

Cobalt, nickel, tungsten, cadmium, selenium, silver and gold-bearing mercurian tetrahedrite from the Saski Rad barite–siderite deposit in the Mid-Bosnian Schist Mts.



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ABSTRACT

In the Saski Rad barite-siderite ore deposit, Hg-tetrahedrite is the main ore mineral, pyrite and some others are only accessories. Two tetrahedrite samples (fresh and weathered) have been analysed in detail: major and minor components, constituent trace elements, REE, and $\delta^{34}\text{S}_{\text{CDT}}$ values. The following microconstituents have been detected: Ni 71 ppm (in fresh sample) and 70 ppm (in weathered sample); Co 113 and 90 ppm; Cd 27 and 20 ppm; W 20 and 5 ppm, Bi 2500 and 1613 ppm; Se >100 and 72 ppm and Au 11 and 9 ppm. These values have been compared with the only currently available analysis of Hg-tetrahedrite from the Duboki Vagan near Kreševo in the Mid-Bosnian Schist Mts. (MBSM) carried out by JURKOVIĆ et al. (2010): Ni 266.2 ppm; Co 63.5 ppm, Cd 319.6 ppm; Bi 1466.0 ppm; Au 38.96 ppm which also agrees with our analysis of Hg-tetrahedrite from the Brixlegg barite deposit in Tyrol, Austria: Co 234.4 ppm; Cd 160.5 ppm; W 6.7 ppm; Sn 1.0 ppm; Bi 909.1 ppm; Se > 100 ppm and Au 2.3 ppm.

The $\delta^{34}\text{S}_{\text{CDT}}$ isotope values of six tetrahedrites from the Saski Rad are on average -10.11% , those of three tetrahedrites from the Duboki Vagan -10.05% and of the tetrahedrite from the Brixlegg deposit -1.60% .

The ΣREE content is lower in two analysed tetrahedrites from the Saski Rad deposit (10 ppm) compared to the tetrahedrite from Duboki Vagan (15 ppm) and the tetrahedrite from Brixlegg (17.4 ppm). The analysed barite sample from the Saski Rad deposit does not contain microconstituents typical of Hg-tetrahedrite.

The distribution and genetic significance of some trace elements, tetrahedrite microconstituents, REE and siderite isomorphic components in the seven most important genetic and paragenetic types of ore deposits in the MBSM and South-Eastern Bosnia have been commented upon.

Keywords: Mercurian tetrahedrite, content of Co, Ni, W, Cd, Se, Ag and Au, sulphur isotope compositions, Saski Rad and Rad barite-siderite deposits, Palaeozoic, Mid-Bosnia

1. INTRODUCTION

In the framework of the Variscan metallogeny in the Mid-Bosnian Schist Mts. (MBSM) and South-Eastern (SE) Bosnia, particular attention has been paid to the problem of tetrahedrites, the main ore minerals of numerous barite and barite-siderite ore deposits (JURKOVIĆ, 1956; JURKOVIĆ et al., 2010).

Two completely different tetrahedrite types have been discovered: a) an initial, older type without mercury characterised by positive $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from $+3.28$ to $+4.0\%$ (KUBAT et al., 1979/80; JURKOVIĆ et al., 2010); and b) a second, younger type mercury-bearing tetrahedrite, characterised by strongly negative $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from -4.95 to -15.40% (JURKOVIĆ et al., 1997).

At present, 16 quantitative chemical analyses of tetrahedrite samples from the MBSM have been performed and published (POECH, 1900; VESELY, 1921; JURKOVIĆ, 1956, 1960, 1986; JURKOVIĆ & MIKO, 1997; JURKOVIĆ et al., 1997). These analyses included only eight major constitutive elements: Cu, Fe, Zn, Hg, Ag, Sb, As and Bi (rarely Au). Tetrahedrite samples have been taken from the following barite and barite-siderite ore deposits: two older tetrahedrite samples (without mercury) from Trošnik (2) and 14 younger Hg-tetrahedrite samples from Maškara (5), Saski Rad (2), Sabiljine Pećine (1), Zlatarica (1), Točak (1), Kostajnica (1), Duboki Vagan (1), Dubrave (1), Vidici (1). Chemical compositions were obtained through various analytical techniques: a) quantitative wet chemical analyses (5 samples); b) the PIXE method with scanning proton microprobe (5 samples); and c) atomic absorption spectrophotometry (AAS) and ICP–AES after Br₂–HCl digestion (6 samples).

The analytical data obtained from these 16 tetrahedrite samples, demonstrate significant differences resulting from a) the distance of the ore deposit from the long and deep Voljevac fault; b) the stratigraphic level (age) of the host rock; c) the type of the host rock (carbonates or metaclastics); d) being overprinted (or not) by ascending mercury-bearing fluids.

The average values of Hg, Fe, Zn and As in the tetrahedrite samples from the barite-siderite deposits of the four most important ore regions of the MBSM are represented in Table 1. Evidently, the mercury content in the tetrahedrite crystal lattice depends on the distance of the deposit from the Voljevac fault. The Maškara vein (No 6) and the Mračaj vein (No 46) are the biggest and the richest Hg-tetrahedrite ore deposits in the MBSM. The Maškara vein is 2 km and the Mračaj vein only 0.5 km away from the first order Voljevac fault. The values of the same elements in tetrahedrites from the Gemericum (Slovakia) (CAMBEL–JURKOVSKY et al., 1985) and from the Brixlegg, Tyrol (Austria) (LUKAS,

1971; GSTREIN, 1983; FRIMMEL and PAPESH, 1990) are included in Table 1 for comparison.

Our initial detailed study of the tetrahedrite genesis in the MBSM and SE Bosnia, demanded additional, more precise analytical methods which ensure the determination of Au intergrowths and microconstituents in the tetrahedrite samples such as Ni, Co, Cd, Sn, W, Se, Te, another 31 trace elements and 14 rare earth elements. The first such determination has been done on Hg-tetrahedrite from the Duboki Vagan deposit (D-VAGT sample) in which the following microconstituents have been detected: 266 ppm Ni, 63.5 ppm Co, <0.5 ppm W, 313 ppm Cd, <1.0 ppm Sn, <0.5 ppm Se and 39 ppm Au (JURKOVIĆ et al., 2011).

In this paper, our objectives are to investigate in great detail the chemical composition of Hg-tetrahedrite from the smaller barite-siderite deposits Saski Rad and Rad. They present the south-eastern prolongation of the Maškara ore deposit, the biggest Hg-tetrahedrite deposit in the MBSM, located in the Silurian–Devonian (S,D) metaclastic rocks, 9 km SE of the town of Gornji Vakuf. In order to elucidate its genesis, Hg-tetrahedrites will be compared with Hg-tetrahedrite samples from other Maškara vein type deposits; the Duboki Vagan (Kreševo) and Brixlegg (Tyrol) barite deposits.

2. GEOLOGICAL SETTING

2.1. Geology of the Gornji Vakuf area

The Gornji Vakuf area is situated in the middle part of the south-western Mid-Bosnian Schist Mts. (Fig. 1.a). Fig. 1.b presents a simplified geological map, compiled from data published by SOFILJ & ŽIVANOVIĆ (1979) and SOFILJ et al. (1980).

The oldest rocks of the area are chlorite-sericite schists and sericite-chlorite-quartz schists, locally interlayered by metasandstones and, in the area of Gromilica, by quartzites.

Table 1: Average values (in wt.%) of Hg, Fe, Zn and As in the crystal lattices of tetrahedrite samples from the barite-siderite deposits located in the four most important regions of the Mid-Bosnian Schist Mountains (MBSM) (JURKOVIĆ et al., 1997). Abbreviations: lm = limestone; do = dolomite; sch = metaclastic rocks (phyllite, metasandstone); S = Silurian; D = Devonian; n = number of analysed tetrahedrite samples; nmrs = numerous; av = average value; rg = range; V. Fault = Voljevac Fault.

Ore district	n		Hg wt. %	Fe wt. %	Zn wt. %	As wt. %	Host rock	Age	Distance to Voljevac fault
Sabiljine Pećine NW of the Gornji Vakuf	1	av rg	7.35	1.10	4.17	2.04	lm (do)	D ₂	0.5–1 km
Maškara – Saski Rad SE of Gornji Vakuf	8	av rg	5.14 (3.69–7.58)	4.29 (2.80–5.77)	0.24 (tr–0.72)	3.82 (1.50–5.84)	sch	S,D	0.5–2 km
Dusina, Deževica Kostajnica	5	av rg	1.62 (0.63–3.40)	1.89 (0.82–3.40)	3.64 (0.77–6.18)	3.05 (0.43–5.41)	do (lm)	D ₂	10–15 km
Kreševo, Tarčin	5	av rg	1.95 (0.33–3.80)	2.27 (0.52–4.15)	3.01 (1.21–4.64)	1.97 (1.41–2.73)	do (lm)	D ₂	15–20 km
Trošnik, Fojnica	3	av rg	0.29 (0.03–0.63)	6.77 (6.00–7.42)	2.24 (1.82–2.41)	1.05 (0.90–1.20)	do (sch)	S,D	>20 km
MBSM	22	av rg	3.07 (0.03–7.58)	3.74 (0.52–7.42)	2.09 (tr. 6.18)	2.77 (0.43–5.84)		JURKOVIĆ et al. (1997, 2010)	
Rudnány, Gemericum, Slovakia	nmrs	av rg	9.70 (0.0–19.80)	2.59 (0.2–5.8)	0.79 (0.1–4.0)	4.87 (2.3–4.7)		CAMBEL & JURKOVSKY (1985), RADVANEC et al. (2004)	
Brixlegg, Tyrol Austria	nmrs	av rg	1.80 (0.0–15.0)	2.60 (2.5–3.0)	5.40 (4.0–6.0)	6.20 (5.0–6.0)		LUKAS (1971), GSTREIN (1983), FRIMMEL & PAPESH (1990)	

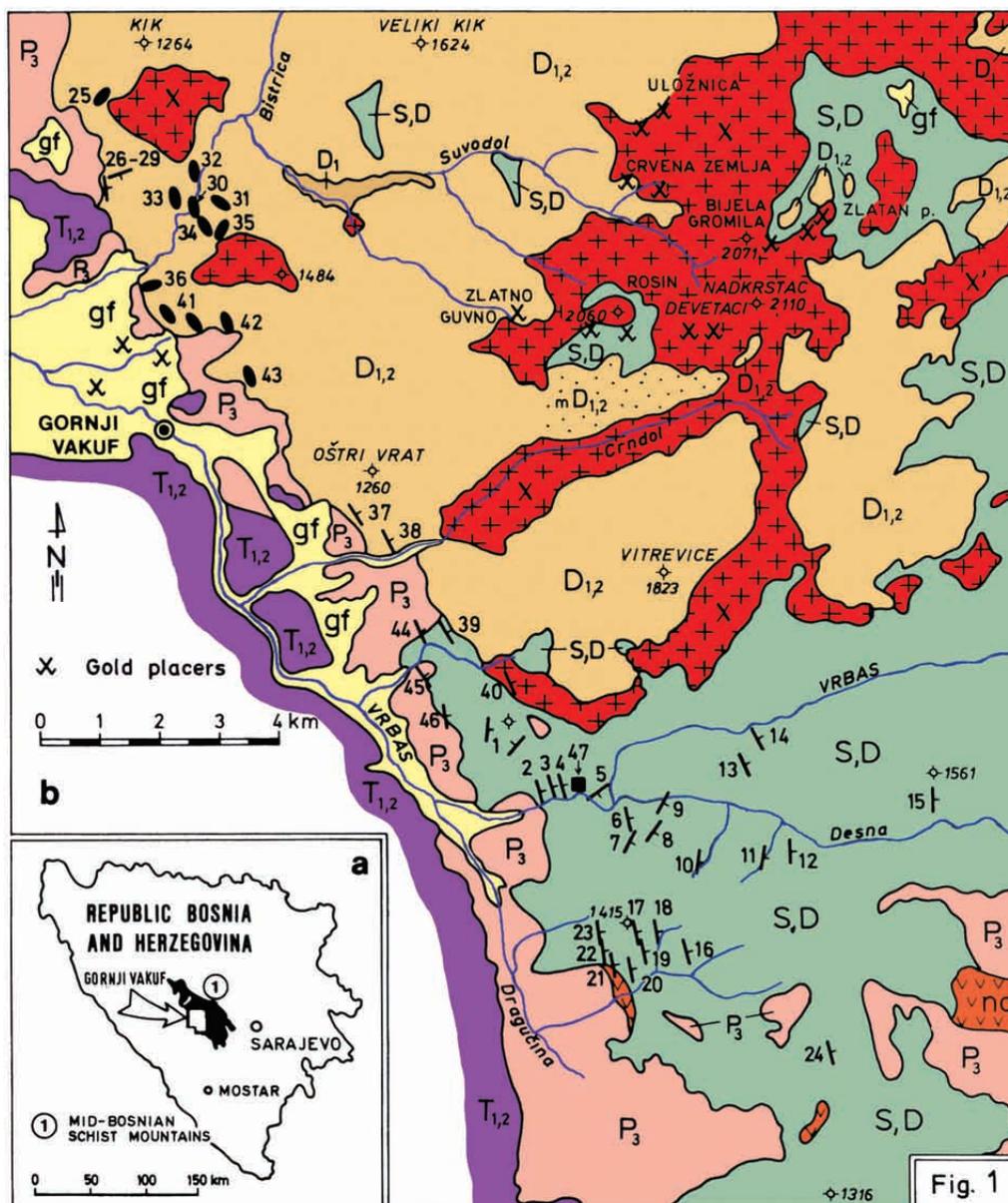


Figure 1: a) Position of the Mid-Bosnian Schist Mountains (MBSM) inside the Republic of Bosnia and Herzegovina; b) Simplified geological map of the Gornji Vakuf area from the Prozor sheet compiled by SOFILJ & ŽIVANOVIĆ (1979). Positions of the 47 ore occurrences, their parageneses, strike and dip are marked by JURKOVIĆ et al. (1994). The Maškara ore deposit is denoted by the number 6, Rad by number 7 and Saski Rad by number 8. Colours are according to the Commission for the Geological Map of the World (CGMW) and the International Commission on Stratigraphy (ICS) (CMYK colour code, 2008). Abbreviations: S,D – Upper Silurian–Lower Devonian schist complex; D₁ – Lower Devonian; D_{1,2} (D) – Middle Devonian carbonate complex; mD_{1,2} – marbleized limestones; X – rhyolite; X' – metarhyolite; nq – quartzkeratophyre; P₃ – Upper Permian sediments; T_{1,2} – Lower and Middle Triassic; gf – fluvioglacial placers; Ore occurrences: Nos 1–15 (in Fig. 1.b) = siderite ± barite + tetrahedrite (in S,D); Nos 16–24 = barite ± siderite + tetrahedrite (S,D); Nos 25–40 = barite ± tetrahedrite (D_{1,2}); Nos 41–43 = bartie ± tetrahedrite (P₃–D_{1,2} thrust/fault zone); Nos 44–46 = siderite ± barite + tetrahedrite (P₃–S,D thrust/fault zone); No 47 = metamorphogenic quartz deposit (S,D).

In the area of the Cvrče Village and in the Desna Valley younger rocks and slates occur. The area near Krugljača is characterised by the occurrence of sandy sericite-chlorite schists and schistose sandstones. Limestone and dolomite lenses are very rare. All these rocks are attributed to the Silurian–Devonian metamorphic rocks of greenschist facies (S,D in Fig. 1.b).

In the Mt. Vranica area, the Silurian–Devonian complex is tectonically covered by Devonian limestones with subordinate dolomites. The lowest part, found only in the Suvodol valley, is built up by the fossiliferous Lower Devonian platy

limestones (D₁). The Middle Devonian consists of zoogene, massive and rarely bedded limestones and subordinate dolomites (D_{1,2}). On the geological map, Prozor Sheet, Carboniferous rocks have not been registered, although ŽIVANOVIĆ (1972) presumes that younger parts of the Silurian–Devonian complex may belong to the Lower Carboniferous.

Shallow subvolcanic rhyolite (denoted as X in the Fig. 1.b) intrusions and extrusions are numerous. JURKOVIĆ et al. (2010) proved by ⁸⁷Sr/⁸⁶Sr ratio that they represent an S-type granitoid magma as previously assumed by MAJER & GARAŠIĆ, 2001. They are mostly transformed into meta-

rhyolites (denoted as X' in the Fig. 1.b) by Variscan regional metamorphism. Keratophyres (nq), are much rarer, younger than (meta)rhyolites and belong to the Permian.

Upper Permian formations are unconformably underlain by older Palaeozoic rocks: breccias, conglomerates, porous limestones ± gypsum, coloured subgraywackes, subarkoses, siltstones.

The Lower Triassic (T₁) is composed of siltstones and limestones, and the Middle Triassic (T₂) by limestones, dolomites and a volcanic-sedimentary formation.

2.2. Ore deposits of the Gornji Vakuf area

In the Gornji Vakuf area JURKOVIĆ et al. (1994) have registered 47 ore occurrences (Fig. 1.b) of the following genetic types:

1) Sedimentary gold deposits: a) Quaternary gold-bearing fluvial deposits; b) gold-bearing Diluvial terraces; and c) Uppermost Pleistocene (Wurm) glacial formations (RUECKER, 1896; JURKOVIĆ, 1951; RADUSINOVIĆ, 1960; JURKOVIĆ et al., 1994).

2) Hydrothermal ore deposits (Nos 1–46 in Fig. 1.b): a) The Maškara vein type, containing siderite, barite and Hg-tetrahedrite, located SE of Gornji Vakuf in metapelites and metapsammities of the lower parts of the Silurian–Devonian complex (Nos 1–15); b) The Cvrče-Borova Ravan type, containing barite, siderite and Hg-tetrahedrite, located in metaclastic rocks of the higher parts of the Silurian–Devonian complex (Nos 16–24); c) The Sabiljine Pećine type, containing only barite, while Hg-tetrahedrite is a very subordinate or even accessory mineral. This type is located in the partly dolomitised Middle Devonian limestones, (Nos 25–43); and d) The Mračaj type, which is characterised by a barite-siderite-Hg-tetrahedrite paragenesis. This type is located along the Voljevac fault zone (the tectonic contact between the Upper Permian and Lower Palaeozoic) (Nos 44–46).

3) Metamorphogenic quartz deposit (No 47 in Fig. 1.b)

The research here is restricted to ore occurrences situated in the triangular area between the western slopes of the Vrbas river, western banks of the river Desna and eastern banks of the river Dragučina, a western tributary of the Vrbas river. There are hydrothermal ore deposits of the Maškara paragenetic type (Nos 5–15 in Fig. 1.b) and the Cvrče-Borova Ravan paragenetic type (Nos 16–24) present in this (~60 km²) area.

Taking into consideration two published detailed studies of the Maškara vein (KATZER, 1907; JURKOVIĆ, 1960), research samples were selected from the old medieval and Austrian mines Rad and Saski Rad, which are a prolongation of the Maškara vein.

2.3. General characteristics of the Maškara vein type

From 15 ore occurrences (Nos 1–15) attributed to this paragenetic type, the biggest one is the Maškara vein (Nos 6). It is 250 to 350 m long, vertically over 110 m high, 0.1 to 1.0 m

thick, dipping 75°/40–60°. This vein produced 8.0 tons of crude ore with 25% of Hg-tetrahedrite. The average content of Hg-tetrahedrite was 9–15 vol.% or 10–16 wt.% in barite crude ore and 20–60 vol.% or 15–65 wt.% in siderite crude ore (KATZER, 1907; JURKOVIĆ, 1960). The Rad (No 7) and Saski Rad (No 8) are ore occurrences which belong to the Maškara genetic type. The quantitative relationship of the main constituent elements in the Hg-tetrahedrite of the Rad and Saski Rad deposits is very similar to that in the Hg-tetrahedrite from the Maškara deposit, indicating that these deposits might represent the broken parts of the Maškara ore vein. The Maškara vein lies at the absolute altitudes of +820 to +930 m, the Rad deposit at an altitude of +1000 m, and the Saski Rad deposit at +1070 m.

On the western banks of the river Desna (a tributary of the Vrbas river), the other ore deposits belonging to the Maškara paragenetic type are located: Desna (No 9 in the Fig. 1.b), Daganj Creek (No 10), Valice Village (No 11), Valice Mlinovi (No 12) and Kulentaš (No 15).

In these deposits, siderite is the main mineral with single Hg-tetrahedrite grains, net-like aggregates or interrupted interlayers of tetrahedrite. Barite is abundant, but subordinate. Ore occurrences Nos 10 and 11 contain an increased quantity of quartz ± pyrite and a decreased amount of tetrahedrite (JURKOVIĆ et al., 1994). All these veined ore occurrences stretch NNE–SSW or NE–SW with a very steep dip. They are short, shallow and very thin veins (from 0.1 to 0.2 m thick). Their outcrops lie at altitudes of +1100 m, hosted by the rocks of the lower part of the Silurian–Devonian complex (phyllite and similar rocks).

The Laznice ore occurrence (No 13) at +1200 m altitude, and Crkvice (No 14) at +950 m, represent an open jointing system (width 0.1–1.0–3.0 m) which is only partly filled with clay gangue, Fe and Mn hydroxides, ankerite, calcite and ore fragments.

In the Cvrče-Borova Ravan area, at altitudes of +1050–+1350 m, similar ore occurrences have been discovered, characterised by barite as the dominant ore mineral, whereas siderite ± quartz are subordinate minerals. Hg-tetrahedrite is scarce or very subordinate. The following ore deposits and occurrences belong to this paragenetic type: Ladina Voda (No 16), Kašli Brdo (No 17), Djamuš Brdo (No 18), Cvrče Village (No 19), Cvrče-Zaganj (No 20), Borova Ravan-Bosnjačica (No 22) and Borova Ravan (No 23). All these veins strike NNW–SSE or NW–SE, dipping towards the NE/25–45°. They are all very thin (Nos 19 and 23 are 0.05–0.10 m thick), only the Djamuš Brdo vein (No 18) is somewhat thicker (0.10–0.40 m). All ore occurrences are hosted by metasandstones and schists are attributed to the higher parts of the Silurian–Devonian complex. ŽIVANOVIĆ (1972) claims that these rocks belong to the Lower Carboniferous.

At Borova Ravan-Guvnanica (No 21) and Ričica (No 24) fragments of ore were only discovered in blocks and not in associated outcrops.

Mineralization of the Maškara vein type occurred inside a system of tensional fissures and joints of variable lengths, widths and depths. The ore occurrences strike mostly NNW–SSE

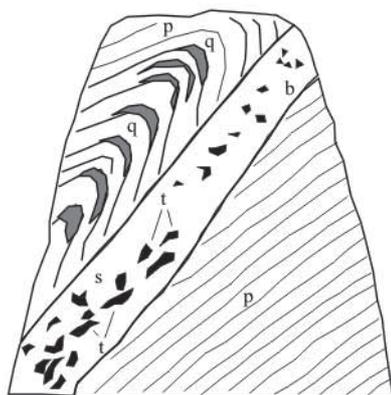


Figure 2: The relationships between tetrahedrite, barite and siderite in Maškara-Saski Rad vein described by KATZER (1907). Siderite gangue contains richer tetrahedrite masses than the barite gangue. Captions: p = phyllite, s = siderite; b = barite; t = tetrahedrite; q = quartz.

and dips towards the ENE with very different angles. The other extensive system, 3.5 km long, has been registered between the Vrbas and Desna rivers (N–S strike, dip towards the E).

In higher levels of the ore deposits, barite predominates over subordinate Hg-tetrahedrite, whereas in the lower levels siderite and Hg-tetrahedrite (\pm quartz) predominate.

Within the geological column, a vertical zonation of the whole Silurian–Devonian complex was also observed. In the lower parts of the complex, siderite with subordinate barite and quartz are common, whereas in the higher parts, barite with subordinate siderite and tetrahedrite are common.

The relationships between tetrahedrite, barite and siderite in Maškara-Saski Rad vein described by KATZER (1907) are shown in Fig 2.

3. THE MAIN GENETIC AND PARAGENETIC TYPES OF MINERAL OCCURRENCES ESTABLISHED IN THE MBSM AND SE BOSNIA

The following main genetic and paragenetic types of mineral occurrences have been established in the MBSM and SE Bosnia:

Ia) The oldest nonmetallic occurrences are numerous Variscan synorogenic and postorogenic sterile, monomineralic quartz veins and irregular quartz bodies located in the Busovača, Fojnica, Kiseljak, and Kreševo area (KATZER, 1926; JURKOVIĆ, 1956; HRVATOVIĆ, 1996).

Ib) The oldest metallic ore deposits, Mačje Jame iron ore deposits (JURKOVIĆ, 1956) and Vranjska Rijeka (JURKOVIĆ and HRVATOVIĆ, unpublished) are located west of the town of Busovača. These deposits are formed at $T = 350\text{--}400^\circ\text{C}$ and $P = 3\text{--}5$ kbars (MAJER et al., 1991). The main minerals are siderite and ankerite (50–90 wt.%), with magnetite, haematite, albite, Ti-oxides (10–30 wt.%). This first phase is followed by a very subordinate pneumatolytic phase with quartz, pyrite, arsenopyrite (5–10 wt.%) associated with cassiterite (0.024 wt.%), and ferberite (0.012 wt.%). The mineralization in these two ore deposits is completed by a

weak hydrothermal phase which consists of Cu, Zn, Fe, As, Bi (cosalite), Sb-sulphides and sulphosalts. The crude ore contains 10 ppm Ag, 0.33 ppm Au, 0.7 wt.% Cu, 0.6 wt.% As, 15 to >230 ppm Bi and to 25 ppm Se. The copper-bearing Sinjakovo siderite deposit, located west of the town of Jajce, also belongs to this genetic type (VASILJEVIĆ, 1972).

BARTALSKY (1991) discovered an almost identical genetic and paragenetic type of ore in the Gemicum (Slovakia). RADVANEC et al. (2004) consider that this is the oldest Slovakian deposit generated at $T = 330\text{--}380^\circ\text{C}$ and $P = 2\text{--}4$ kbars.

II) The Vrtlasce ore deposit is a small, but paragenetically very interesting ore type, located east of the town of Fojnica. Siderite, ankerite and subordinate albite are the main minerals, but the pneumatolytic phase with cassiterite, stannite and molybdenite is clearly noticeable (JURKOVIĆ, 1956; 1958). The hydrothermal phase with 0.02 wt.% Cu, 2.2 wt.% Pb, and 5.0 wt.% Zn is very well developed. This deposit having >300 ppm Ag was a very good supply of silver for the Saxon miners in the Middle Ages. Due to the reduction of Bi and Se, the content of gold was only 0.07 g/t. The silver bearing minerals were galena, boulangerite and other Pb-antimonides.

III) Numerous quartz veins (the longest of which is 1500 m) with silver-bearing sphalerite, antimonite, and Pb-antimonides as the main ore minerals, comprise the Čemernica genetic type, located northwest, northeast and east of the town of Fojnica (KATZER, 1926; JURKOVIĆ, 1956, 1962; JURKOVIĆ et al., 1999). Entire ore reserves (300.000 t) contain 5.9 wt.% Zn, 4.0 wt.% Sb, and 114 g/t Ag. The Au content is only 0.01 g/t, Bi and Se occur in trace amounts. In the Čemernica “Main vein”, RAMOVIĆ (1956) discovered ferberite with 74 wt.% WO_4 ; 18 wt.% Fe and 6.2 wt.% Mn.

IV) The Bakovići gold-bearing pyrite veins with 10–20 wt.% SiO_2 , 5–10 wt.% of Mn-siderite and 50–75 wt.% of gold-bearing pyrite are the richest gold deposits in Bosnia and Herzegovina. The average gold content in the Bakovići ore deposit is 21 g/t Au and 13 g/t Ag. The source of gold in this deposit is presently unknown (JURKOVIĆ, 1995).

V) Barite \pm siderite veins and irregular replacement bodies with 1–10 (max. 15 wt.%) of Fe, Cu, Zn, Pb, and Sb sulphides and sulphosalts characterized by positive $\delta^{34}\text{S}_{\text{CDT}}$ (0.0 to +5‰), are predominantly located in SE Bosnia, rarely in the MBSM (RAMOVIĆ, 1957, 1976; JEREMIĆ, 1963; KULENOVIĆ, 1987; JURKOVIĆ et al., 2010). An identical morphologic and paragenetic type of polysulphide-bearing barite deposits has been found in the Petrova and Trgovska gora Mts. in Croatia (JURKOVIĆ, 1958) and in NW Bosnia (ŠIFTAR, 1988, 1990) but only sporadically in the MBSM (JURKOVIĆ, 1956; JURKOVIĆ et al., 2010). Small quantities of Sb-tetrahedrite do not contain mercury in the crystal lattice, being also characterized by a positive $\delta^{34}\text{S}_{\text{CDT}}$. This type of barite deposit with the polysulphide group of ore minerals, has been formed at moderate temperatures of 140°C as determined by the fluid inclusion studies of BLEČIĆ (1983).

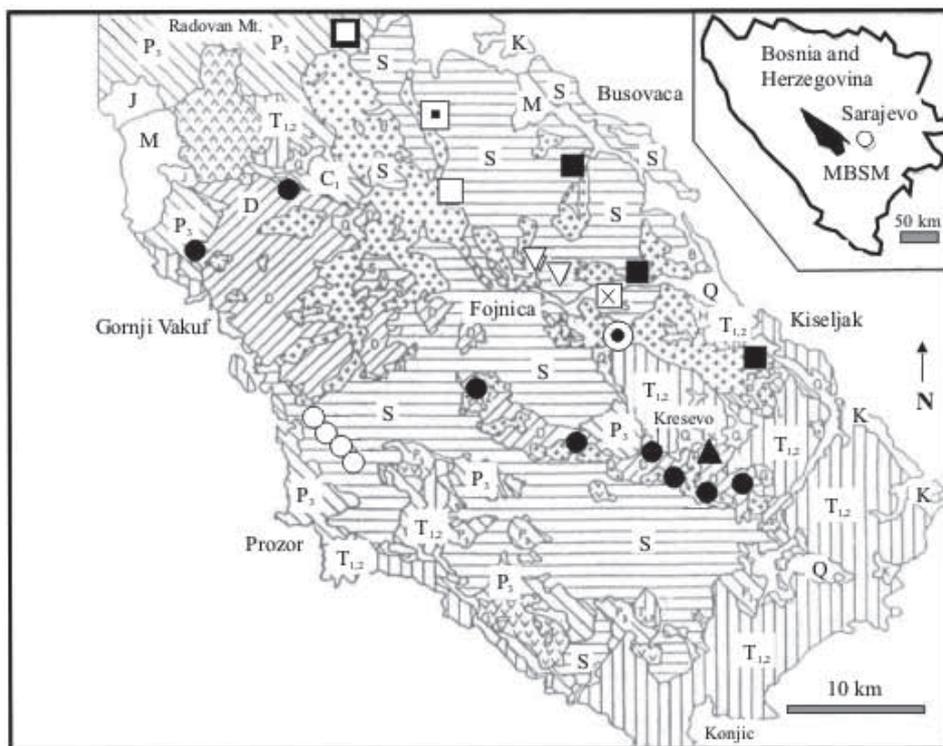


Figure 3: Positions of the most important genetic and paragenetic types of ore deposits in the MBSM area. Geological map after SOFILJ & ŽIVANOVIĆ (1979). Legend: Q-Quaternary, M-Miocene, K-Cretaceous, J-Jurassic, T_{1,2}-Lower and Middle Triassic, P₃-Upper Permian, C₁-Lower carboniferous, D-Devonian, S-pre-Devonian metamorphic rocks, $\Delta\Delta\Delta$ -Triassic diorite, minor gabbro, albite syenite, albite granite; $\vee\vee\vee$ -Middle Triassic volcanic rocks (keratophyre, andesite, dacite); +++ - Upper Palaeozoic rhyolites, metarhyolites. Positions of the ore deposits after JURKOVIĆ et al (1994). Types of ore deposits: ■ Busovača type; □ Mačje Jame type; ▣ Vranjska Rijeka type; ⊠ Vrtlasce type; ▽ Čemernica type; ⊙ Bakovići type; ▲ SE Bosnia type; ○ Maškara – Saski Rad type; ● Kreševo type; ■ Vilenica type.

VI) The youngest group of ore deposits consists exclusively of two morphologic groups of Hg-tetrahedrite-bearing barite deposits. The first morphologic type are quartz-siderite-barite vein deposits; the Maškara-Saski Rad type, rich in Hg-tetrahedrite. Barite crude ore contains 10–16 wt.% of Hg-tetrahedrite, whereas siderite crude ore is richer and contains 20–65 wt.% of Hg-tetrahedrite (KATZER, 1907). All other ore minerals are only accessories or occur in microscopic dimensions. The second morphological type, the Kreševo type, are barite \pm calcite \pm quartz irregular replacement bodies with a very low content of Hg-tetrahedrite (traces or 1 to 5 wt.%) and high temperature, octahedral fluorite. All other microscopically established minor minerals are only accessories (JURKOVIĆ, 1987).

Numerous fluid inclusion studies revealed a strongly increased homogenisation temperature of 230–330°C (PALINKAŠ & JURKOVIĆ, 1994; JURKOVIĆ & PALINKAŠ, 1996; JURKOVIĆ & PALINKAŠ, 2002; JURKOVIĆ et al., 2002). In both types of Hg-tetrahedrite deposits, tetrahedrite is characterized by a strongly negative $\delta^{34}\text{S}_{\text{CDT}}$.

The position of the main genetic and paragenetic types of mineral occurrences are shown in Fig. 3.

4. ANALYTICAL METHODS

Numerous thick opaque polished sections of the tetrahedrite samples were studied using reflected polarized light. Thin-sections of barite and siderite samples were examined using transmitted polarized light. The information obtained enabled separation of the fresh and weathered samples. Selected samples were crushed, hand-picked under binocular microscope and powdered in an agate mortar for chemical analysis.

A relatively high Se content (>100 ppm) was determined for the first time in the fresh Hg-tetrahedrite of the Saski Rad deposit in the MBSM. This led to similar analysis of the weathered Hg-tetrahedrite of Saski Rad deposit in order to confirm a similar high Se content of Hg-tetrahedrite as a typical characteristic of this deposit.

Major and trace elements were analysed by inductively coupled plasma (ICP) mass spectrometry – in ACME Analytical Laboratories, (Vancouver) Ltd. in Canada. Sulphur and oxygen stable isotope compositions were determined at the Stable Isotope Laboratory of the University of Lausanne, using the Finnigan Mat Facility.

The Saski Rad No 7 tetrahedrite sample has been analyzed by atomic absorption spectrometry (AAS) and ICP–AES, after Br₂HCL digestion, in the Croatian geological Institute in Zagreb (JURKOVIĆ et al., 1997), and Saski Rad No 8 tetrahedrite sample by PIXE method with scanning proton microprobe in the Institute Rudjer Bošković in Zagreb (JURKOVIĆ et al., 1997).

5. RESULTS

5.1. Analytical results of the fresh Hg-tetrahedrite (SAS–TET sample)

Results of quantitative chemical analyses of Hg-tetrahedrite samples from the Saski Rad deposit, are presented in Table 2. The first two analyses, performed in 1994 and 1997, contain only the major constituent elements (Cu, Fe, Mn, Zn, Hg, Ag, Sb, As, Bi, Te, S and Au), whereas minor and trace constituents (Ni, Co, W, Cd and Se) as defined by DUDA & REJL (1987) were not analysed. However, the third analysis shown in Table 2 results from the present work and contains major, minor and

Table 2: Quantitative chemical analyses of Hg-tetrahedrites from the Saski Rad deposit. Abbreviations: (1) analysis performed by JURKOVIĆ et al. (1994); (2) analysis performed by JURKOVIĆ et al. (1997); (3) analysis performed for the present work (SAS-TET sample); M.a. – mechanical admixtures; Tr-El. – trace elements, MDL – method detection limit. The difference between 97.5% and 100% is attributed to unanalysed O₂ and H₂O*.

Main element	tetrahedrite		Main element	MDL	MDL	REE	tetrahedrite		Tr. El.	MDL	MDL	Admixture in tetrah.	
	JURKOVIĆ et al., 1994	JURKOVIĆ et al., 1997					SAS-TET this work	SAS-TET this work				ppm	ppm
	wt. %	wt. %	wt. %	ppm	wt. %		ppm	ppm	ppm	ppm			
Cu	38.290	41.770	Cu	39.8100	0.001	La	9.30	0.10	Cr	20.0	10.00	BaSO ₄	0.0467
Fe	5.070	5.030	Fe	5.7010	0.010	Ce	0.60	0.10	Mo	7.3	1.00	SrSO ₄	0.0129
Zn	0.290	0.460	Zn	0.2249	0.010	Pr	0.05	0.02	Tl	91.9	0.10	CaCO ₃	0.3496
Mn	n.a.	n.a.	Mn	<0.0100	n.a.	Nd	<0.30	0.30	Cs	0.2	0.10	MgCO ₃	0.0347
Hg	2.820	4.060	Hg	3.8120	0.001	Sm	<0.05	0.05	Rb	1.2	0.10	Total	0.4439
Ag	0.140	0.149	Ag	>0.0300	2.00	Eu	<0.02	0.02	U	0.1	0.10		
Ni	n.a.	n.a.	Ni	0.0071	0.10	Gd	0.07	0.05	V	0.9	8.00		
Co	n.a.	n.a.	Co	0.0113	0.20	Tb	0.01	0.01	Zr	0.6	0.10		
W	n.a.	n.a.	W	0.0020	0.50	Dy	0.08	0.05	Y	0.3	0.10		
Cd	n.a.	n.a.	Cd	0.0027	0.10	Ho	<0.02	0.02	Total	122.5			
Sb	21.160	16.830	Sb	19.0300	0.001	Er	0.05	0.03					
As	4.010	5.840	As	5.0200	0.010	Tm	<0.01	0.01					
Bi	0.232	0.247	Bi	0.2509	0.010	Yb	<0.05	0.05					
Te	n.a.	n.a.	Te	n.a.	n.a.	Lu	<0.01	0.01					
S	25.440	23.340	S	22.6315	0.005	Total	10.16						
Se	n.a.	n.a.	Se	>0.0100	0.50								
CO ₃ ²⁻	n.a.	n.a.	CO ₃ ²⁻	0.5151									
Au	0.00218	n.a.	Au (ppb)	0.00110	0.50*								
M.a.	n.a.	n.a.	M.a.	0.4439									
Tr-El.	n.a.	n.a.	Tr-El.	0.0122									
REE	n.a.	n.a.	REE	0.0010									
Total	97.450	97.730	Total	97.5170									
Cation proportion													
Cu+Ag+Hg	0.61792	0.67894											
Fe+Zn	0.09522	0.09772											
Sb+Ag+Bi	0.22843	0.21736											
S	0.79341	0.72792											
Me ²⁺ : Me ³⁺ : S	3.12:1.3:3.47	3.57:1.3:3.5											

trace elements, along with the rare earth elements (REE). This analysis represents the SAS-TET Hg-tetrahedrite sample.

According to the analysis of the SAS-TET sample, the studied tetrahedrite represents a Cu-Sb-S tetrahedrite, in which Cu is isomorphically replaced by Fe (5.70 wt.%), Hg (3.81 wt.%), Zn (0.225 wt.%) and Ag (>0.03 wt.%) and also by minor elements (71 ppm Ni, 113 ppm Co, 20 ppm W and 27 ppm Cd). Additionally, Sb is replaced by As (5.02%) and Bi (0.25 %), whereas S is replaced by Se (>100 ppm). This represents the first discovery of selenium in the MBSM and SE Bosnia tetrahedrite samples. Au (11 ppm) is present in microcavities

Table 3: Sulphur isotope composition of six mercurian tetrahedrites from the Saski Rad deposit.

Sample	$\delta^{34}\text{S}_{\text{CDT}}$ ‰	Publication
SAS-41. No 102/a	-9.50	JURKOVIĆ et al., 1994
Saski Rad No 7	-10.69	JURKOVIĆ et al., 1997
Saski Rad. No 8	-9.68	JURKOVIĆ et al., 1997
SAS-41.No 102/b	-9.90	this work
S-RADT	-10.30	this work
SAS-TET	-10.60	this work

Table 5: Trace element and REE contents of the barite sample (S-RAD) from the Saski Rad deposit.

		barite						
		S-RAD						
		this work						
REE	ppm	MDL ppm	Trace elements		Trace elements			
			ppm	MDL ppm	ppm	MDL ppm		
La	1.40	0.10	Be	<1.00	1.00	Mo	0.20	0.10
Ce	0.10	0.10	Co	<0.20	0.20	Cu	68.40	0.10
Pr	<0.02	0.02	Cs	<0.10	0.10	Pb	1.40	0.10
Nd	<0.30	0.30	Ga	<0.50	0.50	Zn	5.00	1.00
Sm	<0.05	0.05	Hf	3.10	0.10	Ni	0.20	0.10
Eu	1.65	0.02	Nb	<0.10	0.10	As	5.40	0.50
Gd	2.04	0.05	Rb	0.30	0.10	Cd	<0.10	0.10
Tb	0.12	0.01	Sn	<1.00	1.00	Sb	21.10	0.10
Dy	0.61	0.05	Ta	7.50	0.10	Bi	<0.10	0.10
Ho	0.18	0.02	Th	<0.20	0.20	Ag	1.00	0.10
Er	0.32	0.03	U	<0.10	0.10	Au*	0.6	0.50
Tm	0.03	0.01	V	<8.00	8.00	Hg	5.25	0.01
Yb	0.15	0.05	W	<0.50	0.50	Tl	<0.10	0.10
Lu	0.01	0.01	Zr	<0.10	0.10	Se	<0.50	0.50
Total	6.61		Y	1.30	0.10	Total	107.95	
BaSO ₄	> 93.00 %		Total	12.20		Sr	29781	
SrSO ₄	6.24 %							

In the first group of trace elements, ranging from Be to Y, 4 elements (Hf, Rb, Ta and Y) were identified accounting for only 12.20 ppm in total.

The second group of trace elements (Mo to Se) contains, among others, Cu (68.40 ppm), Sb (21.10 ppm), As (5.40 ppm), Hg (5.25 ppm), Zn (5.0 ppm), Ag (1.0 ppm) and Au (0.6 ppb), which are the major constituents of Hg-tetrahedrite. Microconstituent elements typical for Hg-tetrahedrite have not been identified in this barite sample. Identical results were recorded in other studied barite samples taken from the various barite deposits throughout the MBSM.

The analysed barite sample is characterised by its extremely low content of REE (6.61 ppm in total), which is similar to the other analysed samples of barite from the MBSM and SE Bosnia. The values for Pr, Nd and Sm were below the MDL.

The BaSO₄ content of this sample is higher than 90.00 wt.% and its SrSO₄ content is 6.24 wt.% (Sr = 29781 ppm).

5.4. Analytical results of siderite

The content of the four major components (mol. and wt.%) of the siderite sample, representative of the Maškara-Saski Rad vein system, analysed by JURKOVIĆ et al. (1994), are presented in Table 6. Molar composition reflects a hydrothermal fluid system characterised by heightened temperature.

Table 6: The content of the four major components of the siderite sample from the Saski Rad deposit (JURKOVIĆ et al., 1994).

components	wt %	mol %
FeCO ₃	81.23	74.39
CaCO ₃	9.52	10.18
MgCO ₃	6.59	12.22
MnCO ₃	2.66	2.47
Total	100.00	99.26

Table 7: Sulphur and oxygen isotope compositions of Hg-tetrahedrites and barites and SrSO₄ content of barites from some barite deposits of the Borova Ravan area. Captions: ¹ – JURKOVIĆ et al., 1994; ² – this paper.

Ore deposit	Tetrahe- drite		Barite	
	δ ³⁴ S _{CDT} ‰	δ ³⁴ S _{CDT} ‰	δ ¹⁸ O _{SMOW} ‰	SrSO ₄ wt.%
Djamaš Brdo ¹	-10.69	18.48	n.a.	2.70
Cvrče / Zaganj ¹	-9.68	17.11	n.a.	2.20
Borova Ravan ¹	n.a.	15.89	n.a.	2.50
Cvrče Village ²	-1.20	15.10	18.10	n.a.

5.5. Analytical results of tetrahedrite and barite from neighbouring ore deposits

For the purpose of the comparison, the sulphur and oxygen isotope compositions of Hg-tetrahedrite and barite from the neighbouring Cvrče Village barite deposit (Fig. 1.b) were also determined within the scope of this work. These results, together with isotopic compositions and SrSO₄ content of barite from the Djamaš Brdo, Cvrče/Zaganj and Borova Ravan barite deposits determined by JURKOVIĆ et al. (1994) are presented in Table 7. All analyzed δ³⁴S_{CDT} values in tetrahedrites are negative (-1.20 to -10.69‰), whereas those in barites are positive (+15.10 to +18.48‰).

6. DISCUSSION

6.1. The problem of microconstituents in the tetrahedrite

According to RAMDOHR (1986) 1/4 of copper places in tetrahedrite must be replaced by Fe, Zn, Co, Ni, Ag and Hg; arsenic and antimony by Bi, Sn, W, Ge and Te, and sulphur by selenium. DUDA & REJL (1987) defined only Ni, Co, W, Cd and Se as trace elements in tetrahedrite. JOHNSON et al. (1988) and FOTT & HUGHES (2004) consider that copper can be replaced by Fe, Zn, Mn, Hg, Cd, and Ag; arsenic and antimony by Bi and Te; and sulphur by Se. They consider that the structure of tetrahedrite must be analogous to the structure of the mineral sodalite.

The microconstituent elements can be inserted in tetrahedrite: (a) as micro-scale inclusions occupying defects in the structure; (b) as myrmekitic intergrowths of various fineness, some of which originate through decomposition and (c) as exsolution textures.

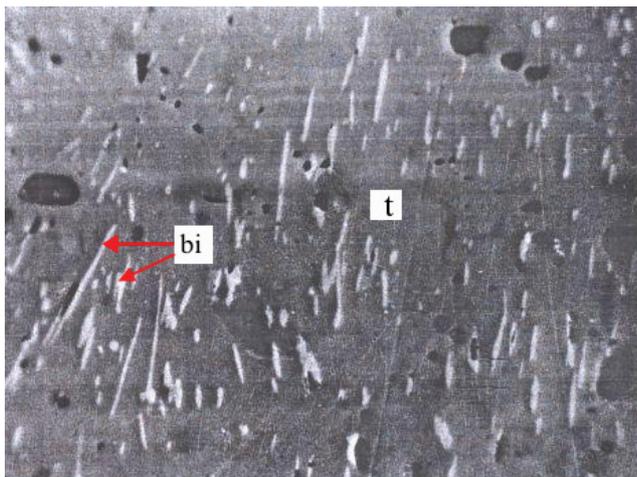


Figure 4: The photomicrograph of the needles of bismuthinite (bi) oriented parallel to (111) as exsolutions in tetrahedrite crystals (t) from the Trošnik, Fojnica deposit. Magnification: 300x.

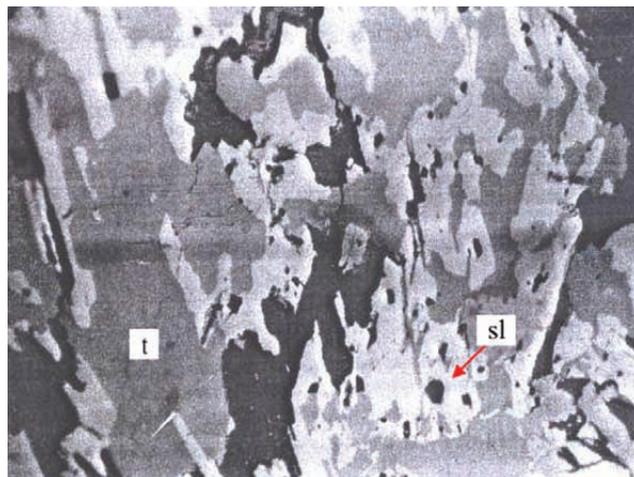


Figure 6: The photomicrograph of myrmekitic intergrowths of tetrahedrite (t) with one sulphide or sulphosalt (sl) from the Trošnik, Fojnica deposit. Magnification: 300x.

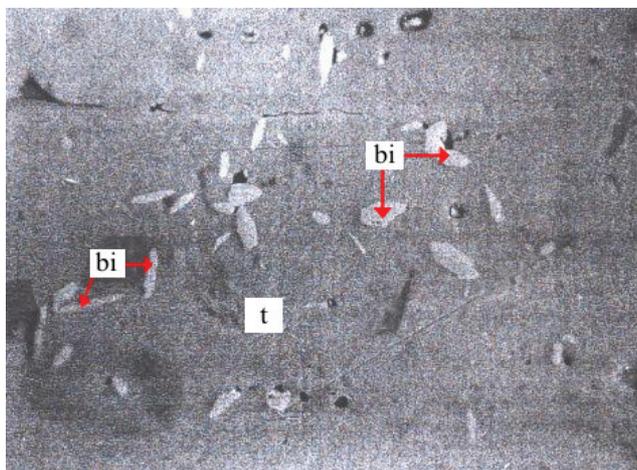


Figure 5: The photomicrograph of the discs and needles of bismuthinite (bi) as exsolutions in tetrahedrite crystals (t) from the Trošnik, Fojnica deposit. Magnification: 450x.

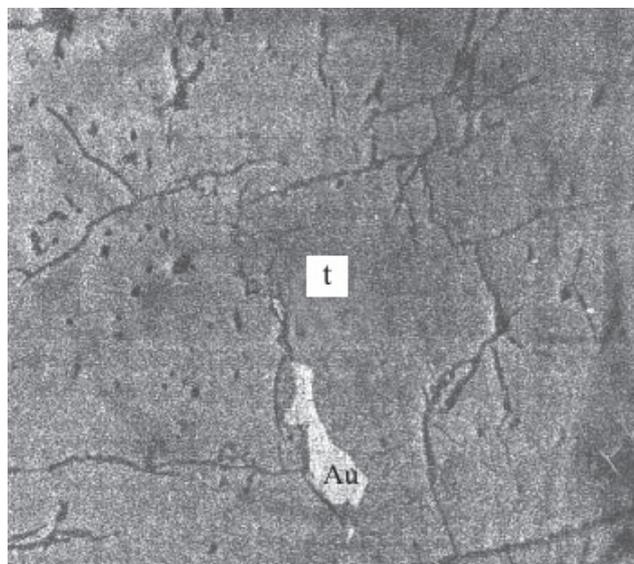


Figure 7: The photomicrograph of gold (Au) occurring as small, irregular masses in tetrahedrite (t) from the Maškara-Saski Rad gold-bearing tetrahedrite. Magnification: 300x.

According to RAMDOHR (1986) exsolutions in tetrahedrite are exceptionally rare (only bismuthinite and questioned “goldfieldite”). The needles of bismuthinite (bi) oriented parallel to (111) (Fig. 3) and discs and needles of bismuthinite (Fig. 4) as exsolutions in tetrahedrite crystals (t) from the Trošnik, Fojnica deposit (MBSM) have been found by the first author of this work during his postdoctoral study (1957) at the Geological Department of Heidelberg University. These results have been confirmed by professor Ramdohr and published by JURKOVIĆ (1958).

Myrmekitic intergrowths of tetrahedrite (t) with one sulphide or sulphosalt (sl), the most probably Ag-mineral according to optical properties, have been also documented by JURKOVIĆ (1958) and are shown in Fig. 5. This texture most likely originated by decomposition of one rich silver-bearing tetrahedrite containing 0.20 and 0.34 wt. % Ag (JURKOVIĆ et al., 1997).

According to our opinion, very often gold occurs mechanically inserted as micro-scale inclusions in tetrahedrite

occupying defect places in its structure. JURKOVIĆ (1958) took photomicrographs of gold also occurring as irregular masses of microscopic dimension (Fig. 6).

6.2. Distribution of the most important tetrahedrite microconstituents as trace elements in the ore deposits located in the MBSM and SE Bosnian areas

The distribution of Co, Ni, Sn, W, Ag, Au, Hg, Bi and Se in the seven main genetic types of ore deposits (Chapter 3) is presented in the Table 8.

Cobalt is the most abundant element in the oldest phase (Mačje Jame, 78 ppm) and in the youngest phase of mineralisation (Maškara-Saski Rad veins, 113 ppm). One unidentified mineral with optical characteristics very similar to a

Co-Ni-arsenide was discovered using a polarised microscope, but only from the Mačje Jame deposit.

Nickel is most abundant in the Mačje Jame deposit (105 ppm) then in the Vrtlasce deposit (78 ppm) and in the Maškara-Saski Rad tetrahedrite veins (71 ppm).

Tin has been found optically as cassiterite and stannite minerals by JURKOVIĆ (1956, 1958a) in the Vrtlasce deposit (average 429 ppm Sn; maximal 900 ppm) and in the Mačje Jame (115 ppm Sn). JURKOVIĆ & HRVATOVIĆ (manuscript) found tin in the Vranjska Rijeka deposit. These three ore deposits are characterized by a well developed pneumatolytic phase. In the hydrothermal phase (Hg-tetrahedrite) tin is very rare and hardly measurable.

Tungsten as the mineral ferberite (Fe,Mn)WO₄ was discovered by RAMOVIĆ (1956), in the silver-bearing sphalerite-antimonite quartz vein named “Main vein” and “NW Čemernica” veins (W = >100 ppm). Small contents of W we found in the Mačje Jame deposit (26 ppm) and in the Maškara-Saski Rad Hg-tetrahedrite veins (20 ppm). The majority of tungsten was consumed earlier by formation of mineral wolframite.

Bismuth and **selenium** are closely genetically related. Their presence was first observed in the Mačje Jame deposit (Bi = 15 and Se = 14 ppm), but they are most abundant in the Vranjska Rijeka deposit (230 ppm Bi and 20 ppm Se), as the minerals cosalite and elemental bismuth (JURKOVIĆ & HRVATOVIĆ, in press). The Vranjska Rijeka deposit contains 0.33 g/t of gold, the Vrtlasce deposit contains 0.07 g/t and there is less in the Mačje Jame deposit at 0.01 g/t. The occurrence of Bi and Se simultaneously with gold in these three deposits indicates their clear positive correlation.

The best positive correlation between Bi, Se and Au has been established in the Hg-tetrahedrite deposits, Maškara-Saski Rad and Kreševo types. The element Bi, having usually microelement status, becomes a very important major element (0.20–0.25 wt.%; max. 0.58 wt.%), whereas the abundance of Se exceeds 100 ppm. Tetrahedrites with such contents of Bi and Se, contain 8 to 62 g/t of Au and between 300 ppm and 0.34 wt.% of Ag (JURKOVIĆ et al., 1997).

In Hg-tetrahedrite, gold is in pronounced positive correlation with **mercury** which in the Hg-tetrahedrite also be-

comes a major element (on average 3.0 wt.%) for the first time. In the earlier mineralization phases, mercury was only a trace element. The occurrence of scarce cinnabar in the Čemernica deposit is an exception, but in our opinion, this phenomenon is only a younger overprint.

Silver is characterized by a positive correlation with Pb–Sb sulphides and sulphosalts in the Vrtlasce and Čemernica deposits. In the Middle Ages, these two groups of silver-bearing deposits were rich suppliers of silver ore for the Saxon miners.

The second bearers of silver are small, but numerous polymetallic barite ± siderite ± calcite ± quartz veins and replacement bodies, and are best developed in SE Bosnia. They are rare in the MBSM. Ag is linked with Fe, Cu, Zn, Pb, and Sb sulphides and sulphosalts, particularly with PbS and Pb-antimonides. The silver content is moderate (some tenths of a gram/t) and gold only occurs as a trace element.

The third, youngest silver mineralization phase is genetically related to the occurrences of Hg-Bi-tetrahedrite in the monosulphide barite-siderite Maškara-Saski Rad veins, and in the barite ± fluorite replacement bodies of the Kreševo type. These deposits contain Hg-tetrahedrite, in which the Ag content ranges between 300 ppm and 3400 g/t, whereas its Au content varies from 8 to 62 g/t. The Bakovići deposit also has a high content of gold (21 g/t) but only 13 g/t Ag.

Cadmium isomorphically substitutes zinc in the crystal lattice of sphalerite and zinc in the Hg-tetrahedrite.

Tellurium in the Hg-tetrahedrite from the MBSM has not, so far, been investigated by chemical analyses. Optical investigations of polished sections of Maškara Hg-tetrahedrites under polarized microscope revealed some minute minerals, with optical characteristics very similar to Au-telluride (JURKOVIĆ, 1960). This suggests that there should be a positive correlation between gold and tellurium.

Thalium with an increased content of 91.9 ppm has been only been discovered in one out of more than fifty analysed samples.

Comparison of the microconstituents of studied Hg-tetrahedrite from the Saski Rad vein deposit, with those of the Hg-tetrahedrite samples taken from the Duboki Vagan de-

Table 8: The distribution of Co, Ni, Sn, W, Ag, Au, Hg, Bi and Se in the seven main genetic types of ore deposits.

Ore types	Co ppm	Ni ppm	Sn ppm	W ppm	Ag ppm	Au ppb	Hg ppm	Bi ppm	Se ppm
Rhy-KREŠEVO	8.0	8.0	3.0	3.00	<0.1	n.a.	0.04	0.1	<0.5
Rhy-BUSOVAČA	6.0	<20.0	2.0	n.a.	<0.5	n.a.	n.a.	n.a.	n.a.
MAČJE JAME	77.7	104.7	114.7	25.80	1.3	n.a.	0.32	15.4	13.5
VRANJSKA RIJ.	25.3	7.7	44.1	1.10	10.3	0.33	2.02	>229.4	20.0
VRTLASCE	13.8	77.7	428.7	0.50	>52.9	0.07	28.00	>36.1	29.9
ČEMERNICA	1.0	n.a.	4.00	>100.00	153.2	0.01	436.8	10.0	n.a.
BAKOVIĆI	1.0	3.0	4.00	n.a.	13.0	21.00	n.a.	10.0	n.a.
SEB–A	4.6	29.7	<1.0	0.70	20 - 50	tr.	0.7	0.3	<0.5
SEB–B	1.0	16.4	<1.0	0.08	0.04	0.30	0.46	<0.1	<0.5
SASKI RAD	113.1	71.3	<1.0	20.00	>300.0	11.00	3.81%	0.25%	>100.0

Table 9: Differences in the content of some microconstituents in the Hg-tetrahedrite crystal lattice between the Duboki Vagan (Kreševo), Saski Rad (Gornji Vakuf) and Brixlegg (Tyrol, Austria) barite deposits. The tetrahedrite sample from the Brixlegg deposit was gifted by prof. W. PROCHASKA, University Leoben.

	Dubrave	Saski Rad		Brixlegg
	D-VAGT	SAS-TET	SAS-41	BRX-1
Ni	266.2	71.0	70.0	<0.1
Co	63.5	113.0	90.0	234.4
Cd	313.6	27.0	20.0	160.5
W	<0.5	20.0	5.0	6.7
Sn	<1.0	<1.0	<1.0	1.0
Bi	1466.0	2500.0	1613.0	909.1
Se	<0.5	>100.0	72.0	>100.0
Au	38.96	11.0	9.0	2.3
Σ REE	15.03	10.16	9.96	17.43

posit (Kreševo, MBSM) and the Brixlegg deposit (Tyrol, Austria) is presented in Table 8. There is an interesting correspondence in the content of Se between Saski Rad and Brixlegg deposits. The Au content in the Saski Rad and Duboki Vagan tetrahedrites is several times higher than that of Brixlegg tetrahedrite. Furthermore, the Saski Rad and Duboki Vagan tetrahedrite have higher Ni and Bi content compared to the Brixlegg tetrahedrite. However, the Brixlegg tetrahedrite contains more Co and Cd than the Saski Rad tetrahedrite.

6.3. Problem of lanthanides (REE)

Table 10 compares the total REE content, and values of the three dominant lanthanides (La, Ce, and Nd), in the (meta)-rhyolite and keratophyre of the Kreševo (KRE) and Busovača (BUS) regions, with the REE contents of some important ore deposits in the MBSM and SE Bosnia. This arose from the suspicion that the oldest Mačje Jame and Vranjska Rijeka iron deposits may have a direct genetic connection with metamorphogenic fluids generated during progressive and retrograde Variscan (Hercynian) metamorphism. The total REE and the contents of the dominant lanthanides (La, Ce, Nd) in rhyolite, keratophyre and the oldest iron deposits of Mačje Jame and Vranjska Rijeka is very high and almost the same, indicating a direct genetic link.

Table 10: The contents of the total REE and the values of the three dominant lanthanides (La, Ce, and Nd) in the (meta)-rhyolite and keratophyre of the Kreševo (KRE) and Busovača (BUS) regions compared with those of some important ore deposits in the MBSM and SE Bosnia.

Localities	Rhyolite-keratophyre				Ore occurrences and deposits in the MBSM and SE Bosnia						
	Kreševo Fojnica	Busovača Vitez	Mačje Jame	Vranjska Rijeka	Vrtlasce Fojnica	SEB-A sd-ba	Trošnik Fojnica	Saski R. tetrah.	Saski R. barite	SEB-B barite	Kreševo fluorite
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
ΣREE	183.1	159.5	216.5	158.8	59.5	33.0	15.6	9.15	8.4	5.14	0.416
La	38.0	29.4	33.1	36.8	9.8	5.9	2.9	8.19	1.8	1.30	0.026
Ce	76.8	64.8	74.6	60.1	23.7	4.9	5.5	0.64	0.3	0.24	<MDL
Nd	30.0	28.4	26.6	30.3	9.6	6.7	3.0	<0.30	<0.3	<0.30	<MDL

Rash reduction of total REE content during the subsequent phase of mineralization (Vrtlasce deposit) is the result of crystallization of some lanthanide minerals in the earlier phase. These were most probably minerals of the bastnaesite group, as described by RADVANEC et al. (2004) in the similar Slovakian ore deposit.

Only partial analytical data is available for the Čemernica type deposit and the later Bakovići ore type mineralisation phase, and therefore they could not be included in Table 10.

Numerous analytical values have been obtained from the fifth phase of mineralization. The highest content of total REE characterizes the siderite from SE Bosnia (33.0 ppm). Lower contents have been found in siderite from the Trošnik ore deposit (15.6 ppm), in the Hg-tetrahedrite from the Maškara-Saski Rad deposit (9.2 ppm) and in barite from the Maškara-Saski Rad deposit (8.4 ppm), whereas barite from the SE Bosnia contains only 5.1 ppm of total REE. Fluorite from the Dubrava (Kreševo) ore deposit is the mineral containing the least REE. Its two analyses contain 0.427 and 0.406 ppm of total REE. These fluorites belong to the latest phase of mineralisation in the MBSM. Analyses of fluorites were performed by INAA facilities in the Institute for Petrology and Geochemistry, Karlsruhe University (PALINKAŠ & JURKOVIĆ, 1994).

The evidence suggests a successive decrease of total REE contents, not only because of the formation of new REE minerals, but also due to insertion of REE in the vacant defect places of the crystal lattices of other minerals, especially siderite, ankerite, barite and tetrahedrite. Evidence suggests that mixed hydrothermal fluids played a specific role in this process during the last mineralization phase. The development of REE from the oldest to the youngest ore deposits indicates gradual reestablishment of a uniform and unique hydrothermal system in the MBSM area.

6.4. Composition of FeCO₃, CaCO₃, MgCO₃ and MnCO₃ isomorphous components of siderite in the different genetic and paragenetic types of ore deposits in the MBSM and SE Bosnia

Table 11 shows six siderite chemical analyses belonging to the six most important genetic and paragenetic ore types from the MBSM deposits: Mačje Jame, Vranjska Rijeka, Vrtlasce, Trošnik, Maškara-Saski Rad and Bakovići-Čemernica.

Table 11: Interdependence between the composition of siderite and its genetic ore type (PT conditions).

	Mačje jame	Vranjska rijeka	Vrtlasce Fojnica	Trošnik Fojnica	Maškara Saski Rad	Bakovići Čemernica
	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
Σ	100.01	100.00	99.82	100.00	100.00	100.69

nica. The paragenesis and some PT conditions of these deposits are described in Chapter 3. Table 11 demonstrates the clear interdependence of the composition of Fe-carbonates and PT conditions during their genesis.

7. CONCLUSIONS

a) Both fresh and weathered Hg-tetrahedrite samples from the Saski Rad deposit have been examined concerning their microconstituents. W (20 ppm) and Se (>100 ppm) have been detected for the first time in the MBSM Hg-tetrahedrite. There is an interesting correlation of the Se content between the Saski Rad and Brixlegg deposits. The Au content of the Saski Rad Hg-tetrahedrite is relatively high (11 ppm), four times lower than in the Duboki Vagan tetrahedrite, but four times higher than in the Brixlegg Hg-tetrahedrite.

b) The low content of total REE (10 ppm) and strong negative $\delta^{34}\text{S}_{\text{CDT}}$ values (average: -10.09%) in the Hg-tetrahedrite samples of the Saski Rad vein deposit are in accordance with 18 other previously analysed Hg-tetrahedrite samples from the whole of the Mid-Bosnian Schist Mts.

c) The quantitative relationship of the main constituents in the studied tetrahedrite is very similar to that in the tetrahedrite of the Maškara deposit, confirming the earlier assumption that the Saski Rad vein deposit represents the broken part of the Maškara ore vein.

d) The Co, Ni, Sn, W, Ag, Au, Hg, Bi and Se distribution in the seven most important paragenetic types of the MBSM and SE Bosnia ore deposits is significant in several ways. Optical studies suggest that Co and Ni, are most probably present as Co-Ni arsenides in the oldest iron deposits (Mačje Jame and Vranjska Rijeka), and also occur as microconstituents in Hg-tetrahedrite. Sn is completely consumed in the pneumatolytic-hydrothermal Pb, Zn and Cu sulphide deposits as cassiterite and stannite. The first Sn occurrence is detected in the Mačje Jame deposit. W, as the mineral ferberite, was found in the silver-bearing Čemernica sphalerite-antimonite deposit. Bi with 230 ppm and Se with 20 ppm drew attention to the first gold (0.33 ppm) presence in the Vranjska Rijeka copper (0.7 % Cu) deposit. The second very strong occurrence of Bi (with 0.25–0.58 wt.%) and Se (with >100 ppm) is observed in the last hydrothermal Hg-tetrahedrite-bearing barite \pm siderite phase. Hg (average 3.07 wt.%),

occurs in association with Bi and Se as a major constituent, whereas in all other deposits it is absent or present only as a trace element. There is a positive correlation between Bi, Se, Hg and Au, Ag presence in studied ore deposits.

e) A review of numerous previous scientific investigations of parageneses, isotope composition (C, O, S, Sr, Pb), fluid inclusion, trace elements, and REE data analysis, suggests that the seven main paragenetic and genetic types of the MBSM and SE Bosnia ore deposits are generated dominantly from metamorphogenic fluids. The important masses of (meta)-rhyolites and keratophyres are formed by anatexis, as evidenced by Sr isotope data. Palaeozoic protoliths, metamorphosed by several stages of Variscan progressive and retrograde metamorphism, are the sources of hydrothermal fluids. A similar opinion concerning the genesis of siderite \pm barite deposits of Rudnány (Slovakia) was published by GRECULA et al. (1989); ŽAK et al. (1950) and RADVANEC et al. (2004).

The most convincing evidence of the metamorphogenic origin of the hydrothermal fluid is the strong similarity of total REE and the dominant La, Ce and Nd elements in the meta-rhyolite and their pelitic and psammitic metamorphosed protoliths on one hand and the oldest Mačje Jame and Vranjska Rijeka iron ore deposits on the other (Table 10).

f) Previous investigations of the MBSM and SE Bosnia ore deposits established unexpected contrasting parageneses that indicate several different hydrothermal fluids and PT conditions. The best example is Čemernica, an important rich silver-bearing deposit containing >150 g/t Ag, only traces of Au and >100 ppm W, in relation to the richest gold-bearing pyrite deposit Bakovići having 11 g/t Au and only 13 g/t Ag, but without W.

Deposits differ in salinity and in homogenization temperature (T_h). SEB-A and SEB-B barite-siderite deposits associated with polymetallic sulphides (the SE Bosnia type) are characterized by lower salinity (<10 wt.% NaCl) and low $T_h = 100\text{--}150^\circ\text{C}$. Polymetallic monomineral barite-siderite \pm octahedral fluorite ore deposits, Hg-tetrahedrite-bearing Maškara-Saski Rad and Kreševo types are characterized by high salinity (15–25 wt.% NaCl) and high $T_h = 230\text{--}330^\circ\text{C}$.

g) The composition of FeCO₃, CaCO₃, MgCO₃ and MnCO₃ isomorphous components of sideritic gangue in the MBSM and SE Bosnia ore deposits are dependent upon PT conditions and the hydrothermal fluid system.

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