cu, Zn, Pb and Sb sulphides and sulphosalts. Mining investigations at the locations of Rudno and Brizove stijene only involved the oxidation zone of both ore occurrences, whereas the Mačje Jame deposit had been mined in the primary ore zone as well (KATZER, 1905, 1910, 1924) (**Fig. 1**).

The Vranjski Potok ore deposit is situated on the west bank of the Vranjski Potok (Creek), 150 m above its bed. The ore occurrence is located in the strongly tectonized Palaeozoic metasandstone of pre-Devonian age, approximately ten metres thick. Metasandstones are fine to coarse-grained rocks giving the appearance of a conglomerate (**Fig. 2**). Green-grey metarhyolite is located at the footwall of the metasandstone, in the Duboki Potok creek, the tributary of the Krušćica river. The ore deposits are friable at the outcrops and the interstices are filled with limonite and different sulphides. The most abundant mineral is quartz, followed by muscovite as deformed ribbons, while sericitized feldspars, pyrite, limonite and clay minerals are sporadic. Layers of quartz and mica-schists, mm-cm thick, are interbedded in the faulted host rock.

2. GEOLOGY

2.1. Pre-Variscan metamorphic rocks

The oldest rocks in the Mid-Bosnian Schist Mountains (MBSMts) are phyllites and mica schists, interlayered with metavolcanics, amphibolites and flaser gneisses. These rocks are exposed in a zone several km long at Modri Kamen and Zahor in the Busovača region. KATZER (1906,1924) interpreted these rocks as being Azoic. ŽIVANOVIĆ and MILOJEVIĆ (1975) interpreted them as being of Ordovician age. KARAMATA and KRSTIĆ (1996) supposed a Cambrian-Ordovician age for these rocks. According to PAMIĆ and JURKOVIĆ (2002) and PAMIĆ et al., (2004), the pre-Variscan metamorphic rocks could be compared not only to the Ötztal complex of the Eastern Alps, but also to Palaeozoic metamorphic complexes of the Drina-Ivanjica area (SW Serbia) and of Eastern Macedonia. According to HRVATOVIĆ (1999, 2006) the oldest rocks in the MBSM are Ordovician metaclastics and metabasalt.

Dinaridic Cambrian-Ordovician formations were metamorphosed during the Late Ordovician deformation, under P-T conditions of greenshist facies, and to a lesser extent of epidote-amphibolite facies (400-500°C; 4-5 kbars), in conformity with the statement of MATTÉ (1984) for Central Europe (PAMIĆ et al., 2004).

A detailed microscopic study performed by MAJER et al. (1991) of the pre-Variscan metamorphic rocks (Cambrian-Ordovician) in the Busovača zone demonstrated a significant difference compared to the Silurian-Devonian Variscan rocks. The pre-Variscan rocks include: a) phengitic muscovite containing more than 10 mol % celadonite; b) chloritoid with 23-26 mol % of a Mg-chloritoid component; c) chlorite richer in the Mg-component and d) barroisitic type amphibole.

MAJER et al., (1991) carried out a phase analysis of pyrophyllite, white micas, chlorite, chloritoid and amphibole from the metamorphic rocks in the Busovača-Fojnica-Kiseljak-Kreševo region. These analyses demonstrated very low to low grade metamorphism of rocks in the SW part of the MBSM, and the local presence of barroisitic amphibole in the NE part of this territory (south of Busovača) indicating higher P - T conditions.

2.2. Variscan rocks

The Silurian metaclastic formations, scarcely intercalated with pelagic limestone chert interlayers and metavolcanic rocks are represented by slates, phyllites, quartz-muscovite schists, black graphite-bearing quartzitic schists, chlorite-muscovite-quartz schists, chloritoid schists, calcic phyllites (calcareous schists) with subordinate pyrophyllite schists, metasandstones and quartzites (KARAMATA & KRSTIĆ, 1996, HRVATOVIĆ, 1996, 2006). According to MAJER et al., (1991) the predominant Variscan rocks of Silurian age contain phengitic muscovite with less than 10 mol % celadonite, chloritoid with mainly 8-15 mol % of Mg-chloritoid component and chlorite rich in the Fe-component. These rocks were generated under low-grade P-T conditions ranging between 350 - 400°C and approximately 300-400 MPa. A group of pyrophyllite-bearing rocks originated under P-T conditions of 350-430°C and 300-400 MPa. The first dating of the MBSM rocks was performed on a phyllite sample from the Fojnica area by BALOGH at the Institute of Debrecen, Hungary, PALINKAŠ et al., (1996). The obtained K-Ar age of 343 ± 13 Ma suggests a Middle Viséan (Carboniferous) thermometamorphic event, a metamorphic overprint of an inferred pre-Variscan complex in the Busovača-Fojnica region (PAMIĆ et al., 2004).

Devonian. The Silurian rocks are overlain by massive reef limestones, dolomites, locally marbles characterized by tabular coral *Favosites vranicae* and stromatoporoid *Amphipora ramosa*. Lower parts of the carbonate sequence belong to the Early Devonian (Emsian), whereas the upper parts belong to the Middle Devonian, mostly to the Eifelian and to a lesser extent to the Givetian (ŽIVANOVIĆ, 1979). Upper Devonian formations, which belong to the Frasnian, contain conodont *Ancyrodella ooids* (ŽIVANOVIĆ, 1972), only recorded at the village of Dusina.

MUDRENOVIĆ et al., (1969) consider that greywacke-sandstones, without fossils, which overlie Devonian layers with **conodonts** at Jezero (Jajce) are of the Lower Carboniferous age. ŽIVANOVIĆ and MILOJEVIĆ (1975) stated that argillites and clay shales at Medenik (Rostovo), although without fossils, but covering fossiliferous Devonian sediments must be attributed to the Lower Carboniferous. VUJNOVIĆ (1981) included greywacke sandstones and chlorite-sericite schists with locally rare phyllite breccias located at the village of Komar (Travnik), into the Lower Carboniferous.

A dry land period existed from the end of the Lower Carboniferous to the Upper Permian.

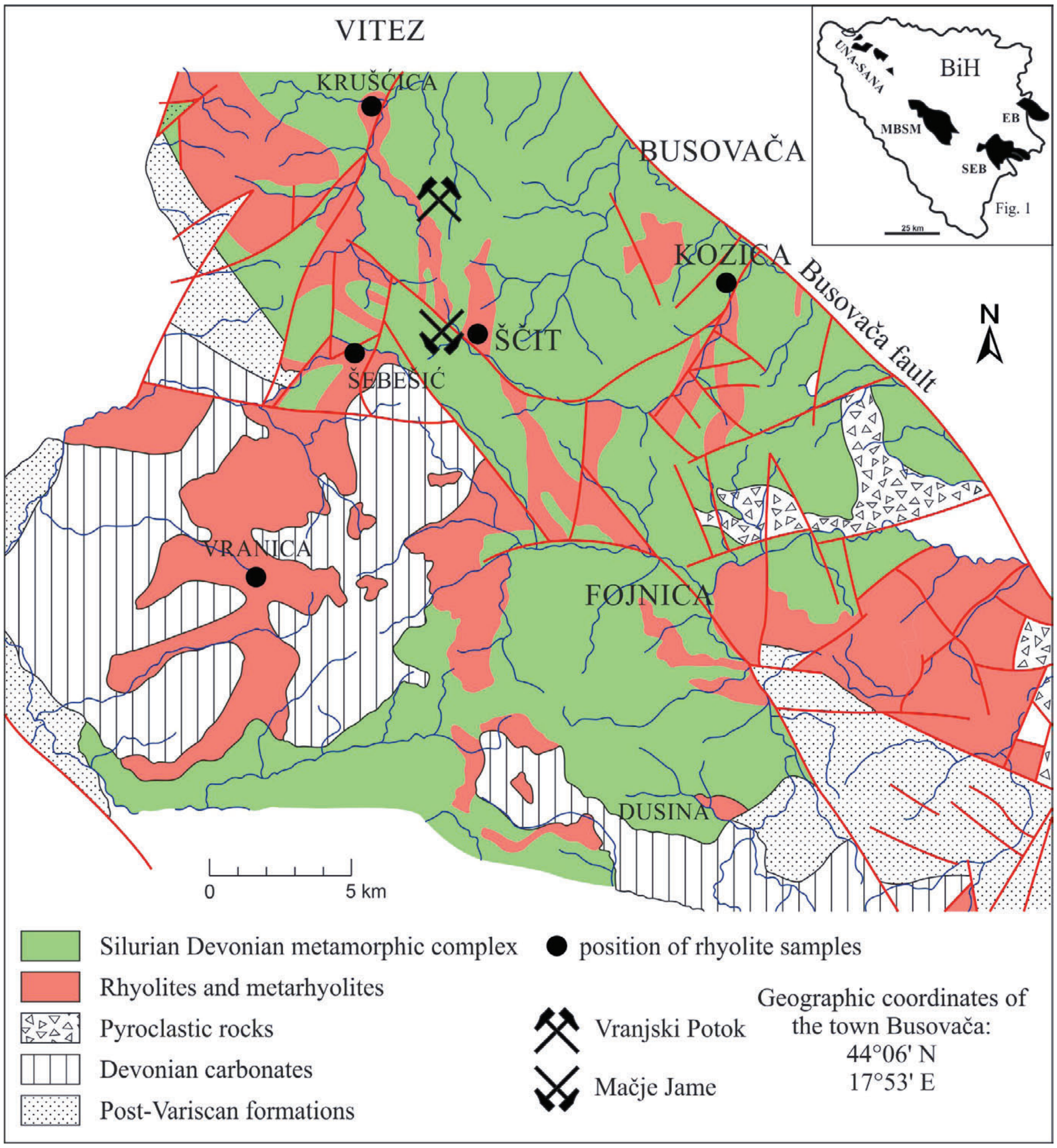

Figure 1: Simplified geological map of the northeastern part of the Mid Bosnian Schist Mountains.

Figure 2: Vranjski Potok ore deposit. On the right side of this photo are visible outcrops of thick banded coarse-grained quartz sandstones and conglomerates inserted with different ore and gangue minerals.

Three Upper Permian formations have been identified: (1) Upper Permian Bojska series in the region of Bugojno, Kalin; **(2) Upper Permian Opara series**; **(3) Permo-Triassic series in the area of Travnik**.

2.3. Variscan magmatic rocks

Detailed microscopic and chemical investigations of quartz-porphyry and metaquartz porphyry of Vranica Mountain (2107 m) and albite porphyry of Sinjakovo (Jajce) were conducted by JURKOVIĆ and MAJER (1954). The rocks have been identified as rhyolites, metarhyolites and albite rhyolite, generated from magma of a leucogranitic-aplitic character. Southwest of Jezero-Jajce, near the village of Aljinovac, in the western tributary to the Perućica river, the authors established contact metamorphism between albite rhyolite and crinoid limestone at that time supposed to be of Lower Permian age (KATZER, 1906, 1924. geological map (M 1: 200 000). In addition, on Vranica Mountain they established contact metamorphism between rhyolites and at that time considered Carboniferous phyllite. Further data concerning chemical compositions of the MBSM rhyolites are found in the explanations of the basic geological maps (M 1 : 100 000).

According to ŽIVANOVIĆ and MILOJEVIĆ (1975), four successive eruptive phases of rhyolites in the MBSM have been established: the first phase as shallow Silurian intrusions in the Gornji Vakuf area; the second phase between the Lower Carboniferous and the Upper Permian; the third phase, very subordinate, during the Permo-Triassic and the last phase, only locally in the Lower Triassic. ŽIVANOVIĆ (1979) and JOVANOVIĆ et al. (1978) presented the case for a two-stage magmatic history: 1) the older stage resulted in porphyrite sills found in the Silurian muscovite-chlorite schists (^{1}Pz) and quartz-sericite schists (^{3}Pz), and 2) the younger one which occurred in Carboniferous-Permian time and produced quartz porphyries penetrating Silurian and Devonian rocks, thus causing contact metamorphic changes in carbonate rocks. They considered that quartz keratophyres were partly Carboniferous-Permian and partly Triassic in age. TRUBELJA (1978) and SOFILJ et al. (1980) suggested that metarhyolites intruded as intrusive and extrusive rocks during Carboniferous and early Permian time. They considered that quartz keratophyres are partly of Triassic age. HRVATOVIĆ (1996, 2006) considers that most of rhyolites are synsedimentary with presumed Silurian metasediments and are of Silurian age. Some hypabyssal rhyolites intruded into the Late Silurian and Early Devonian limestones which also occur as xenoliths within the volcanic body. Large masses of pyroclastics are either interlayered with metaclastics or represent shallow hypabyssal bodies.

MAJER and GARAŠIĆ (2001) defined the composition of the major elements, compatible elements (Ni,Cu,Co) as well as incompatible elements with low (K, Rb, Ba, Th) and high ionic potential (Y, Zr, Nb). A low content of compatible elements and a high content of incompatible elements in rhyolites compared to the average contents in chondrites prompted the authors to express their doubt as to the juvenile origin of rhyolites from the mantle, and to attribute them to a crustal origin. JURKOVIĆ et al. (2010a) determined in one Vranica Mountain rhyolite sample an extremely high ^{87}Sr/^{86}Sr ratio of 0.776995 ± 2 s, performed by thermal ionisation mass spectrometry (TIMS) in the Activation Laboratory, Ancaster, Ontario, Canada. This high strontium ratio of rhyolite might indicate the crustal source of an S-type of granitoid magma.

3. PARAGENESIS OF THE MAČJE JAME AND VRANJSKI POTOK ORE DEPOSITS

A significant difference exists between the paragenesis of the ancient, abandoned mine Mačje Jame characterized by opened primary and oxidation ore zones and the paragenesis of the recently discovered ore locality Vranjski Potok, open only in the oxidation zone. The difference is also between host rocks: schists are present in the Mačje Jame and metasandstones (conglomerates) in the Vranjski Potok ore deposit.

3.1. Petrography of ore and gangue minerals

3.1.1. The ore deposit Mačje Jame

JURKOVIĆ conducted the first unpublished microscope study of the Mačje Jame ore and gangue minerals as early as 1956a and 1958 (references). These minerals were identified exclusively under polarizing microscope using thin transparent (petrographic) and polished ore sections (hereinafter **marked with an asterisk, ***). Quantitative values of their amounts were performed exclusively by recalculation from chemical analyses performed during this study (2012-2013), displayed in **Tables 2a, 2b, 4a, 4b, 5a, 5b, 6a, 6b and 9b**. Minerals marked with a dot (●) were identified by combining microscopic analyses and analyses of trace elements and REE analyses. Minerals identified by trace element analyses, anticipating genetic type of ore deposits, are marked with a symbol (○). Minerals identified during this study using optical methods are marked with a symbol (**).

The earliest phase of mineralization which makes up 90 to 99 % of the ore, is characterized by different Fe-Mg-Ca-Mn carbonate minerals (siderite, ankerite, dolomite) as the main minerals, and by subordinate magnetite, haematite, albite and scarce pyrite I and quartz I.

Magnetite I. (*****, content: < 5 wt%) is the earliest mineral component, idiomorphically developed, isometric, and marginally **martitized**. **Haematite I** (*****, content: < 5 wt%) is rod-shaped, rodlike formed, 1-4 mm long, 30-60 μm thick. It forms parallel, radial, or bent bundles densely or thinly scattered within carbonates. Basal cross–sections or irregular small aggregates are very rare. A significant amount of haematite I was transformed into **magnetite II** (*****) most probably at the beginning of the sulphide phase. Particular bundles and even particular sticks of haematite I were replaced to different degrees during the process of reduction in which enlargement of magnetite II crystals occurred, and therefore the margins are less acute (**Plate I, photo 1, 2, 5**). Calculation of amounts of irregularly martitized magnetite and oxidized haematite were not calculated individually but alongside goethite.

Siderite (*****, content: 64.7 wt %), is in rombohedral habit with a diameter of up to 0.5 mm. These crystals build up subparallel or radial bundles as siderite II. In **Table 9** isomorphic components of the Mačje Jame siderite-ankerite

Table 1: Paragenesis of the Mačje Jame deposit (Table 1a) and Vranjski Potok deposit (Table 1b) located in the MBSMts (Captions: see text).

Parageneses ANALYTE	Method of identification	MAČJE JAME wt. %	Method of identification	VRANJSKI POTOK wt. %
quartz (SiO_2)	⁎	5.665	▲	61,000
albite ($K(Na)AlSi_3O_8$)	⁎	5.680	▲▲	0,570
siderite ($(Fe,Ca,Mg,Mn)CO_3$)	⁎	45.695		–
pyrite (FeS_2)	⁎	3.090	▲	–
arsenopyrite (FeAsS)	⁎	1.745	▲▲	0,018
magnetite (Fe_3O_4)	⁎	SEE content of goethite		–
haematite (Fe_2O_3)	⁎			
marmatite (Zn,Fe)S	⁎	0.107		–
tennantite (tetrahedrite)	⁎	0.086		–
chalcopyrite ($CuFeS_2$)	⁎	0.058	▲	1,993
boulangerite ($Pb_5Sb_4S_{11}$)	⁎	0.029		–
chalcedony (SiO_2xH_2O)	⁎	<0.100		–
cassiterite (SnO_2)	⁎	0.024	▲▲	0,006
galena (PbS)	⁎	0.018		–
wolframite ($(Fe,Mn)WO_4$)	●	0.012		–
cosalite ($Pb_2Bi_2S_5$)	●	0.010	▲▲	0,058
sphalerite (ZnS)	●	<0.010	▲	0,023
enargite (luzonite) ($Cu_3As(Sb)S_4$)	⁎	<0.005		–
sternbergite ($AgFe_2S_3$)	⁎	<0.005		–
silver (Ag)	⁎	ppm <1.6	▲	0,001
gold (Au)	●	ppm 0.029	▲	0,339
bismuth (Bi)	●	<0.010	▲▲	0,329
molybdenite (MoS_2)	○	<0.001	▲▲	0,0004
barite ($BaSO_4$)	●	0.004	▲▲	0,040
cobalite (CoAsS)	○	0.022	▲▲	–
gersdorffite (NiAsS)	○	0.030		–
columbite (FeMn) ($(Nb,Ta)_2O_6$)	○	0.012	▲▲	–
allanite ($(Ce,Y)\cdot(Al,Fe)_3(SiO_4)_3\cdot OH$)	⁎⁎	<0.100	▲▲	–
Trace elements (Tr-El)	●	0.071	▲▲	0,109
REE	●	0.017	▲▲	0,018
goethite ($FeO\cdot OH$) + magnetite + haematite	⁎	39.315	▲	26,955
kaolin ($Al_2Si_2O_5(OH)_4$)	ppm ○	56.800	▲▲	10,164
calcite ($CaCO_3$)	⁎	trace		–
Pb-As-Sb oxydes	●	trace	▲	>0,016

(FeO, CaO, MgO and MnO) ore samples were calculated: 62.5 wt % $FeCO_3$; 8.8 wt % $CaCO_3$; 19.3 wt % $MgCO_3$ and 9.4 wt% $MnCO_3$. These values are significantly elevated, particularly the values of $MgCO_3$ and $MnCO_3$ in relation to the younger Maškara siderite-barite-tetrahedrite ore deposit in the MBSM. Obviously siderite-ankerite generation in the Mačje Jame deposit represents the earlier generation of iron carbonates in the MBSMts generated under higher P-T conditions (350-400°C and 1.5 kPa) (**Plate I, photos 1, 4, 5**).

Albite (* content: 5.7 wt %), develops as single crystals, twins or polysynthetic crystals: 0.5 to 1 mm long, even 3 to 4 mm in druses. Greater albite crystals occlude fragments or crystals of older carbonates, magnetite and Ti-oxides. Albite is very irregularly distributed in the ore.

Quartz I (*, 5.7 wt %) is very coarse-grained, cataclased and optically anomalous. Quartz is mostly concentrated along salbands. It is younger than carbonate minerals replacing their particular zones (**Plate I, photo 3**).

Pneumatolytic-katathermal phase of mineralization

This phase accounts for between 2 and 4 wt.% of the ore of the Mačje Jame deposit **(Table 1.)**.

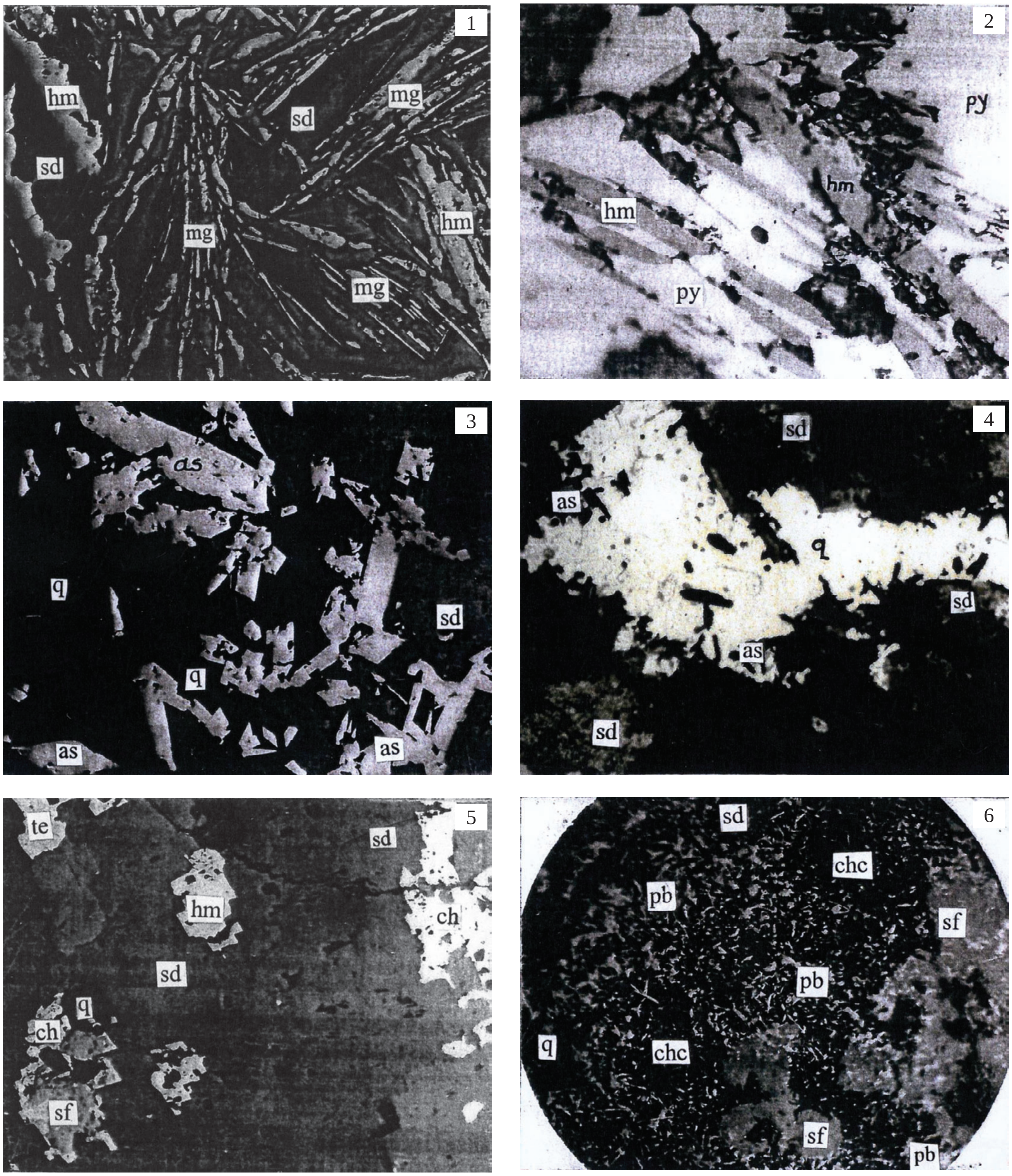

Plate I

Six photomicrographs of the Mačje Jame ore samples. Legend: hm – haematite, sd – siderite, pb – galena, mg – magnetite, py – pyrite, q – quartz, as – arsenopyrite, tennantite, chc – chalcedony, sf – sphaterite, ch – chalcopyrite

Pyrite II (*, 3.1 wt %) is partly or strongly oxidized. Unoxidized relicts of pyrite of two ore samples gave 0.65 and 5.62 wt.%. Many bigger crystals are cataclased and locally mylonitized. It is the most abundant sulphide mineral (**Plate I, photo 2**).

Quartz II (*) is coarse-grained, most often associated with arsenopyrite crystals.

Arsenopyrite (*, 1.8 wt %) has been found in the three ore samples which gave 2.70, 0.79 and 0.36 wt.% FeAsS. It is most abundant within carbonate minerals and as single crystals, and as aggregates 50-200 μm in diameter. Arsenopyrite crystals are sometimes occluded and associated in the coeval quartz crystals and distinguished predominantly with idiomorphic (rhombic) forms (**Plate I, photos 3, 4**).

Mesothermal-epithermal phase of mineralization

During this phase some Co, Fe, As, Sb, Bi and Pb sulphides and sulphosalts were formed.

Marmatite (*) **(**average content is **0.11 wt%)** is the oldest mineral of this phase replaced by other younger minerals, particularly by boulangerite in the form of small irregular masses or as bands of needles or crystals characterized by rhombic sections. Marmatite is distinguished by yellow-brownish, red-brownish and red internal reflections, which indicate sphalerite, rich in iron. It is visible to the naked eye and its content in the ore is 0.107 wt. % (**Plate I, photos 5, 6**).

Chalcopyrite (*) (average content is **0.06 wt.%**) and associated **tennantite** (*) (av. content is **0.086 wt.%**) **are the main copper minerals** (**Plate I, photos 5, 6**).

Enargite-luzonite (*) (average content is **0.005 wt.%)** is a very rare mineral in the form of minute crystals some tens μm in diameter, most often occluded in chalcopyrite. It is partly lamellar in habit (luzonite).

Galena (*) (average content is < **0.018 wt.%**) is associated with other sulphides, or it selectively replaces haematite.

Drusy epithermal-hydatogene mineralization phase

Small irregular cavities in the ore have their interior walls encrusted with small **quartz III** crystals or with chalcedony showing relicts of primary colloid structure. Using optical methods, the following drusy minerals were identified (**Plate I, photos 4, 6**).

Chalcedony (*) (average content is **< 0.1 wt%**) is the main gangue mineral of this mineralization phase. Small grains of chalcedony are often characterized by their radial-concentric structure. **Quartz III** (*) grown on the drusy walls has a bipyramidal-prismatic habit.

Boulangerite (*) (average contents in three different samples calculated from the trace element analyses are **0.029, 0.019, 0.012 wt.%).** It predominantly occurs within chalcedony in the form of numerous small aggregates or as very dense needle bundles or particular needles marked by rhombic cross-sections. Droplets of pinkish **bismuth** (*) (average content **< 0.01 wt.%)** are noticeable within boulangerite. Locally, there is a single grain or densely arranged minute yellow-pinkish grains with higher relief than that of the boulangerite replacing it, probably of **argyropyrite (X)** or **sternbergite (X)** (average content **< 0.005** wt.%), goldish-yellow coloured and of higher reflection than boulangerite (**Plate I, photo 6**).

Yellow sphalerite (*) (average content **< 0.01 wt.%)** mostly within chalcedony is distinguished by clearer internal reflection, preponderantly yellowish. It forms minute drops reminiscent of a colloid structure.

Marcasite (*) is associated with **gel-pyrite** indicating generation from older weathered pyrrhotite.

Hypergene mineralization

During the oxidation phase of the Mačje Jame ore deposit, the main mineral that formed is **goethite**, whereas **lepidocrocite** is rare. C**ovellite, chalcocite, malachite, azurite and Sb (As) oxides** are subordinate or occur as accessories. Small masses of **elemental silver** (ϕ 100-150 μm) were observed in two polished sections of the ore.

3.1.2. Minerals identified during this study

Minerals identified using the data of trace element analyses, REE analyses and detailed microscopic investigations are indicated **with a small black dot** (●) and probable minerals **with the symbol** (○) (see **Table 1a**).

Cassiterite (●) (average content **0.024 wt%)** was observed in some ore samples (polished sections) as microscopically fine masses, distinguished by high relief, and great hardness. It is dark-grey or pinkish, characterized by low reflectivity, clear anisotropy and white-light-dark brown internal reflection. Trace element analysis indicate 189 and 151 ppm **Sn** which equates to 0,024 and 0,019 wt.% SnO_2. The Mačje Jame ore deposit is the second cassiterite bearing locality in the MBSM, the first locality being Vrtlasce several km east of the town of Fojnica (JURKOVIĆ, 1956).

Wolframite (○) (average content **0.012 wt%)** is a presumed mineral, because trace element analysis of one ore sample produced a high content of 71.6 ppm W. The second reason for this presumption is the discovery of wolframite in the Main Vein of the big Čemernica quartz-antimonite-sphalerite-veiny system (RAMOVIĆ, 1956). Wolframite crystals in the Čemernica ore deposit are visible to the naked eye and contain 74 wt.% WO_3, 18 wt.% FeO and 6.2 wt.% MnO which corresponds to the mineral **hibernite**.

Gersdorffite (○) (average content **0.03 wt %)** is also a presumed mineral in the Mačje Jame ore deposit. Trace element analyses produced 182 ppm of Co and 244.2 ppm of Ni. The recalculation of these values gives 0.022 wt.% of CoAsS (**cobaltite**), and 0.030 wt.% of NiAsS (**gersdorffite**). Their isomorphic arsenide (gersdorffite) is a typical pegmatitc-pneumatolytic high-temperature mineral (RAMDOHR, 1983).

Columbite-tantalite (○)**.** **(**average content **0.012 wt%)** Heightened contents of Nb (26.8 ppm) and Ta (10.9 ppm) in the same ore sample indicate presumed minerals from the isomorphic pair columbite-tantalite. Recalculation gives $\mathbf{(Fe,Mn,Nb_{0.711}Ta_{0.289})_2O_6}$ with the participation of **0.012 wt.%.**

The high presence of **Y** (58.8, 70 and 90.4 ppm) and 129 ppm of **Ce (Table 5a)** proves formation of the mineral **allanite** (**), whereas the presence of 28.1 ppm of Th indicates **monazite**.

3.1.3. Microscopic investigation of ore samples from the Vranjski Potok deposit

Twelve mineralized rock samples marked by symbols BOS-1, 2, 3, 4, 5, 6, 9, 10, 11, 13, 15 and 25 were investigated under the ore microscope. The mining investigations were conducted recently (in 2013, **Table 1b**) in the initial phase, and therefore the ore samples have been picked up only in

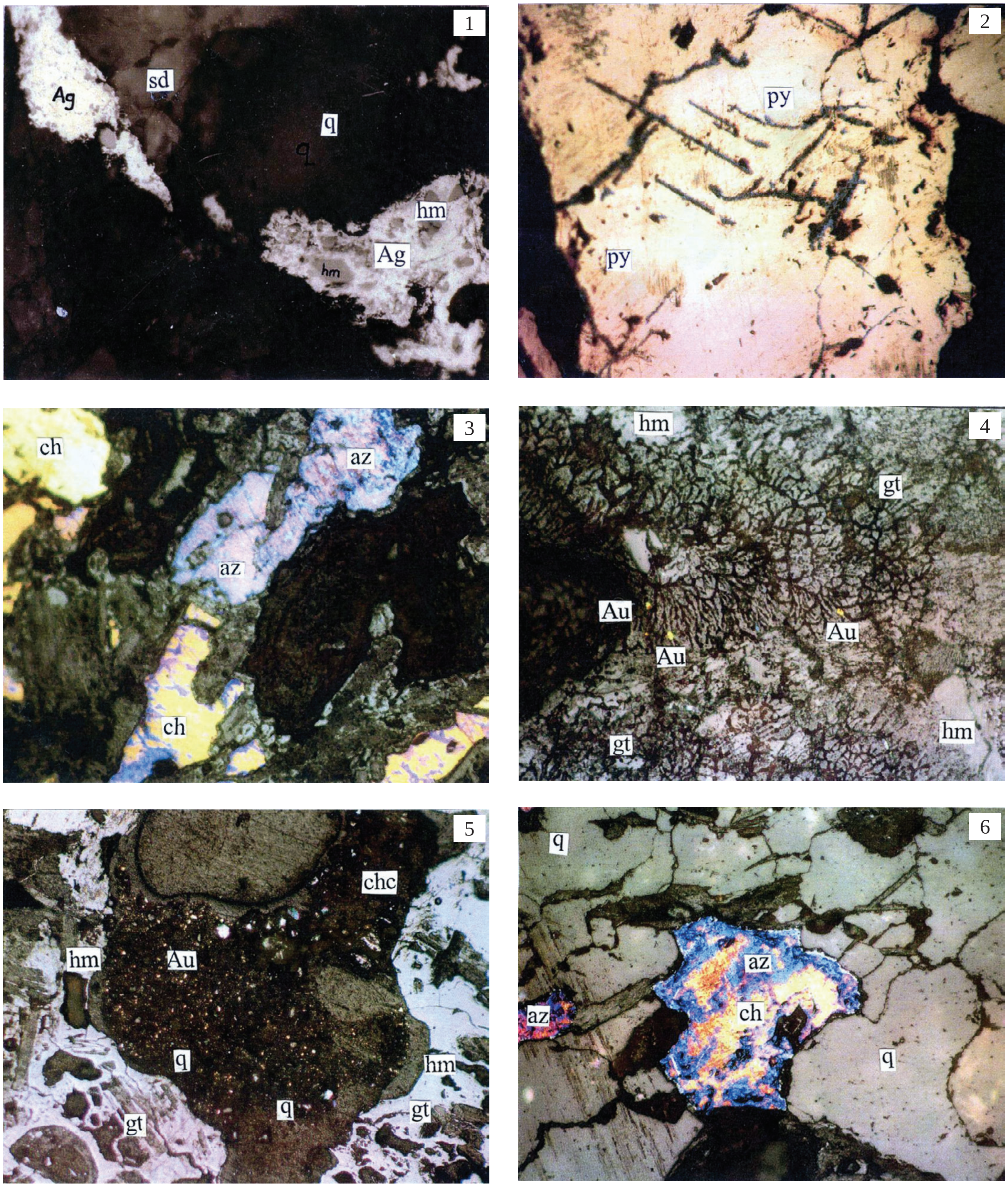

Plate II

Photos 2-6 are photomicrographs of the Vranjski Potok ore deposit. Photo 1 is from Mačje Jame ore deposit. Legend: hm – haematite, sd – siderite, pb – galena, mg – magnetite, py – pyrite, q – quartz, as – arsenopyrite, tennantite, chc – chalcedony, sf – sphaterite, ch – chalcopyrite, Ag – silver, Au – gold

the oxidation zone of the Vranjski Potok deposit. All minerals are displayed in **Table 1b**. Minerals identified under the microscope during this study in 2013 are indicated by a small darkened triangle (▲), and their contents were calculated from the chemical analyses. Minerals identified by trace element analyses anticipating a genetic type of ore deposits, were indicated by two small darkened triangles (▲▲).

The polished sections of BOS-1, 3, 4, 15 and 25 samples were taken from quartzose conglomeratic metasandstone composed of rounded or semirounded particles. In the BOS-

Table 2: Chemical analyses of two ore samples from the Mačje Jame ore deposit (Table 2a) and five samples from the Vranjski Potok ore deposit (Table 2b).

MAČJE JAME					Table 2a
Sample		MA-JA	MA-JS		
Chemical method	MDL	FUS-ICP	FUS-ICP	Average	
Analyte	wt. %	wt. %	wt. %	wt. %	
SiO_2	0.010	14.380	5.060	9.720	
Al_2O_3	0.010	2.320	0.180	1.250	
Fe_2O_3	0.010	27.240	39.990	33.610	
FeO	0.010	17.990	17.310	17.650	
MnO	0.001	2.050	2.670	2.360	
MgO	0.010	4.350	3.630	3.990	
CaO	0.010	3.130	1.460	2.290	
Na_2O	0.010	1.300	0.040	0.670	
K2O	0.010	0.030	0.010	0.020	
TiO_2	0.001	0.020	0.100	0.060	
P_2O_5	0.010	<0.01	0.010	<0.01	
As	5 ppm	1.290	0.360	0.830	
LOI		26.520	30.410	28.470	
Total	0.01	100.620	101.230	100.980	
		Table 2 (a+b)			

			VRANJSKI POTOK				Table 2b
Sample	MDL	BOS-9	BOS-10	BOS-12	BOS-13	BOS-15	Average
Analyte	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
SiO_2	0.010	69.000	41.000	61.000	50.000	78.000	59.800
Al_2O_3	0.010	5.330	4.910	2.140	7.160	3.040	4.520
TiO_2	0.010	0.020	0.010	0.010	0.020	0.010	0.010
Fe_2O_3	0.040	17.470	42.810	29.640	30.730	12.210	26.570
CaO	0.010	0.030	0.030	0.520	0.040	<0.01	0.120
MgO	0.010	2.630	1.760	0.430	2.310	0.810	1.590
Na_2O	0.010	<0.01	0.004	0.020	0.005	0.005	0.010
K_2O	0.010	0.024	0.060	0.080	0.120	0.070	0.070
MnO	0.010	0.100	0.080	0.270	0.080	0.030	0.110
P_2O_5	0.010	0.030	0.120	0.160	0.130	0.030	0.090
S		0.170	0.080	0.170	0.180	1.510	0.420
H_2O+ (gt)		1.970	4.840	3.350	3.470	1.380	3.000
H_2O+ (kl)		3.550	3.280	1.420	4.780	2.030	3.010
Total	0.010	99.728	99.809	99.220	99.034	99.137	99.320

25 sample microbrecciated and mylonitized particles of host rock are visible. Polished sections of these ore samples studied here contain different **colloform limonite structures** (Fe oxides and hydroxides). Irregular relict patches of **pyrite I** and coarse-grained porous and strongly cataclased **pyrite II** are also present. Locally, small masses of **chalcopyrite**, rarely **sphalerite** and one very weathered copper mineral, associated with **malachite** and **azurite**, probably **tetrahedrite**, are observed. Hollows in the rock are encrusted with fine layers of **younge**r **pyrite** and **Fe-hydroxide**. Sample BOS-25 contains partly **metasandstone** and partly **micrograined quartz** as the main gangue, coloured by iron oxides (**Plate II, photos 1-6**).

The BOS-2, 5, 6, 9, 10, 12 and 13 samples are composed only of ore with predominantly **micrograined quartz** (diameter in μm). Many quartz grains contain occluded pyrite and micrograins or micromasses of **elemental gold or electrum** which is bright yellow or silver-yellowish in colour. Pyrite, gold and silver occluded in quartz grains are not oxidised because they are totally isolated in quartz grains. **Younger pyrite II** and **mica** flakes often occur in the fine fractures and rarely on the short faults in the **quartz gangue**. Fine encrustations of **arsenic and antimony oxides** formed by weathering of **arsenopyrite**, **tetrahedrite and lead antimonides** are also visible in the small masses of **chalcopyrite** and **malachite**.

3.2. Chemical composition of the ore of both deposits

3.2.1. The chemical composition of the main components of the Mačje Jame deposit

By recalculating the data of two samples (**Table 2a**) on the minerals identified earlier by optical methods (JURKOVIĆ, 1956), a mineral composition model was obtained as displayed in **Table 3c**. It is for the most part an **iron carbonate deposit** with different Fe-Mg-Ca-Mn carbonates and with subordinate iron oxides **magnetite** and **haematite**. Almost 50% of the siderite has been oxidized to **goethite** and lepidocrocite. Only **pyrite I, II** (av. content 3.1 wt%) and **arsenopyrite** (max. value 2.7 wt%) are visible to the naked eye, all other numerous sulphides and sulphosalts are accessories (**Table 1**). Although pyrrhotite was not identified microscopically, the presence of typical **"birds eye" structure** of gel-pyrite-marcasite indicates its formation. When we attempted to recalculate all TOT/S (total sulphur) only on pyrite, we obtained a lack of sulphur.

3.2.2. Chemical composition of the ore in the Vranjski Potok ore deposit

Quartz occurs partly as detrital particles of quartzose metasandstone, and partly as a chemically precipitated gangue mineral (**Table 2b, Table 2c**). The quartz content is approximately calculated at 60.6 wt %. **The main ore mineral is goethite**, whereas lepidocrocite is markedly subordinate. In the oxidation zone of the Vranjski Potok ore deposit, the primary hypogene siderite is almost completely oxidized into goethite, whereas pyrite, magnetite and haematite are partly altered to goethite. The average calculated content of these minerals amounts to 26.8 wt% and varies between 13.6 and 47.7 wt%.

Minerals of the clay group. Due to the minute available amounts of the elements Ca, K and Na, conversion into kaolinite was performed out of the three possible minerals (kaolinite, illite and montmorillonite).. The obtained values range between 5.04 and 17.41 wt. % (the average value is 10.09 wt. %). The average content of **albite** is low (0.6 wt. %), and it is unevenly distributed in the ore. The content of albite is probably greater in the primary zone. Contents higher than 1 wt% were only observed for oxidized copper minerals: **malachite, azurite, cuprite, Cu–sulphate** etc. **Table 2c** shows that the values of $CuFeS_2$ in the primary zone would range between 0.6 and > 2.9 wt. %. The calculated content of Fe_2O_3 (12.2 up to 42.8 wt.%) belongs to the mineral goethite. The Al_2O_3 (with 2.1, and 7.2 wt. %) is locked into the clay minerals. A high content of H_2O^+ (crystal water) between 1.4 and 4.8 wt% is linked to goethite, whereas 1.4 to 4.8 wt% of crystal water is attributed to clay minerals.

Table 3: Main mineral components in the Mačje Jame and Vranjski Potok ore deposits.

Main mineral components in the Mačje Jame and Vranjski Potok ore deposits				Table 3
Ore deposit	MAČJE JAME		VRANJSKI POTOK	
Number of samples	three		five	
Analyte	wt. %		wt. %	
Quartz	5.665	–	60.573	–
Siderite	44.730	47.241	–	–
Albite	5.680	5.999	0.566	1.435
Pyrite I, II	3.090	3.264	–	–
Arsenopyrite	1.814	1.916	0.018	0.046
Chalcopyrite	0.058	0.062	>1.979	>5.019
Clay mineral	trace	trace	10.093	25.596
Goethite+Fe_3O_4 + Fe_2O_3	39.315	41.520	26.766	67.879
TOTAL	100.352	100.002	99.995	99.975

3.3. Trace elements in the Mačje Jame and Vranjski Potok ore deposits

3.3.1. Trace elemets in the Mačje Jame deposit

Trace element contents in the Mačje Jame deposit are displayed in **Table 3.** The most characteristic trace element is **As** predominantly as the mineral **arsenopyrite**. The heightened contents of **Co** (182 ppm) and **Ni** (244 ppm) also indicate the presence of **cobaltite** and **gersdorffite.** High contents of **Sn** (151 and 189 ppm) is evidence of **cassiterite** and 71.6 ppm of **W** suggests the probable presence of the mineral **wolframite.** The ore sample MA-JS contains 26.8 ppm of **Nb** and 10.9 ppm of **Ta,** which probably reflects the presence of the mineral **columbite.**

Among **non-ferrous** metals, **Zn** is the most abundant (989 and 220 ppm) occurring in the minerals **marmatite**, **tetrahedrite** and in **yellow sphalerite**, **Cu** (20, 25 and 370 ppm) is a constituent of **chalcopyrite, tetrahedrite,** and **enargite-luzonite. Pb** (419 ppm) with **Sb** (74, 35 and 30 ppm) formed the mineral **boulangerite** and with **Bi** (44 ppm) the mineral **cosalite.** It is very interesting to note the low contents of **Ag** (< 1.6 ppm)**, Au** (0.029 ppm), **Hg** (0.95 ppm) and **Se** (2.5 ppm). JURKOVIĆ et al., 2010a, 2011 proved mutual (reciprocal) genetic interdependence among **Bi**, **Ag**, **Au, Hg** and **Se**. These trace elements are trace elements in the oldest MBSM deposit (Mačje Jame). In the youngest MBSM ore deposits with Hg-tetrahedrite as the main, almost the only ore mineral (Maškara, Trošnik, Glumac), the very high values of these elements incontestably suggest two different mineralising fluids in terms of time and space (JURKOVIĆ et al., 2010a).

3.3.2. Trace element contents in the Vranjski Potok deposit

High values of **Sn** (50 and 181 ppm) indicate relicts of the resistant hypogene **cassiterite**. Likewise, the values of **Zr** (average 57 ppm) prove the presence of the mineral **zircon**. The heightened contents of **Y** (16 to 47 ppm) and of **Ce** (av-

Table 4: Trace element contents in the Mačje Jame ore deposit Ba-Y group and Mo-Se group.

Trace element contents in the Mačje Jame ore deposit — Table 4

Sample		MA-JA	MA-JS		MA-JP	Trace Elements		MA-JA	MA-JS		MA-JP
Anal. Method	MDL	FUS-MUS	FUS-MUS	MDL	4B	Method	MDL	FUS-MUS	FUS-MUS	MDL	IDX
Analyte	ppm	ppm	ppm	ppm	ppm	Analyte	ppm	ppm	ppm	ppm	ppm
Ba	3.00	7.00	6.00	1.00	31.00	Mo	2.00	<2.00	<2.00	0.10	3.700
Be	1.00	<1.00	<1.00	1.00	<1.00	Cu	10.00	20.00	370.90	0.10	25.100
Co	1.00	31.00	20.00	0.20	182.00	Pb	5.00	6.00	<5.00	0.10	418.500
Cs	0.10	0.10	0.20	0.10	0.10	Zn	30.00	220.00	<30.00	1.00	989.000
Ga	1.00	3.00	4.00	0.50	2.40	Ni	20.00	40.00	30.00	0.10	244.200
Hf	0.10	<1.00	8.10	0.10	<0.10	As	5.00	1.29 wt%	0.36 wt%	0.50	see Table 2a
Nb	0.20	1.00	26.80	0.10	4.90	Cd		n.a.	n.a.	0.10	1.800
Rb	1.00	2.00	2.00	0.10	1.30	Sb	0.20	74.40	34.60	0.10	30.200
Sn	1.00	4.00	189.00	1.00	151.00	Bi	0.10	1.80	0.60	0.10	43.700
Sr	2.00	58.00	9.00	0.50	11.90	Ag	0.50	<0.50	<0.50	0.10	3.900
Ta	0.01	<0.01	10.90	0.10	<0.10	Au*		n.a.	n.a.	0.50	29.20*
Th	0.05	0.27	28.10	0.20	0.30	Hg_x		n.a.	n.a.	0.01	0.95x
U	0.01	1.66	4.57	0.10	1.90	Tlx	0.05	<0.05	0.07	0.10	0.10x
V	5.00	51.00	101.00	8.00	127.00	Se_x		n.a.	n.a.	0.50	2.50x
W	0.50	2.20	71.60	0.50	3.70	Ge	0.50	1.70	1.30		n.a.
Zr	1.00	<1.00	269.00	0.10	2.70	Scx	1.00	11.00	16.00		n.a.
Y	0.50	58.80	70.00	0.10	90.40	Cr	20.00	<20.00	<20.00		n.a.
Total		220.03	820.27		610.60	Total		374.90	453.47		1763.65

erage 77 ppm, **Table 6b**) suggest relicts of the mineral **allanite**. In the BOS-13 sample, 22.8 ppm of **Nb** is presumed to represent relicts of **niobite** or **columbite**. The obtained values of **Co** (83 ppm) and of **As** (558 ppm) in the BOS-12 sample presume the relicts of hypogene **cobaltite** and **arsenopyrite** (**Tables 5a and 5b**).

In Vranjski Potok, the third hydrothermal phase is two to three times (see **Table 3**) better developed than in the Mačje Jame deposit (**Table 4** and **Tables 5a and 5b**), which indicates a stronger Late Variscan overprint.

Cu is the predominant trace element with contents of 0.19, 0.44, 0.48, > 1.0 wt%. The dominant copper minerals in the oxidation zone are **malachite**, **azurite**, **cuprite**, **tenorite**, **Cu-sulphates**, **chrysocolla**. The element **Pb** with the average values of 422 ppm occurs as **cerussite** and **anglesite.**

3.4. Rare earth elements

3.4.1. REE contents in the Mačje Jame ore deposit

Three analyzed ore samples gave completely different Σ REE values (**Tables 7a and 7b**). The sample MA-JS is characterized by an exceptionally high Σ REE content of 353 ppm. La participates with 57 ppm, Ce with 129 ppm and Nd with 44 ppm (**Table 6a**). Heightened contents of Y (70 ppm) and Th (28 ppm) in the same sample prove the presence of **allanite** and **monazite** as accessory minerals. Unusually elevated values of Pr, Gd, Dy, Er and Yb reflect probably other, not yet identified lanthanide accessory minerals.

The sample MA-SP is distinguished by a negative slope of the Σ LREE/ Σ HREE by the lowered negative Eu-anomaly, redoubled positive Ce anomaly and negative La/Sm_N and La/Yb_N fractionation factors (**Fig 3**).

3.4.2. REE contents in the Vranjski Potok ore deposit

Five analyzed ore samples (**Table 6b**) gave very different REE contents. The BOS-10 and BOS-13 samples have 275 ppm, BOS-12 175 ppm, BOS-09 122 ppm and BOS-15 68 ppm. The main cause for this difference is the share of sandstone as the mother rock in the analyzed sample and the intensity of overprint. Despite this, the majority of REE parameters, with the exception of BOS-12, are roughly equal (**Table 7b**). The Eu-anomaly is negative, whereas the Ce anomaly is positive. All three fractionation factors are positive, particularly the slope of the (La/Yb_N) curve.

These five samples were affected by Late Variscan overprints, particularly the BOS-12 (**Table 6b**), and then BOS-15 and BOS-10. The BOS-12 sample contains > 1.0 wt.% of Cu (> 2.9 wt% of $CuFeS_2$), then > 0.2 wt% of Bi (as cosalite and as Bi), 74 ppm of Se, 7.2 ppm Hg, 178 ppm Sb, 471 ppm of Pb, 172 ppm of Zn. The occurrence of Bi, Se, and Hg is regularly associated with the presence of Ag (32 ppm) and Au (381 ppb).

The average content of lanthanides in 5 ore samples from the Vranjski Potok deposit amounts to 183 ppm, ranging between 68 and 275 ppm (**Table 6b**). Three lanthanides (La, Ce and Nd) stand out among other lanthanides in terms of their content. Lanthanum is present with an average value

Table 5: Content of trace elements in the Vranjski Potok deposit Ba-Y group (Table 5a) and Mo-Se group (Table 5b).

Trace elements (Ba-Y) in the Vranjski Potok deposit						**Table 5a**
Sample	MDL	BOS-09	BOS-10	BOS-12	BOS-13	BOS-15
Anal.Method	4B	4B	4B	4B	4B	4B
Analyte	ppm	ppm	ppm	ppm	ppm	ppm
Ba	1.0	48.00	172.00	165.00	360.00	605.00
Be	1.0	<1.00	<1.00	<1.00	1.00	<1.00
Co	0.2	14.90	17.50	83.20	11.80	5.80
Cs	0.1	0.40	1.80	0.50	3.80	1.40
Ga	0.5	13.00	15.60	5.10	25.40	10.30
Hf	0.1	1.70	1.70	0.10	2.30	2.00
Nb	0.1	7.50	9.70	3.10	22.80	7.70
Rb	0.1	5.80	44.90	13.80	93.60	44.80
Sn	1.0	49.00	54.00	181.00	28.00	16.00
Sr	0.5	8.00	12.30	11.20	13.10	8.40
Ta	0.1	0.60	0.80	0.10	1.30	0.60
Th	0.2	6.60	10.40	0.80	17.00	5.50
U	0.1	1.10	2.80	1.20	3.00	0.80
V	8.0	39.00	55.00	13.00	83.00	38.00
W	0.5	<0.50	3.40	<0.50	3.90	0.90
Zr	0.1	60.50	54.70	5.30	85.60	56.80
Y	0.1	15.20	25.80	46.70	26.30	7.40
Total		271.30	482.40	530.10	781.90	811.40
Trace elements (Mo-Se) in the Vranjski Potok deposit						Table 5b
Sample	MDL	BOS-09	BOS-10	BOS-12	BOS-13	BOS-15
Anal.Method	4B	4B	4B	4B	4B	4B
Analyte	ppm	ppm	ppm	ppm	ppm	Ppm
Mo	0.10	4.90	2.50	2.20	1.00	0.60
Cu	0.10	1.954.00	4.807.00	>10.000.00	4.417.00	>10.000.00
Pb	0.10	190.40	562.30	471.40	821.40	63.30
Zn	1.00	155.00	407.00	172.00	84.00	57.00
Ni	0.10	3.00	7.10	21.90	4.30	2.00
As	0.50	25.90	19.80	551.17	24.70	<0.50
Cd	0.10	<0.10	0.20	0.90	0.20	0.20
Sb	0.10	2.10	4.70	178.40	22.10	0.80
Bi	0.10	125.80	81.00	>2.000.00	63.40	14.80
Ag	0.10	1.90	15.30	32.40	1.20	8.70
Au* (ppb)	0.50	240.50	181.00	380.80	89.90	772.10
Hg^x	0.01	0.98	0.71	7.15	0.31	2.69
Tl^x	0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Se^x	0.50	9.60	10.50	74.00	19.50	11.80
Total		2.714.08	6.099.11	>13.892.30	5.549.01	>10.934.00

of 40 ppm, Ce with 77 ppm, and Nd with 32 ppm. The average value of all three lanthanides (La + Ce + Nd) is 146 ppm, which accounts for 82 wt. % of the content of all 14 lanthanides in the Vranjski Potok deposit.

In view of the fact that metarhyolite and its protolith contain the same or very similar REE and La, Ce and Nd values as the predominant REE elements, it was concluded that the metamorphogenic **fluids** generated in the

Table 6: REE content of the samples from the Mačje Jame deposit (Table 6a) and from the Vranjski Potok deposit (Table 6b).

REE content in the Mačje Jame deposit							Table 6a
Sample		MA-JA	MA-JS		MA-JP		
Chemical method	MDL	FUS-MUS	FUS-MUS	MDL	4B	Average	
Analyte	ppm	ppm	ppm	ppm	ppm	ppm	
La	0.050	9.62	56.60	0.1	2.90	23.04	
Ce	0.050	20.10	129.00	0.1	6.50	51.87	
Pr	0.010	2.48	14.20	0.02	0.95	5.88	
Nd	0.050	9.21	43.70	0.3	4.80	19.24	
Sm	0.010	3.27	11.70	0.05	2.64	5.87	
Eu	0.005	1.28	4.89	0.02	1.98	2.72	
Gd	0.010	4.50	13.70	0.05	5.23	7.81	
Tb	0.010	1.16	3.41	0.01	1.49	2.02	
Dy	0.010	8.90	25.60	0.05	11.43	15.31	
Ho	0.010	2.06	5.73	0.02	3.03	3.61	
Er	0.010	6.93	18.60	0.03	9.87	11.80	
Tm	0.005	1.18	2.98	0.01	1.58	1.91	
Yb	0.010	8.23	19.90	0.05	9.85	12.66	
Lu	0.002	1.21	2.80	0.01	1.46	1.82	
Total		80.13	352.81		63.71	165.55	

REE contents in the Vranjski Potok ore deposit							Table 6b
Sample	MDL	BOS-09	BOS-10	BOS-12	BOS-13	BOS-15	Average
Analyte	ppm	ppm	ppm	ppm	ppm	ppm	ppm
La	0.10	30.00	57.60	39.80	60.00	13.60	40.02
Ce	0.10	56.30	114.40	68.30	117.10	29.70	77.16
Pr	0.02	5.47	13.67	8.20	13.42	3.41	8.83
Nd	0.30	17.10	51.10	29.60	50.90	12.90	32.32
Sm	0.05	2.82	10.22	4.47	9.80	2.29	5.92
Eu	0.02	0.87	4.56	1.77	3.07	0.92	2.24
Gd	0.05	2.36	8.61	5.59	8.37	1.80	5.35
Tb	0.01	0.43	1.33	1.08	1.12	0.27	0.85
Dy	0.05	2.43	6.31	6.63	5.09	1.43	4.38
Ho	0.02	0.55	1.03	1.41	0.91	0.23	0.83
Er	0.03	1.63	2.63	3.75	2.39	0.66	2.21
Tm	0.01	0.25	0.40	0.53	0.39	0.10	0.33
Yb	0.05	1.51	2.41	3.19	2.35	0.66	2.02
Lu	0.01	0.23	0.36	0.43	0.35	0.09	0.29
Total		121.95	274.63	174.75	275.26	68.06	182.75

S-granite magma and their pre-Palaeozoic and Lower Palaeozoic protoliths, might be a source of mineralizing fluids for the generation of the Mačje Jame and Vranjski Potok deposits.

3.4.3. Comparison of the REE contents between the Mačje Jame and Vranjski Potok ore deposits, and the metarhyolites and keratophyres from Busovača-Fojnica-Kreševo region

The range of REE contents between the ore samples and magmatic rock samples is displayed in **Table 8.**

The range of REE content values range from 158 to 197 ppm (average 180 ppm) for 5 samples of rhyolite and metarhyolite from the Fojnica-Kiseljak-Kreševo region. These 5 samples have the following average content of dominant elements: **La** 35 ppm, **Ce** 76 ppm and **Nd** 33 ppm.

Furthermore, the 3 rhyolite samples from the Šebešić-Kozica-Kruščica (Busovača) region show values of between 205 to 214 ppm (average 209 ppm) with the following dominant values: La 43 ppm, Ce 88 ppm and Nd 35 ppm. Five samples from the Vranjski Potok ore deposit produced values between 68 and 275 ppm, with an average value of 183

Table 7: REE parameters in the ore samples from the Mačje Jame deposit (Table 7a) and from the Vranjski Potok deposit.

REE parameters in the ore samples from the Mačje Jame deposit — **Table 7a**

Sample	MA-JA	MA-JS	MA-JP	Average
Mineral	sd	sd	sd	
ΣREE	80.13	352.81	63.71	165.55
ΣLREE	44.68	255.20	17.79	105.89
ΣHREE	32.96	89.92	42.48	55.12
ΣLREE ΣHREE	1.36	2.86	0.42	1.55
Eu/Eu*	0.34	0.39	0.53	0.42
Ce/Ce*	4.12	4.55	10.79	6.49
(La/Sm)N	1.90	3.12	0.71	1.91
(Gd/Yb)N	0.45	0.57	0.44	0.49
(La/Yb)N	0.84	2.04	0.21	1.03

REE parameters in the Vranjski Potok ore deposit — Table 7b

Sample	BOS-09	BOS-10	BOS-12	BOS-13	BOS-15	Average
ΣREE	121.95	274.63	174.75	275.26	68.06	36.83
ΣLREE	111.69	246.99	150.37	251.22	61.90	148.56
ΣHREE	9.16	22.72	22.18	20.62	5.15	13.85
ΣLREE ΣHREE	12.19	10.87	6.78	12.18	12.02	10.75
Eu/Eu*	0.34	0.49	0.35	0.34	0.45	0.40
Ce/Ce*	4.40	4.08	3.78	4.13	4.36	3.95
(La/Sm)N	6.87	3.64	5.75	3.95	3.83	4.23
(Gd/Yb)N	1.29	2.96	1.45	2.95	2.26	2.17
(La/Yb)N	14.26	17.14	8.95	18.32	14.79	14.55

Table 8: Comparison of the REE contents between rhyolite-keratophyres and ore samples from the Mačje Jame and Vranjski Potok ore deposit.

	LOCALITIES rocks and ore samples	KREŠEVO Rhyolite	KREŠEVO Keratophyre	BUSOVAČA Metarhyolite	BUSOVAČA Metarhyolite	MAČJE JAME	VRANJSKI POTOK
	Analyte	ppm	ppm	ppm	ppm	ppm	ppm
1	La	34.60	16.60	43.00	22.30	33.10	40.00
2	Ce	75.70	37.70	87.00	43.90	74.60	77.20
3	Nd	32.70	17.80	43.50	16.30	30.00	32.30
4	La+Ce+Nd	143.00	72.10	174.20	82.50	137.70	149.50
5	ΣREE	179.60	95.40	209.30	105.30	216.80	187.90
6	La+Ce+Nd/ ΣREE	0.80	0.76	0.83	0.78	0.60	0.84

ppm. The average values for La, Ce and Nd were 40 ppm, 77 ppm and 32 ppm, respectively.

4. Genesis of the iron deposits Mačje Jame and Vranjski Potok

The **first mineralization phase** of the Mačje Jame deposit (> 90-95 wt. %) is composed of 44.7 wt. % of Fe (Ca, Mg, Mn)CO_3 carbonates, 39.3 wt. % of magnetite, haematite and goethite, 5.7 wt. % of albite, 3.1 wt. % of pyrite, 1.8 wt. % arsenopyrite, 0.06 wt. % chalcopyrite, 0.05 wt. % of REE and 0.42 wt. % are trace elements. Siderite as the predominant ore mineral is composed of 62.5 wt. % $FeCO_3$, 8.8 wt. % $CaCO_3$, 19.3 wt. % $MgCO_3$ and of 9.4 wt. % $MnCO_3$ (**Table 9b**) indicating formation under elevated PT conditions (350–400°C and 3.5 kbars), MAJER et al., (1991).

During the very subordinately developed pegmatitic-pneumatolytic phase, numerous scarce or accessory minerals were formed: quartz II as gangue and as ore minerals, arsenopyrite (average content 1.81 wt. %), pyrrhotite, cassiterite (0.024. wt %), wolframite (0.012 wt. %), cobaltite (0.02 wt. %), gersdorffite (0.03 wt. %). One of the three analysed Mačje Jame samples contained elevated contents of Nb (26.8 ppm) and Ta (10.9 ppm), indicating the presence of the mineral columbite (0.012 wt. %).

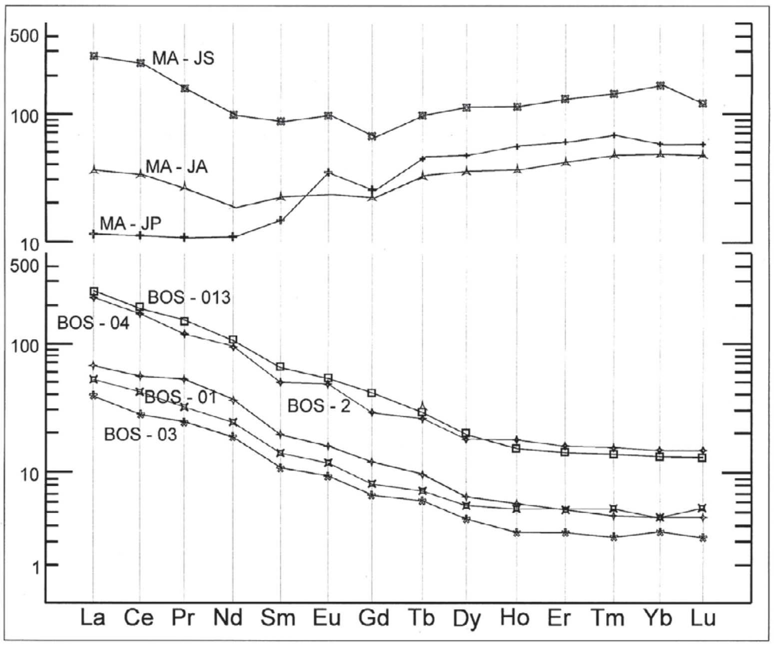

Figure 3: Plot of rare-earth elements normalized to C1 chondrites (SUN & McDONOUGH, 1989). MA–Mačje Jame deposit; BOS–Vranjski Potok deposit.

The first and second mineralization phases were most-probably formed during the **Middle Carboniferous (Visean-Moscovian)** derived from metamorphogenic fluid generated from S-granitoid magma and its protoliths.

The third, hydrothermal phase, (very poorly developed, 1-4 wt. %) is characterized by the following minerals: marmatite, tetrahedrite, chalcopyrite, boulangerite, galena, cosalite, yellow sphalerite, enargite–luzonite, sternbergite, elemental bismuth, "birds-eye" structures of gel-pyrite-marcasite, traces of silver (4 ppm) and traces of gold (29.2 ppb). Gangue minerals are quartz III, chalcedony, and rarely calcite. **The third mineralization phase** of both deposits is characterized by trace elements which are genetically the most important for the youngest deposits in the MBSM: siderite-barite-Hg tetrahedrite deposits. These elements are Bi, Se, Hg, Ag and Au, built up in the tetrahedrite lattice as the main constituents. These five elements reached Mačje Jame and Vranjski Potok ore deposits as an overprint of post-Variscan Permian or Permo-Triassic magmatic activity (JURKOVIĆ et al., 2011).

In the Jezero-Jajce part of the MBSM, there is an old, abandoned Austro-Hungarian copper mine at Sinjakovo, with the ores in the Carboniferous sediments associated with numerous contemporaneous rhyolite sills and veins. Gangue minerals consist of siderite, ankerite, ferrodolomite, with chalcopyrite as the main ore mineral (VASILJEVIĆ, 1972). A very similar paragenesis occurs in Gemericum (Slovakia), in the root zone of siderite veins at the boundary between greenschist and amphibolite facies, as reported by RADVANEC & BARTALSKY (1987), BARTALSKY (1991) and BARTALSKY and RADVANEC (1993).

Because MAJER and GARAŠIĆ (2001) expressed their doubt about the juvenile origin of the rhyolite magma from Vranica Mountain, JURKOVIĆ et al., (2010a) investigated the $^{87}Sr/^{86}Sr$ isotopic ratios in the rhyolite sample from this magma. They obtained the first, extremely high result of strontium isotope ratio of 0.776995 which indicates the previously suggested crustal origin. During further scientific investigation, they presented an additional four $^{87}Sr/^{86}Sr$ isotopic ratios obtained from the rhyolite samples collected from outcrops in the Kruščica and Kozica river valleys and in the mountains of Ščit (Busovača) and Međuvršje (Kreševo). The results were lower than in the first sample from Vranica Mountain, but still high. Finally, the last sample taken at the end of 2013 was collected from four separate rhyolite outcrops in the Jezernica river valley. These four samples have been combined and prepared for determination of their $^{87}Sr/^{86}Sr$ isotopic ratio. The amazingly high result of 0.808079, (greater than the first value), proves that the whole Vranica Mountain rhyolite block is one unique laccolite of the same granitic magma.

These results convinced us that the metamorphogenic fluids derived from an S-granitoid magma and their protoliths were the most probable source for the origin of the Mačje Jame and Vranjski Potok ore deposits.

Recently, GARAŠIĆ et al., (manuscript) performed detailed chemical and geochemical analyses of numerous rhyolite, metarhyolite, keratophyre and quartz keratophyre samples from the Busovača-Fojnica-Kiseljak-Kreševo areas. GARAŠIĆ et al. (manuscript, 2014) also accepted our suggestion to use the discrimination diagrams for the MBSM granite classification in accordance with their tectonic setting. Therefore, they continued to work on this problem and the results should be published very soon in a new scientific article.

Similar opinions with respect to Variscan granitic rocks in the Moldanubian, and in the Eastern and Southern Alps were published by NEUBAUER (1988) and FINGER and STEYRER (1990).

Table 9: Carbon, oxygen and sulphur isotopic values of siderite and pyrite minerals (Table 9a). Isomorphic composition of the different siderite samples in the MBSMts (Table 9b).

Carbon, oxygen and sulphur isotopic values of siderite and pyrite in the Mačje Jame deposit						Table 9a
Mineral	Sample	$\delta^{13}C_{PDB}$	$\delta^{18}O_{VSMOW}$	$\delta^{34}S_{VCDT}$		
sd	MA-JA	–9.5	18.0			
sd	MA-JS	–10.1	17.2			
py	MA-JP			+5.3‰		

	Isomorphic composition of the different siderite samples in the MBSMts					Table 9b
Ore deposit	Mačje Jame	Vranjski Potok	Vrtlasce Fojnica	Trošnik Fojnica	Maškara – Saski Rad	Bakovići – Čemernica
Analyte	wt. %.	wt. %.	wt. %.	wt. %.	wt. %.	wt. %.
$FeCO_3$	62.53	70.13	71.75	74.39	81.23	86.66
$CaCO_3$	8.78	3.55	15.75	12.89	9.52	1.43
$MgCO_3$	19.30	24.13	10.30	10.03	6.59	2.50
$MnCO_3$	9.40	2.20	2.02	2.69	2.66	10.10
Total	100.01	100.00	99.82	100.00	100.00	100.69

5. CONCLUSION

The Mačje Jame and Vranjski Potok iron ore occurrences situated in the north-eastern part of the MBSM, are the earliest postorogenic ore deposits in the MBSM. They formed from the metamorphogenic fluids generated from S-granitoid magma and its protoliths for the most part during the period between the Visean-Moscovian stages partly even earlier. Both ore deposits are located in the biotite-chlorite zone, the transition zone between amphibolite and greenschist metamorphic zones. In the Late-Variscan time (290-260 Ma and in the Upper Permian-Lower Triassic (260-240 Ma) time), Mačje Jame and Vranjski Potok were caught by a younger overprint which brought along Bi, Se, Hg, Ag, Au elements as well as non-ferrous metals Cu, Pb, Zn. A very similar paragenesis of siderite veins is present in the Gemericum (Slovakia), reported by RADVANEC et al. (2004) who consider that this deposit represents the oldest ore occurrence in the Gemericum Palaeozoic complex.

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