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CHEMICAL AND GEOCHEMICAL CHARACTERISTICS OF THE ČEMERNICA ANTIMONITE DEPOSIT IN THE MID-BOSNIAN SCHIST MOUNTAINS

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The Čemernica Sb-Zn-Hg-W quartz vein system is situated in Lower Palaeozoic metasediments formed under 3–5 kbars and 350° to 450°C, intruded by Upper Palaeozoic rhyolites. K-Ar dating indicated three metamorphic phases. The first, 343 Ma old affected phyllite rocks, the second 120–90 Ma metamorphosed rhyolites and the third one, 46 to 37 Ma caused formation of otrelite schist, host rocks of ore deposit. The Čemernica vein (NW-SE), 1.5 km long, and over 350 m deep, on average 0.67 m thick, is faulted in four separated parts:

»Southern vein«; »Erbstollen vein«; »Main vein« and »NW-vein«. Structures of the veins are massive, banded, rarely brecciated. Paragenesis: quartz I (50–95% of ore mass) as the main gangue mineral; antimonite I, II, sphalerite I, II, cinnabar as the main ore minerals; subordinate are chalcodony, siderite, ferberite, jamesonite, berthierite, boulangerite, plagiionite, arsenopyrite, scarce are pyrite I, II, marcasite, pyrrhotite, barite, chalcopyrite I, II, tetrahedrite and enargite, whereas accessories are galena, quartz II, realgar, gold and mineral »X«.

Chemical analysis of 177 ore samples taken from old Saxon and Austrian mining works gave 4.33% Zn, 2.22% Sb and 137 gr/t Ag. Fifteen samples gave trace to 0.1% Hg and eight samples trace to 0.1 gr/t Au. Untouched part of the »Main vein« gave 5.90% Zn, 8.93% Sb and 126 g/t Ag. Remnant ore gave 2.60–3.28% Zn, 0.69–0.73% Sb and 161 to 190 gr/t Ag. Entire proved, probable and possible ore reserves (306.000 t) have 5.9% Zn, 4.0% Sb and 114 gr/t Ag.

The $\delta^{34}\text{S}$ of antimonite is +2.6‰ and of sphalerite +3.7‰ indicating juvenile origin of sulphur. Fluid inclusion study of quartz identified three types of fluids: Variscan NaCl-KCl-H₂O type related to the Late Palaeozoic granite (rhyolite) magmatism, post-Variscan NaCl-CaCl₂(±MgCl₂)-H₂O type formed by admixing of hot saline connate waters originated from the Late Permian evaporite complex and metamorphogenic aqueous-carbonic fluids which overprinted ore deposit with CO₂, CH₄ and N₂ components in Late Tertiary.

Sb-Zn-Hg-W kvarcne žice Čemernice nalaze se unutar donjopaleozojskih metasedimenata formiranih uz 3–5 kbar i 350–450°C probijeni gornjopaleozojskim riolitima. Datiranje K-Ar metodom indiciralo je tri faze metamorfizma. Prva faza, 343 Ma stara djelovala je na filite, druga 120–90 Ma stara metamorfozirala je riolite, a treća između 46 i 37 Ma uzrokovala je formiranje otrelitskih škriljaca, nosilaca ležišta. Rudna žica u Čemernici (NW-SE) pružanja, i padom na NE) debela je prosječno 0.67 m, duga je 1.5 km i proteže se u dubinu preko 350 m. Rasjednuta je u četiri dijela: »Južna žica«, »Rudnički potok žica«, »Glavna žica« i »SZ-žica«. Struktura je masivna, trakasta, rijetko brečasta. Parageneza: kvarc I (50–95% rudne mase) je glavna jalovina, a antimonit I, II, sfalerit I, II, i cinnabarit su glavni rudni minerali. Podređeni su kalcedon, siderit, ferberit, demsonit, bertijerit, bulanžerit, plagiionit, arsenopirit; oskudni su pirit I, II, markazit, pirotin, halkopirit I, II, tetradrit i enargit dok su galenit, kvarc II, realgar, zlato i mineral »X« akcesorije.

Kemijske analize 177 rudnih uzoraka iz starih saskih i austrijskih radova dale su 4.33% Zn, 2.22% Sb i 137 gr/t Ag. Samo 15 uzoraka pokazalo je tragove do 0.1% Hg, a 8 uzoraka tragove do 0.1 gr/t Au. Netaknuti dijelovi »glavne žice« pokazali su 5.91% Zn, 8.93% Sb i 126 gr/t Ag. Preostale rude starih radova dale su 2.6–3.3% Zn, 0.69–0.73% Sb i 161–190 gr/t Ag. Ukupne dokazane, vjerovatne i moguće rezerve rude (306.000 t) sadrže 5.9% Zn, 4.0% Sb i 114 gr/t Ag. $\delta^{34}\text{S}$ antimonita je +2.6‰, a od sfalerita +3.7‰ što ukazuje na juvenilno porijeklo sumpora. Studija fluidnih inkluzija u kvarcu identificirala je tri tipa fluida: variscijski NaCl-KCl-H₂O tip genetski vezan za granitski (riolitski) magmatizam, postvariscijski NaCl-CaCl₂(±MgCl₂)-H₂O tip formiran miješanjem sa vrućim, slanim konatnim vodama koje vuku porijeklo iz gornjopermskog evaporitnog kompleksa te metamorfološki fluidi koji su u mladom tercijeru donijeli CO₂, CH₄ i N₂ komponente.

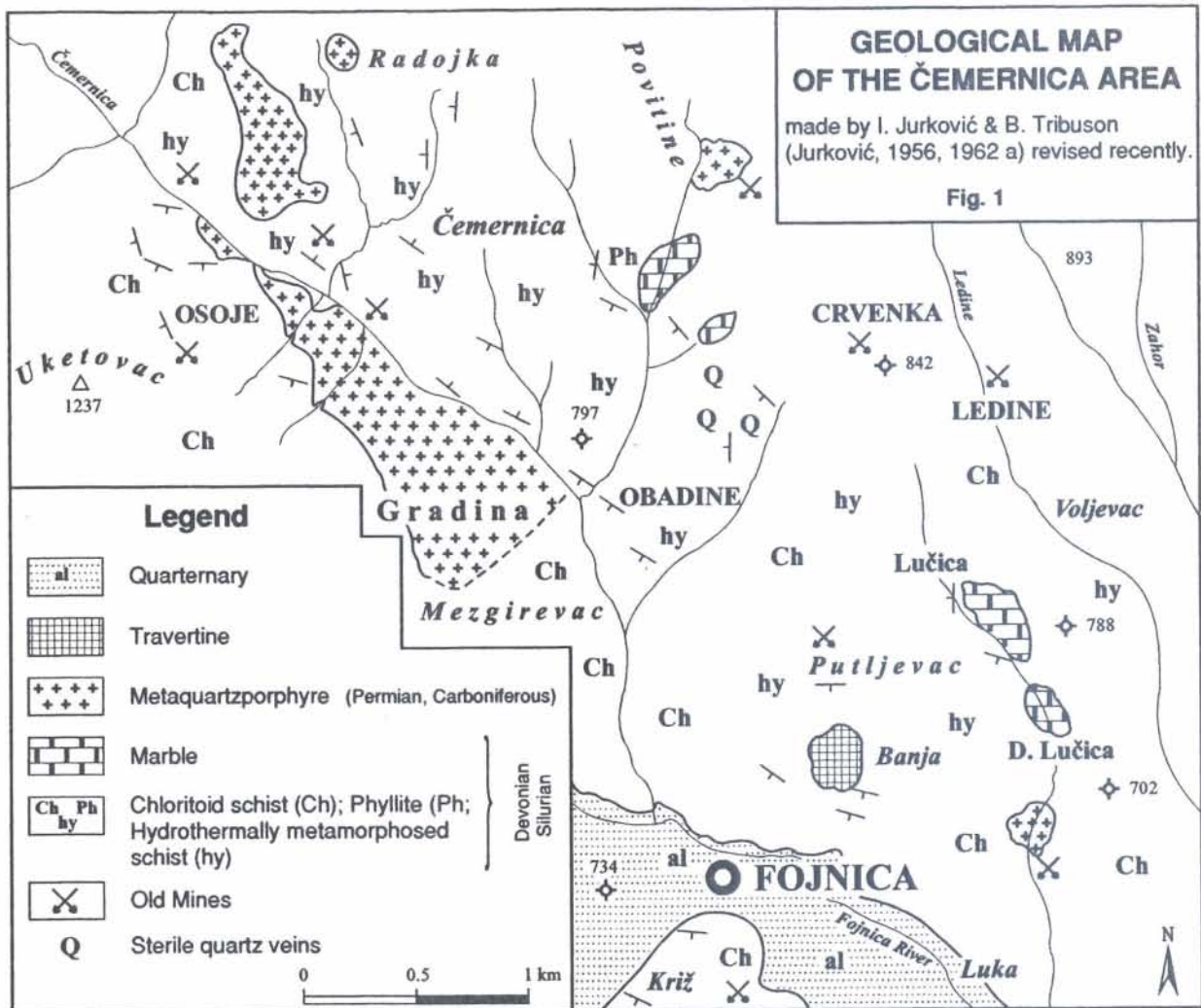
Introduction

The Čemernica area is located 3–4 km northwest of the town of Fojnica in the Middle Bosnian Schist Mountains (MBSM) (figs. 1 and 2).

The ore-bearing area covers the surface of 18 km² (7x 2.5 km). Ore occurrences are found at Osoje, Čemernica, Putljevac, Donja Lučica, Povitine, Crvenka and Ledine (fig. 1). Economically significant occurrences are found at Čemernica whereas the another ones are less significant (Katzner, 1925; Jurković 1956, 1962a).

The abandoned Čemernica mine is located on both sides of the Čemernica Creek. Remnants of older works can be traced for 1.5 km in length and 300 m along dip. The ore-vein outcrops are found at the altitude of +1035 m in the northwest (Brist location) and at +720 m in the southeast (Dedina Špilja location).

Very intensive exploration works were carried out from 14th to 16th centuries by Saxon miners, however there are some indications on the activity of ancient Romans and Illyrians (Hauer, 1884; Walter, 1885, 1887). Austrian miners found on dumps and in underground works sphalerite and certain quantity of silver-bearing antimonite and on some places nests and impregnations of cinnabar. These findings caused dilemma and confusion concerning the real object of the Saxon exploitation in the Čemernica mine. The most surprising fact was complete absence of galena in the ore, galena was only inferred. Walter (1887) and Schönbucher (1898) were of the opinion that the Saxons used in Čemernica silver and gold, whereas Foullon (1892), Rücker (1896) and Richter, who was a director of the Austrian exploration works considered that the Saxons produced mercury ore needed for gold



amalgamation. Most data on the cinnabar were presented by Walter (1885; 1887) who continued Austrian exploration works. His papers were considered by Gezell (1888), Pavlović (1889) and Hauer (1884). Bordeaux (1895), Poech (1900) and Rucker (1896) presented also data on cinnabar of the Čemernica area. John & Foulton (1893) analyzed a selected ore with 6.83 % Hg. On the basis of summarized published data and personal communication of F. Richter, Katzer (1907) writes that cinnabar was main ore mineral of the »Southern vein« which contained 2% Hg and that the ore was enriched by hands to 15% Hg. In »Erbstollen vein«, cinnabar is also main ore constituent and ore contains on average 1% Hg. Katzer (1907) and 1925) was confused with the objectives of the Saxonian mining activity due to the fact that the Saxons did not exploited sphalerite and antimonite which contains in average more than 50 g/t silver and sometimes neither cinnabar because the ore remained on some places in veins. Based on microscopic work, Jurković (1956, 1962a) found in mineral paragenesis tetrahedrite, berthierite, jamesonite, boulangerite and plagioclase instead of lacking silver-bearing galena. The Čemernica deposit was explored during the period 1880–1885 by Austrian miners. They separated by hands from old wastes antimony ore which was melted in a small foundry constructed in 1894 by »Bosnia Company« (Anonymus, 1899). Antimony-crudum production was 56 t in 1884/1885, 108,6 t in 1891, 153 t in 1890–1893 and 73 t

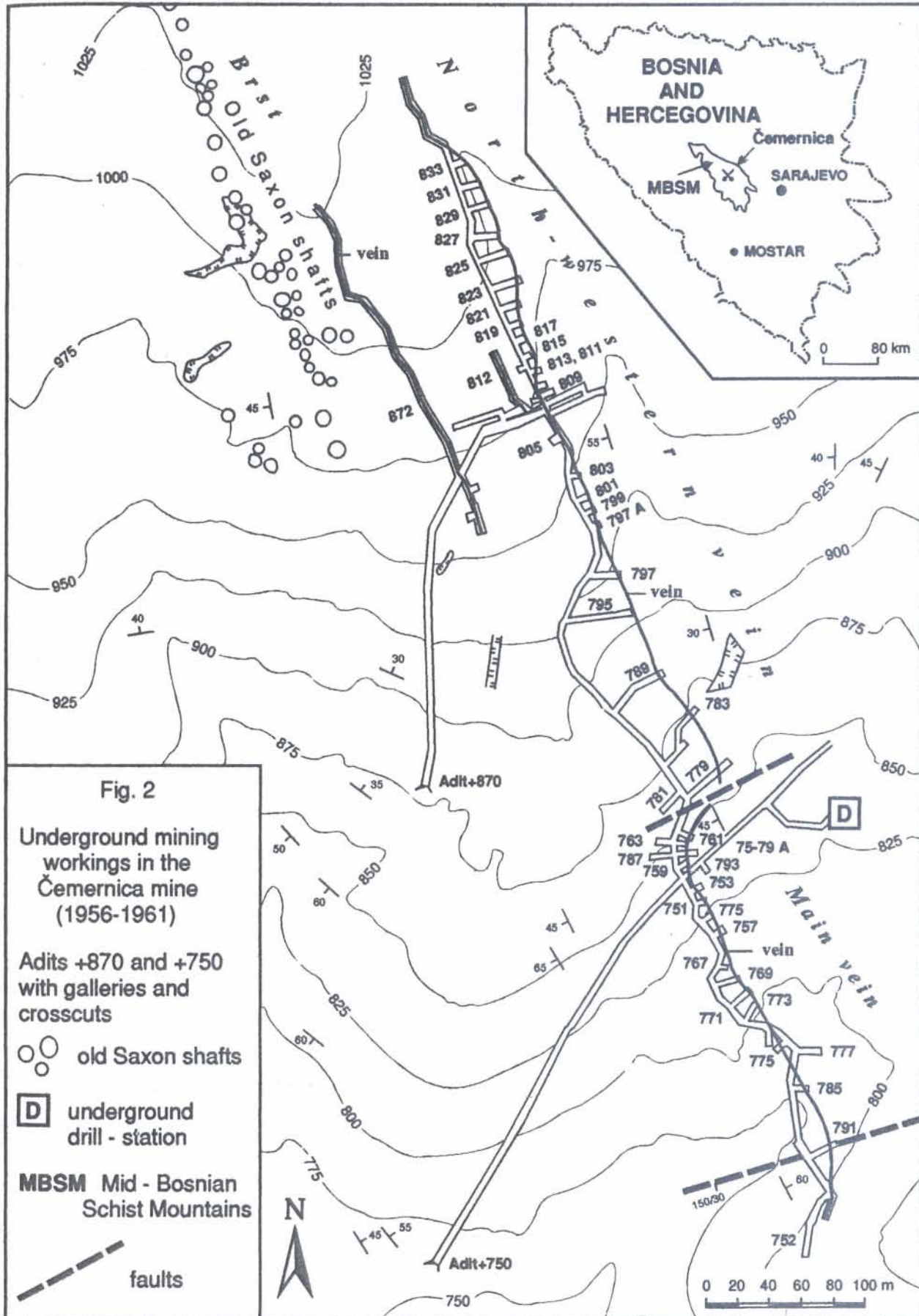
in 1917 (Simić, 1951), whereas production of mercury reached 33,6 to 50 quintals (Anonymus, 1892, 1899) and 6 t, respectively (Katzer, 1907).

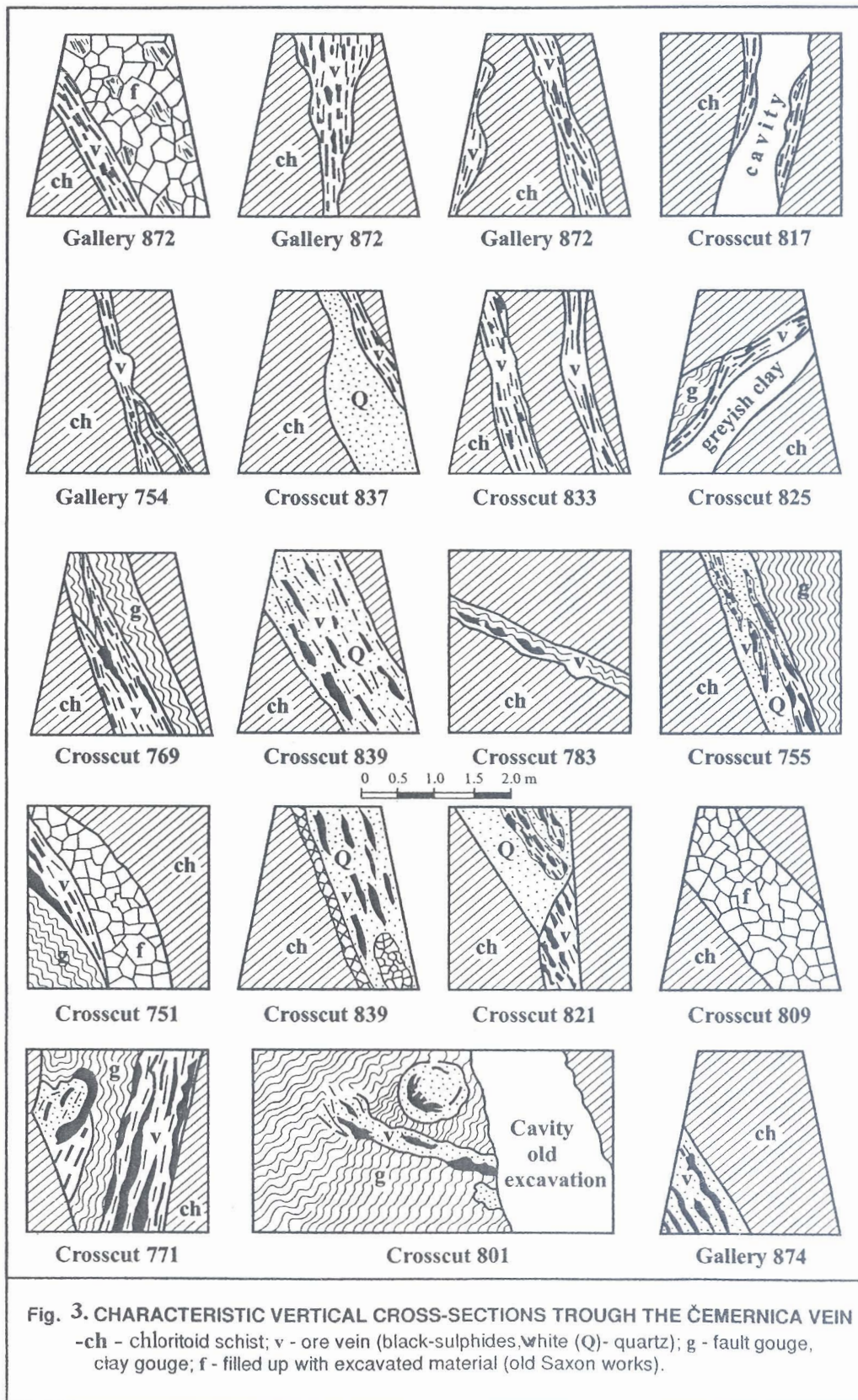
In the next period until 1948 the mine was abandoned. The Copper company, Sarajevo performed during the period 1948–1951 a new 80 m long adit, located 10 m above the main water-pipe shaft. The Geological Survey, Sarajevo, carried out in 1956 extensive exploration works (Ramović & Zec, 1959, 1962), which comprised 2000 m adits, galleries, crosscuts and 200 m inclines. Three boreholes, one vertical (100 m) and two inclined (75 and 50 m) were drilled from underground chamber at +750 m. Geodetic surveying of the surface area scaled 1:200 and of the underground works scaled 1:1000 and 1:250 were performed. Geological recordings of the surface and underground works and sampling of ore veins and old wastes were carried out. The exploration works terminated by the end of 1961.

The exploration works carried out in 1880–1885 and 1956–1961 nowhere reached utmost depth of Saxon works and therefore there are no data about the dipping depth of the Čemernica vein.

Geology of the Čemernica area

The Čemernica area is composed mainly of Azoic or Lower Palaeozoic phyllites and otrelite schists which are intruded by schistose metarhyolites Katzer (1925). First detailed geological map of the Čemernica area





1:25.000 including all ore locations was carried out by Jurković & Tribuson (Jurković, 1956, 1962a) – **fig. 1**. Most of the area is composed of Lower Palaeozoic chloritoid (ottrelite) schist interlayered by quartz schists, phyllites and gneiss-looking phyllites. K-Ar apparent age of 343 ± 13 Ma was obtained on a phyllite, indicating Visean age of metamorphism (Palinkaš et al., 1996; Jurković et al., 1999). Protolith of these rocks must have been pre-Carboniferous. In the area of the adjoining map sheet Prozor Sofilj et al. (1980) included rocks of the same kind, in lower parts of the metamorphic complex ascribed to the Silurian.

North and particularly south of the Čemernica deposit larger intrusions of Upper Palaeozoic schistose metarhyolites (characterized by the $K_2O > Na_2O$) are common, and two smaller volcanic occurrences are found at Povitine and Donja Lučica. Schistosity of metarhyolites is conform with the schistosity in the surrounding schists. K-Ar measurements carried out on one sample of metarhyolite (characterized by the $Na_2O > K_2O$) in the neighbouring Busovača area gave 256 ± 28 Ma indicating their Kungurian (Permian) age (Palinkaš et al., 1996). This rock represents probably product of the final phase of rhyolite volcanism or initial phase of Permo-Triassic magmatism. Hrvatović (1996) emphasizes, the opinion that metarhyolites are older than the unconformably overlying Krušćica Permian Formation in whose conglomerates metarhyolite pebbles are included. Earlier Jurković & Majer (1954) and Sofilj et al. (1980) considered that the rhyolite volcanism lasted from Middle Carboniferous to Middle Permian. K-Ar dating performed on numerous samples of metarhyolites from the Busovača and Fojnica areas yield apparent ages from 92 to 121 Ma, indicating Alpine overprint.

In the area east of Čemernica and between Lučica and Donja Lučica, two intercalations of dolomitized limestones are found in schists. Between the villages Putljevac and Fojnica at Banja, a travertine body, about 50–100 m in diameter occurs from which spout out an active radioactive warm spring with temperature of 29.5°C .

According to Majer et al. (1991) paraschists and metarhyolites are composed of quartz, muscovite, phengitic muscovite and chlorite (mainly ripidolite). Chloritoid contains 8–15, rarely up to 23–26 mole % of Mg-chloritoid and phengitic muscovite with elevated content of celadonite component. The phase analyses indicate low-grade metamorphic conditions under very low to low pressure ($350\text{--}450^\circ\text{C}$ and 2–4 kbars). Based on textural deformations, the authors point out to polyphase metamorphism (the internal helicitic deformations of chloritoid porphyroblasts). Palinkaš et al. (1996) determined the overprint age of the last metamorphic phase on chloritoid schists from the Čemernica area of 46.2 ± 2.4 Ma (Lutetian) and 37.7 ± 1.5 Ma (Priabonian) on chloritoid schists from the Fojnica area. Hrvatović (1996) gave an K-Ar age of 35 Ma obtained on fresh biotites separated from paraschists from the Modri Kamen Mt. nearby Čemernica.

Ore veins

Walter (1887) and Kater (1907) considered that the Čemernica village area comprises six ore veins: (roof vein, main vein, foot vein, »Erbstollen vein«, western and southern veins) Ramović (1957) mentioned eight ore veins. Jurković (1956, 1962a) asserted that this is most probably one single vein which was strongly faulted and thus dismembered, as proved by subsequent exploration

works (Ramović & Zec, 1962). NE–SW trending faults generated four separate parts of the vein: »Southern vein«, »Erbstollen vein«, »Main vein« and »Northwestern vein«.

All four segments of the ore vein are NW–SE directed ($22\text{--}23^\circ$) with the dip towards the northeast between $30\text{--}70^\circ$, most commonly $55\text{--}65^\circ$.

»The southern vein« is 280 m long, representing a crack, up to 3 m thick, filled by crumbled material composed of chloritoid schist, metarhyolite, clay, crushed quartz and smaller or larger fragments of ores (cavernous or chert-like dense quartz with cinnabar and subordinate antimonite and sphalerite and scarce pyrite and arsenopyrite). The second segment named »Erbstollen vein« only 80 m long was shifted eastward for 100 m in relation to the southernmost segment. This part of the vein is 0.5–1.2 m thick and faulted along the flat dip; it is poor in ore and quartz contains scanty impregnations of cinnabar, sphalerite and antimonite. The third vein segment »Main vein«, 275 m long was shifted westward for 160 m from the second segment. Its outcrops occur at +800 m, in the southeastern part, up to +850 m on the northwestern part and thus its depth, based on the dip of 60° to the adit +750 m, is between 60 to 110 m. »Main vein« represents the best explored part of the Čemernica ore vein from the Saxonian time to the present days. Fine-grained quartz, frequently cavernous and in places dense like chert is the main vein mineral. Ore minerals only in some places fill whole vein together with quartz. The ore commonly occurs in form of strips, nests or impregnations in the quartz. Major ore mineral is antimonite with abundant sphalerite and subordinate cinnabar, whereas pyrite and siderite are scarce. The cinnabar occurs mainly in hanging parts of the vein, which were mostly mined by the Saxons, whereas the antimonite is located mainly in its footwall parts.

The last fourth vein segment named »Northwestern vein« was shifted eastward along the NE–SW trending fault for 50 m and was explored for 500 m along the strike (**fig. 2**). The »Northwestern vein« – is marked at the surface by numerous Saxon trenches and shafts which can be traced for 350 m at the altitudes from +1035 m to +975 m (position Brst). This part of vein was opened by adit +870 m in its upper parts and by prolongation of the adit +750 m from the »Main vein« segment in NW direction crossing very strong NE–SW stretching fault in its lower parts. On the level +870 m the vein was explored in SE direction only for 40 m because the vein, suddenly thinned to 0.2–0.4 m. The northwestern part was explored for 220 m. Lower horizon (+750 m), which was not found by Austrian miners, was not detected until 1959. This gallery 754 was parallel to the old works and cut the remnants of the vein with shorter or longer crosscuts. At the distance of 270 m in this gallery an incline up to the level of +870 was carried out. The same level was explored further northwestward for next 230 m.

A new incline from the gallery 754 m to the adit +870 m, 130 m long, parallel in distance of 20 m to the dip of vein and crosscut the vein and on each 33 m. The first crosscut was not checked, whereas the second one cuts the vein at the altitude +812 m (interlevel) 45 m long and sampled along the length for 30 m. An 15 m long incline located below the level of +750 m came across the Saxon works. **Table 1** illustrates that vein is thickest at higher level +870 m, i.e., 0.900 m and the thickness decreases to 0.776 m in the gallery +812 m, whereas in the horizon +750 m the vein thickness is nearly equal along the total length for 700 m ranging between 0.490

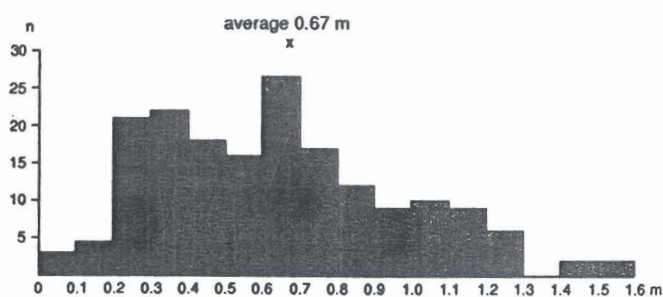


Fig. 4. Distribution of 181 measured values representing the thicknesses of the Čemernica vein; n - number of measurements.

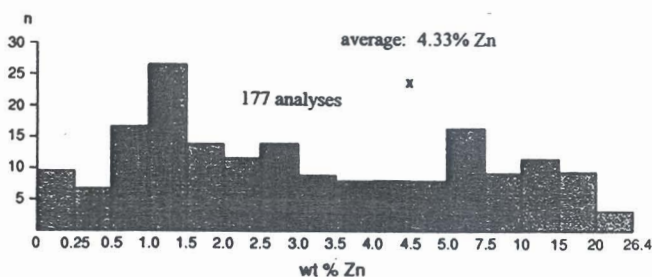


Fig. 4a Frequency of zinc content.

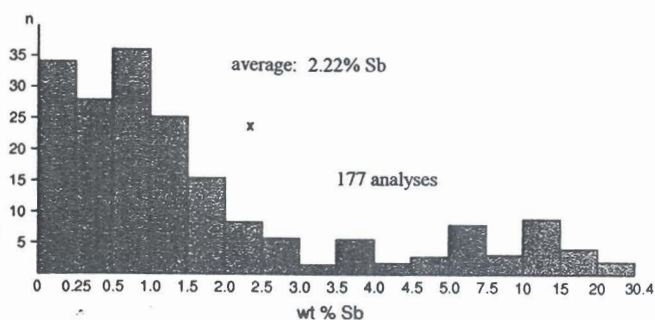


Fig. 4b Frequency of antimony content.

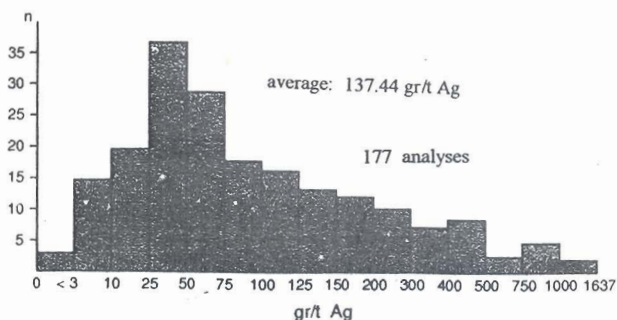


Fig. 4c Frequency of silver content.

m to 0.590 m. It can be realistically presumed that the vein thickness should be 0.35–0.45 m on still lower horizon +650 m. The vein on the outcrops at Brst (+1035 m) was locally up to 2–3 m thick.

The Čemernica ore vein was explored during the period 1956–1961 for 775 m along strike only on the segments »Main vein« and »Northwestern vein«. Other segments (»Southern vein« and »Erbstollen vein«) were only prospected, partly cleaned up and sampled. The

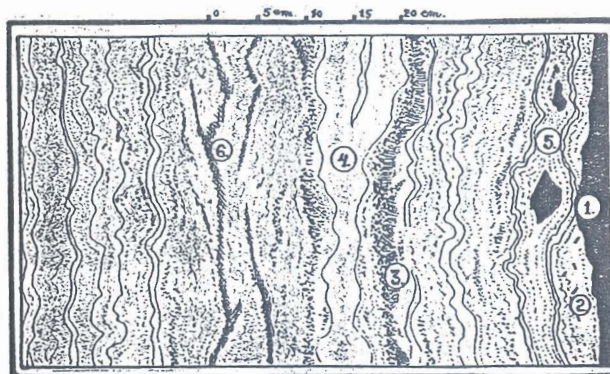


Fig. 5. Asymmetric stripped (ribboned) structure of the »Main vein« in the Čemernica mine. 1-chloritoid schist; 2-fine grained quartz associated with sphalerite and wolframite; 3-antimonite with Pb-antimonides; 4-coarse grained whitish-grayish quartz; 5-finegrained quartz with ribbons of antimonite, berthierite, boulangierite, jamesonite; 6-siderite with cinnabar, tetrahedrite, pyrite, arsenopyrite (Ramović, 1957).

mining activity was focussed to old Saxonian and Austrian underground works on the horizon +750 m. Old galleries were not cleaned but followed by approximately parallel galleries 752 (Main vein) and 754 (NW-vein). From these galleries old works were crosscut by shorter (a few metres) or longer (30–40 m) crosscuts. On most intersections were found spaces filled up with excavated gangue material, depleted of silver and mercury rich ores with more or less pieces of sphalerite and poor antimonite ores which were later manually selected and dumped outside of mine. On some intersections smaller or larger cavities of completely mined richer parts of the vein were found, whereas parts of the vein with abundant and subordinate sphalerite were left. Only on some intersections unmined thinner parts of the vein (<30–40 cm) with poor ore or with predominant sphalerite, or functioned as safety-blocks were found (fig. 3). Horizon +870 m of the »NW-vein« was cleaned 260 m along the vein exploited by Saxon miners. This cleaning enabled ventilation of the whole mine and access into portion of Saxon exploitation. The last 180 m of the »NW-vein« on the horizon +750 m (untouched by Saxon miners) were also opened along the vein.

Mineral paragenesis of the Čemernica deposit

By Austrian exploration works (1880–1885), the following minerals were recognized by naked eyes: quartz as major vein constituent, antimonite as main ore mineral with abundant sphalerite and cinnabar and subordinate pyrite and siderite. »Black sphalerite« (by Ramović, 1956. identified as wolframite) was noticed in »Main vein«. Silver and gold content was identified by chemical analysis and the presence of galena was inferred.

First detailed microscopic study of ore samples from the Čemernica area, was carried out by Jurković (1956, 1962a). In his papers, microphysiography of minerals, their main microstructural, microtextural and optical characteristics were presented. Jurković (1962b) carried out: quantitative optical determination on antimonite crystals reflection: power »r« for E, D and C spectral areas by using »Berek's Spaltmicroscopephotometer« and the determination of τ angle, η_2 - η_1 , χ_2 - χ_1 , R_2/R_1 , R_2 - R_1 and R_1 and R_2 values. Ramović (1956, 1957) found wolframite in »Main vein«, scarce galena in »Northwestern vein« and some gold leaves. Ramović et al. (1979) and Barić &

Trubelj (1984) gave a shorthistorical review of all known data concerning mining works and minerals of the Čemernica ore deposit.

Paragenesis of the Čemernica vein comprises: **quartz I** as the main gangue mineral and **antimonite I, II, sphalerite I, II**, and **cinnabar** as the main ore minerals. Subordinate minerals are **chalcedony, siderite, manganese siderite, ferberite, jamesonite, berthierite, boulangerite, plagiopyrite, arsenopyrite**. Scarce are **pyrite I, marcasite, pyrrhotite, pyrite II, barite, chalcopyrite I, chalcopyrite II, tetrahedrite and enargite**, whereas as accessories are **galena, quartz II, realgar, mineral »X« and gold**.

Quartz is major vein mineral with 50–95% in ore mass. It is mainly dense, milky- or smoky-white in colour. Microcrystalline varieties similar to chert are yellowish, reddish and grayish in colour. **Quartz II** occurs in druses. Coarse-crystalline quartz is zoned and its external zones are full of needle-like minute crystals of antimonite and lead-antimonides and thus are black or darkgray in colour.

Antimonite is the main ore mineral which occurs in needle-like crystals and fills smaller or larger hollows in cavernous quartz forming star-like and fine-grained aggregates. Dense antimonite masses occur rarely. There are two generations of antimonite: as automorphic crystals in sphalerite and siderite and as metasomatic antimonite replacing frontally sphalerite. Post-ore tectonic activity is indicated by optical anomalies on antimonite crystals showing undulose or irregular extinction, polysynthetic polylamellar banded and fragmented pressure twins, cataclastic grains or recrystallized elongated antimonite grains with the same optical orientation. Semiquantitative spectrographic analysis of antimonite crystals gave (in ppm): >10 Zn, Bi, Cd; >100 Ag, Pb, Cu, Fe (Jurković 1962b). Quantitative analysis gave (in ppm): 220 Ag, 310 Pb, 145 Cu; 540 As and >3000 Zn (C. Mudrinić, 1981, published in Ramović, 1991).

Sphalerite is, besides the antimonite, the most abundant ore mineral with the increasing abundance in the »Main vein« and especially in the »NW vein«. The older sphalerite generation is brown or darkbrown in colour with reddish internal reflections and scarce exsolutions of chalcopyrite I, whereas the younger generation, in druses, is lightbrown in colour due to a less iron content with lighter internal reflections. Sphalerite is coarse-grained and lamellar and in some parts is major vein constituent. Quantitative spectrographic analysis gave (in ppm): 5 Ag, 200 Pb, 70 As and 125 Sb (analyst C. Mudrinić, 1981, published in Ramović, 1991).

Cinnabar occurs in form of impregnations, rarely as smaller masses, nests, network of veinlets and strips. The cinnabar aggregates are composed of very indented grains averaging 70–150 micrometers in diameter, which are commonly cataclastic or optically anomalous. Recrystallized textures can also be recognized.

Pyrite I occurs as subordinate mineral in immediate salbands or as minute grains included in quartz, rarely in siderite and sphalerite and very rarely in antimonite and cinnabar.

Siderite, which is the most common in cavernous quartz of the »Main vein«, contains locally up to 10–14% Mn. It includes minute pyrite and arsenopyrite crystals but it can be replaced by antimonite and barite.

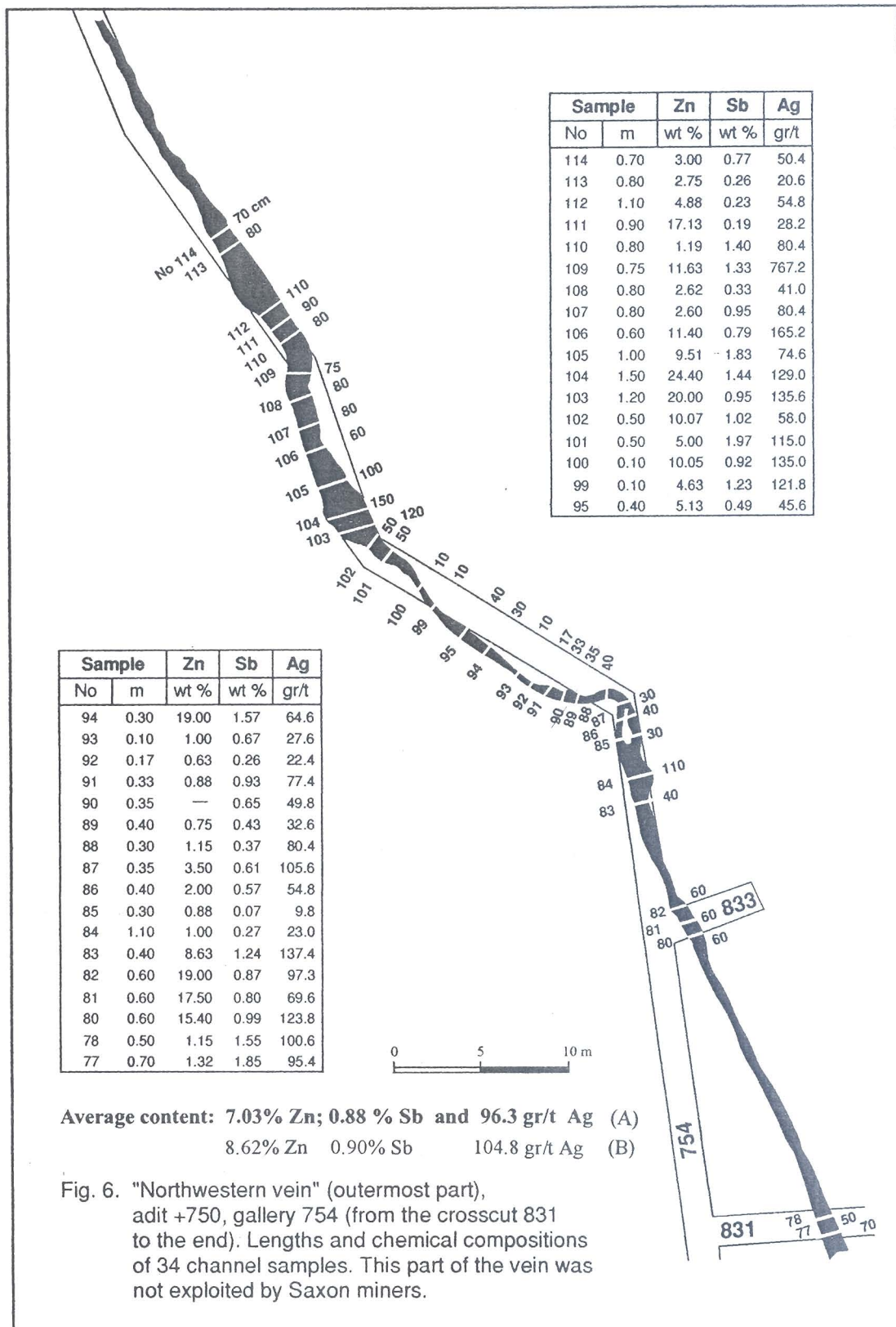
Arsenopyrite occurs mainly as automorphic crystals, 50–100 micrometers in diameter, sometimes elongated and 0.6 mm long. Its larger crystals are frequently cata-

clastic and replaced by antimonite. It is abundant in the Osoje vein. **Pyrrhotite** is almost completely weathered into crypto-microcrystalline mass of **pyrite II** and **marcasite** (bird-eye structure). **Jamesonite**, which is identified in »Main vein«, fills micropores of quartz in form of microscopic needles, frequently indented and mutually-grown into grained masses of boulangerite. **Berthierite** was found in »Main vein« associated with antimonite. Berthierite forms subparallelly elongated aggregates, 1–2 mm long and 0.3 mm thick, which are composed of subparallel crystals arranged parallel to the c-axis. Aggregates are in some places replaced by antimonite. **Boulangerite**, which is much more rare than jamesonite, forms equigranular or elongated aggregates composed of subparallelly arranged lath-like crystals. **Plagiopyrite** occurs as prismatic and needle-like crystals, rarely as grained aggregates. **Wolframite** was found in those parts of »Main vein« and »NW vein« which are enriched in sphalerite or are poor on younger sulphide generation. The crystals are a few micrometers to 3 cm long, 1.2 cm wide and 0.5 cm thick, in druses developed with terminal planes. Wolframite contains 74% WO₃, 18% FeO and 6.2% MnO indicating low-temperature ferberite (Ramović, 1956). **Metacinnabar** (black HgS), which is associated with cinnabar in microcavernous quartz, was found in »Footwall vein« and »Main vein«. **Chalcopyrite I** is extremely rarely exsolved in sphalerite I. **Chalcopyrite II** occurs in form of incrustation around single or aggregated sphalerite grains. **Enargite** is found in the Osoje vein associated with abundant chalcopyrite II. **Chalcedony**, as spherulites with radiating zoned structure, occurs in some parts of ore veins full of needlelike lead-antimony-sulphosalts and antimonite crystals. In some places it is replaced by kidney-like masses of originally colloidal sphalerite. **Barite** associated with quartz, siderite and sphalerite rarely occurs in druses. In some places barite includes antimonite and berthierite crystals and becomes skeletal in appearance. Ramović (1957) first found **galena** in »NW vein«, in »tectonized zone« (»Ruschelzone«) composed of tectonic breccias in which some fragments contained pyrrhotite, galena and an unidentified **mineral X** which is also rarely found in »Southern vein« as cement in cataclastic sphalerite.

Mineral X is characterized by high reflectivity, yellowish colour and optical anisotropy, it belongs to younger sulphide generation. **Native gold**, recognized by microscope, occurs as smaller leaf or grain a few micrometers to 1 mm in diameter. **Tetrahedrite** which is rarely found in analyzed polished sections, belongs to younger sulphide generation; in reflected light it is gray-yellowish with reddish-brown tint. **Realgar** is very rare mineral. **Goethite, lepidocrocite, valentinite, bindheimite and wolfram ocher** are minerals found in the oxidation zone of the Čemernica deposit.

Ore textures and structures

Structures are commonly massive but also frequently symmetrically or asymmetrically banded. In the banded structures (fig. 5) thin quartz bands of variable size grains rhythmically alternate with bands of different ore minerals. The sample presented in the fig. 5 comes from »Main vein« and represents typical asymmetrically banded ore (Ramović, 1957). In banded structures, bands with high-temperature minerals, commonly formed close to salbands, alternate with the bands of lower-temperature minerals in central parts of veins. In some areas, brecciated structures can



be noticed. »Southern vein« is almost completely crushed by post-ore tectonics and ore fragments, together with fragments of host rocks area are embedded in clay-quartzose mass.

Chemical composition of ores

There are no available data on ore composition from the Middle Age period. H a u e r (1884) and W a l t e r

(1887) write that quartz is main gangue mineral whereas antimonite predominates in the ore paragenesis over sphalerite, pyrite and siderite. Galena was only inferred. W a l t e r (1887) gave chemical analyses (made by Patera in Vienna) of two selected antimonite ore samples: 42.37 and 53.98% Sb, 18.86 and 8.63% Zn; 3.27 and 5.32% Fe, 27.20 and 28.20% S; 8.20 and 2.40% SiO₂ and traces to 264 gr/t Ag. J o h n & F o u l l o n (1893) claim

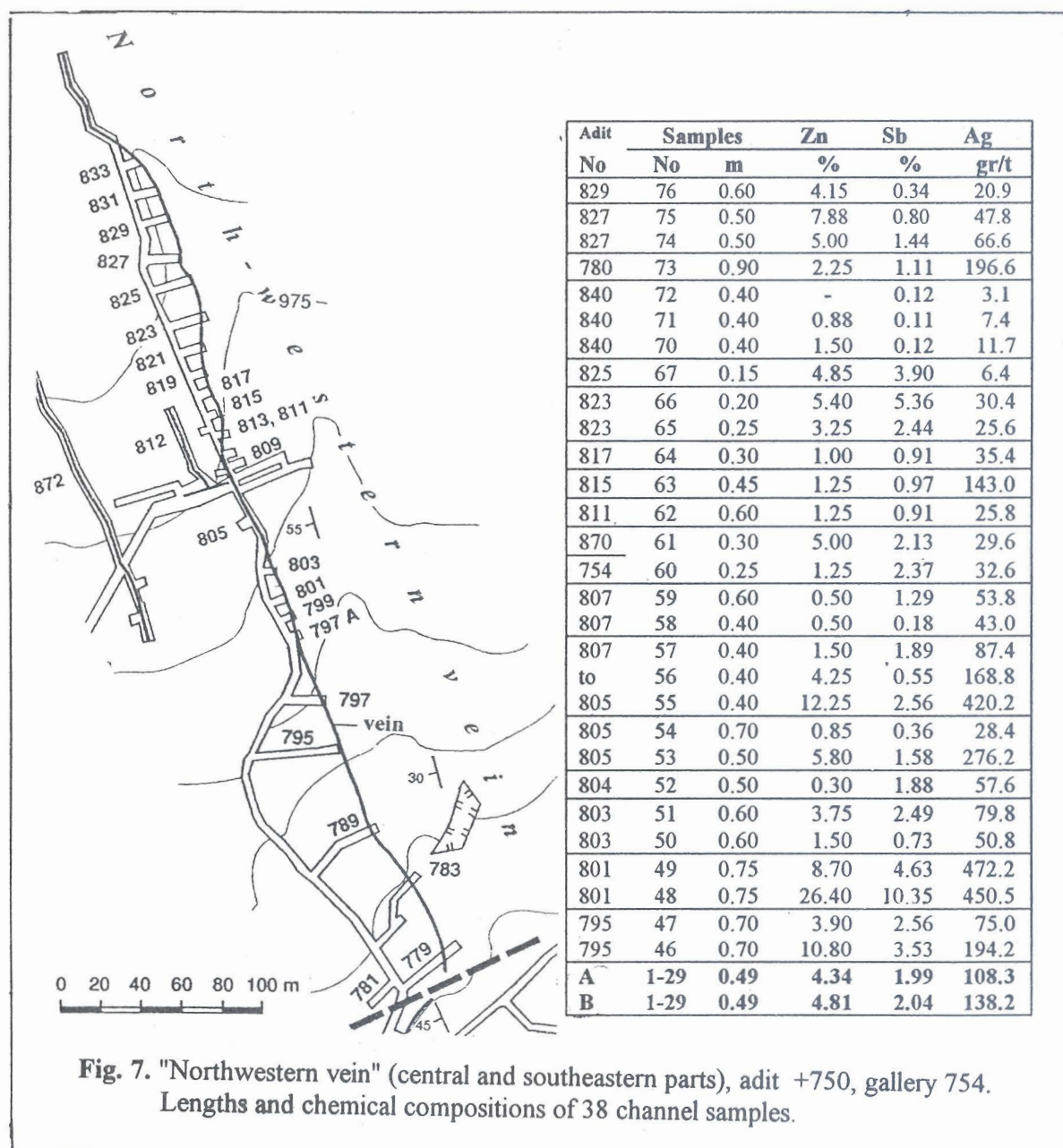


Fig. 7. "Northwestern vein" (central and southeastern parts), adit +750, gallery 754. Lengths and chemical compositions of 38 channel samples.

that the ores from the Ostružnica foundry, supplied from the Čemernica mine, contained 8.92% Sb and 130 gr/t Ag. Chemical analysis of one sample taken in the foot-wall part of vein gave (in wt. %): 0.96 Sb, 1.96 Zn, 2.17 As, traces of Cu and Pb, 5.51 Fe and 64 gr/t Ag.

Systematic sampling by Ramović & Zec (1962) was carried out during the period from 1956 to 1961 on all intersections of old works except 5 ones not available, on the excavated material in galleries, on remnants of ore veins and on the untouched parts of veins themselves. All 177 channels were 121,01 m long, the total length of sampled ore vein was 990 m (Table 1).

Sampling was carried out as follows: (a) on the intersections of new crosscuts and old Saxon gallery found on the horizon +750 m; (b) along cleaned Saxon gallery on the horizon +870 m; (c) on the outermost northwestern part of the »NW-vein« untouched by old miners and (d) on ore pieces found in the gallery 2 on the horizon +720 m (»Southern vein«) (Table 1).

The main purpose of our detailed sampling and analyses was to be acquainted with the composition of remnant ore in the mine and with the minerals as object of Saxon exploitation.

In the initial stage each sample was analyzed for mercury and each fifth sample for zinc, antimony, silver and gold. Later on, chemical analyses were done only for Zn, Sb and Ag, because results of 34 analyzed samples on mercury were disappointed. 18 analyses were negative, 12 samples contained only 0.01 to 0.05 % Hg, 3 samples between 0.06 and 0.09% Hg and only one 0.96% Hg. Mercury was determined in the laboratory of the Idrija mercury mine (Slovenia) and several last analyses in the laboratory of the Tarčin barite mill (Bosnia and Herzegovina). Zinc, antimony, silver and gold analyses were done in the laboratory of the big copper-gold mine in Bor (Serbia). Total of 177 chemical analyses for zinc, antimony and silver was carried out, 74 out of them were analyzed for gold and 22 out of them for mercury. Sepa-

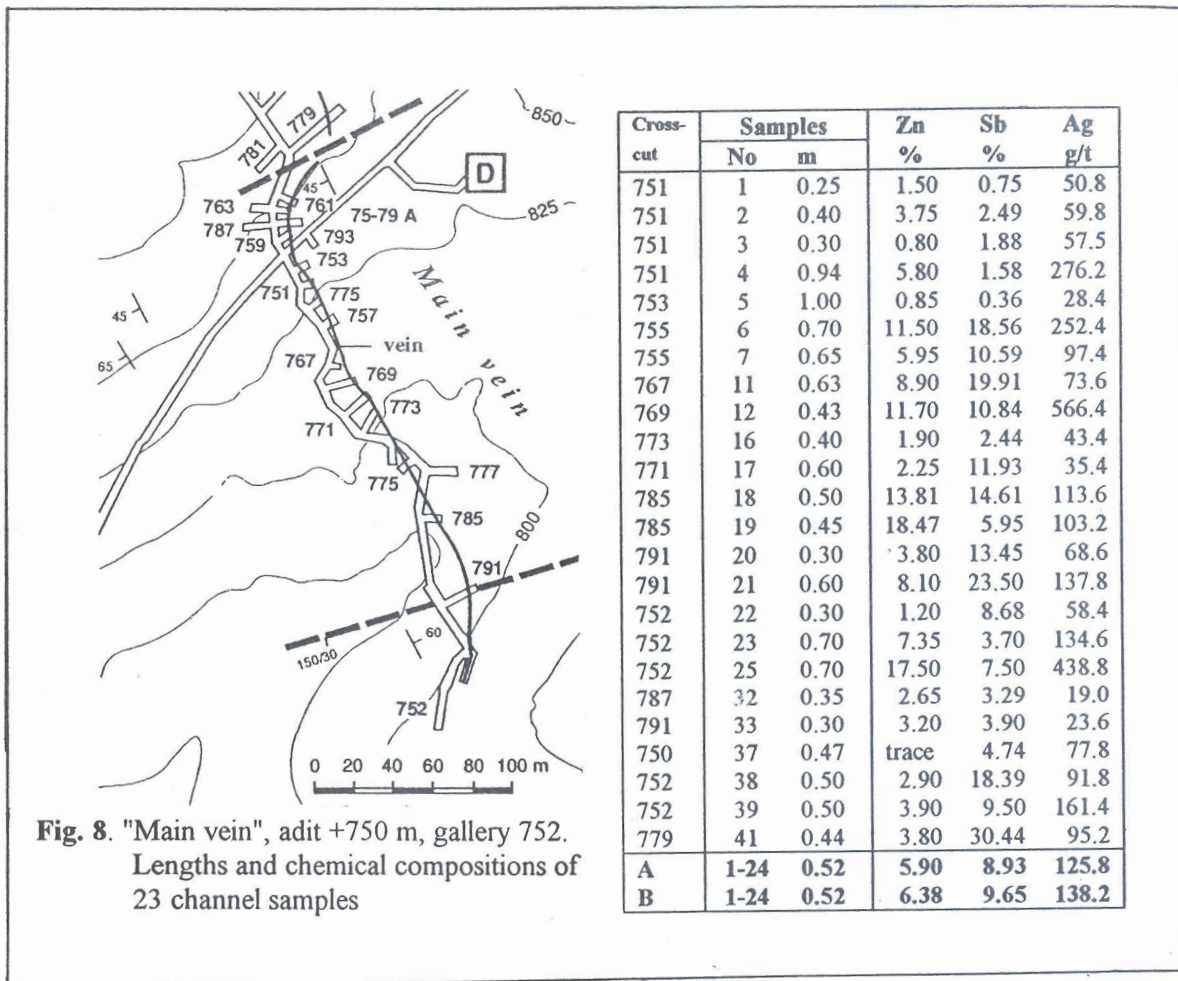


Fig. 8. "Main vein", adit +750 m, gallery 752. Lengths and chemical compositions of 23 channel samples

rately, 12 samples yet were analyzed only for mercury, 6 from the gallery 752, 4 from the gallery 754 and 2 from adit +720 m.

From seventy five ore samples analysed for gold sixty four samples gave negative results, four samples only traces of gold (the gallery 752); three samples 0.1 gr/t (the gallery 754, NW vein), and only one sample 0.7 gr/t (the gallery 872). These results confirm that the Čemernica vein is not economically gold-bearing.

In the table 1 are presented average values of Zn (4.33%), of Sb (2.22%) and of Ag (137.44 g/t) obtained as arithmetically values of all analyses (marked with A).

In table 1 are presented also average contents of zinc, antimony and silver in ores taking into consideration proportional influence of the length of channel samples: Zn 4.34%; Sb 1.84% and Ag 153.18 g/t (marked with B). This table includes also data on the pertinent sector, number of analyzed samples, total channel length, average vein thickness and length of the analyzed section for each sector.

The contents of zinc, antimony and silver are unevenly distributed along length and dip of the Čemernica ore vein (fig 6, 7, 8, 9, 10). Fig. 10 shows instructively swift changes of values for all three elements. The values for zinc are ranged between zero and 26.42%, for antimony from zero to 30.4%, and for silver from zero to 1637 g t.

Frequencies of zinc, antimony and silver contents are different: relatively uniform for zinc, irregularly bisymmetric concave for antimony, and regularly bisymmetric

convex for silver (fig. 4a, 4b, 4c). These differences are due to selection of ore which was exploited by old miners. They left untouched all richer antimonite ore »in situ« or insofar, as excavated, were left in galleries as small or bigger pieces included in quartz gangue. High average antimony content of antimony in untouched parts of »Main vein« in the gallery 752 with 9 to 10% represents probably approximate real value of original vein. In comparison with average values of 0.6 to 2% Sb in the strongly exploited parts of the »NW-vein« in the galleries 754 and 872, the ore with values from 2 to 10% of antimony were object of the exploitation in the Čemernica vein. These values lack in the concave part of the fig. 4b. On the assumption that antimonite contains on average 200 g t Ag, 10% of Sb, or 14% Sb_2S_3 in the vein are responsible only partly for the silver content in the vein. Sphalerite with 5 g/t of silver is negligible bearer of silver. Regarding the lack or scarcity of silver-bearing galena, follows the necessity of the existence of other silver-bearing minerals. Lead, iron and copper antimonides found microscopically (Jurković, 1956, 1962a) in the »Main-vein« and »NW-vein« represent silver-bearing minerals instead of galena. These minerals are coeval with antimonite and therefore intimately associated with antimonite in the Čemernica vein.

Antimonides and antimonite were object of Middle-age exploitation.

There is only a general correspondence between antimony and silver contents in the Čemernica vein. On some segments of the vein rich antimonite ore is poor on

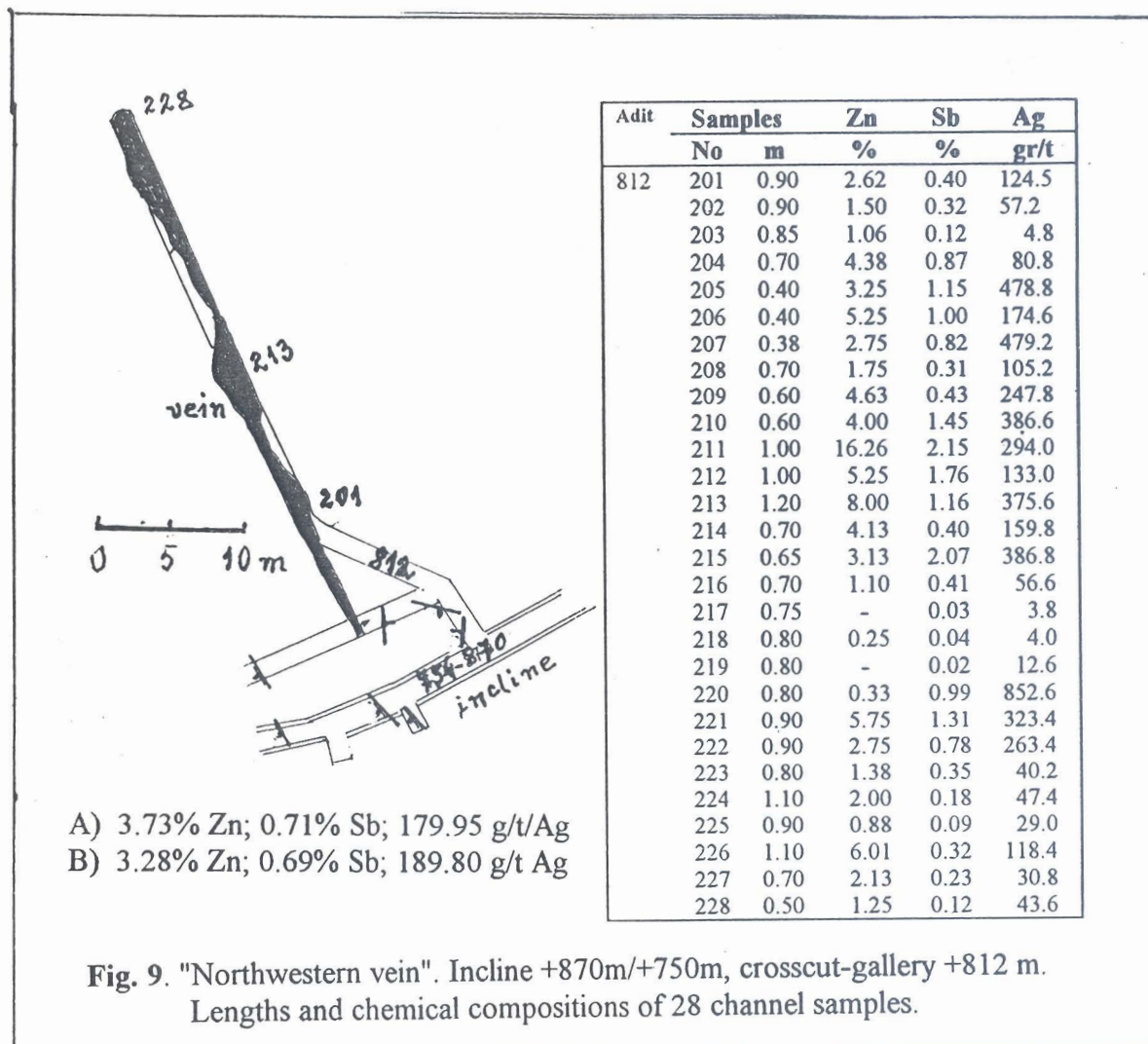


Fig. 9. "Northwestern vein". Incline +870m/+750m, crosscut-gallery +812 m. Lengths and chemical compositions of 28 channel samples.

Table 1. Average contents of zinc, antimony and silver in the investigated parts of the Čemernica vein. A. Arithmetical average values. -B. Values obtained taken into consideration lengths of channel samples.

Vein	Horizon (adit)	Gal- lery	Length of sam- pled vein	Average thickness of veins	n	Length of channel samples	Average chemical composition			
							Zn wt %	Sb wt%	Ag gr/t	
North- western vein	+870 m	872	175 m	0.900 m	57	51.30 m	A	2.60	0.73	161.30
		874					B	2.59	0.64	172.96
	+812 m	812	30 m	0.776 m	28	21.73 m	A	3.73	0.71	179.95
							B	3.28	0.69	189.80
	+750 m	754	80 m	0.590 m	34	20.05 m	A	7.03	0.88	96.32
		NW					B	8.62	0.90	104.75
	+750 m	754	385 m	0.490 m	29	14.20 m	A	4.34	1.99	108.30
		SE					B	4.81	2.04	138.20
Main vein	+750 m	752	280 m	0.517 m	24	12.41 m	A	5.90	8.93	125.80
							B	6.38	9.65	138.20
Southern vein	+720 m	2	40 m	0.264 m	5	1.32 m	A	4.03	5.87	76.56
							B	4.03	5.87	74.44
In total			990 m	0.684 m	177	121.01 m	A	4.33	2.22	137.44
							B	4.34	1.84	153.18

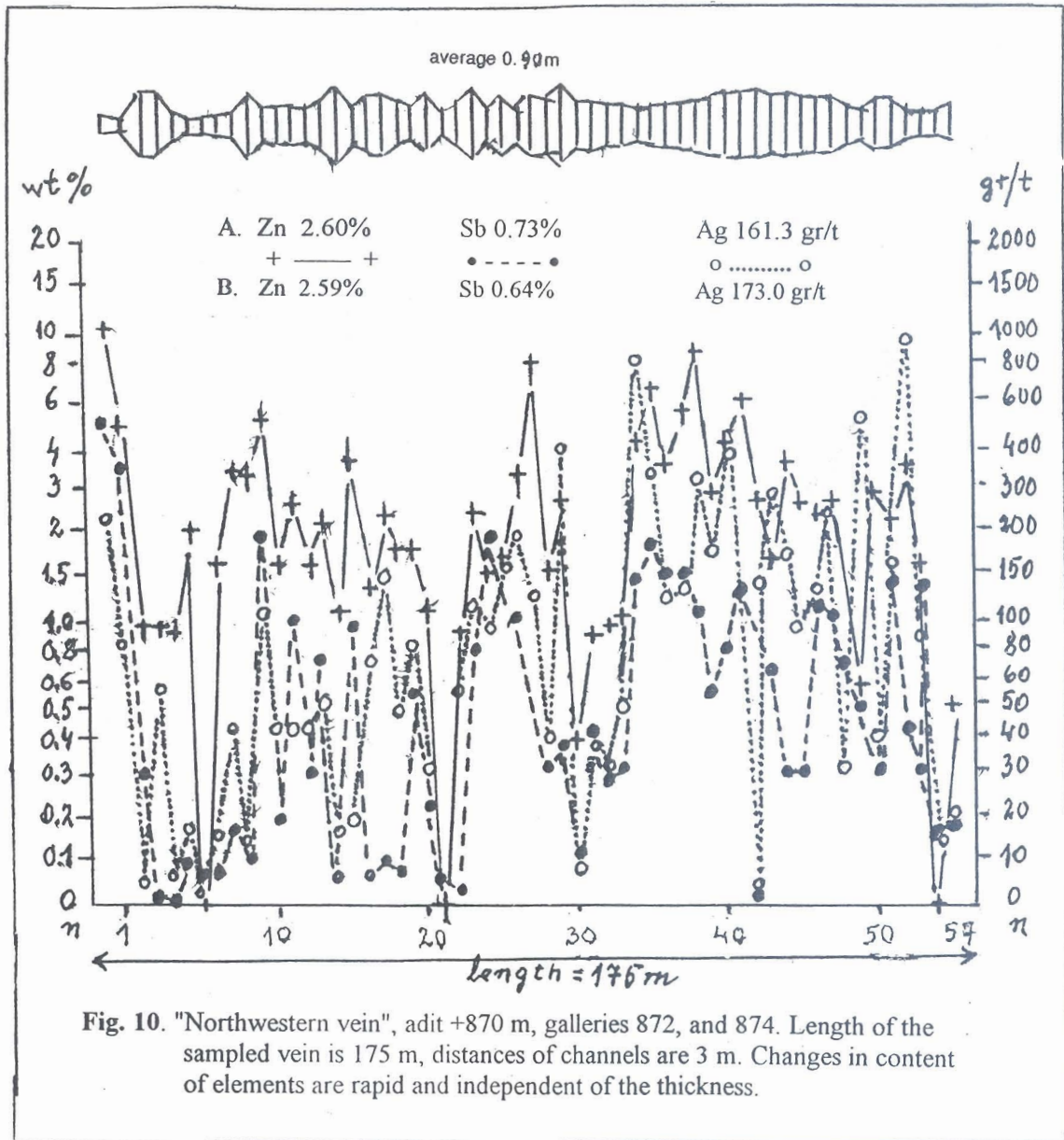


Fig. 10. "Northwestern vein", adit +870 m, galleries 872, and 874. Length of the sampled vein is 175 m, distances of channels are 3 m. Changes in content of elements are rapid and independent of the thickness.

Table 2	High content of Sb, low content of Ag			
Sb	30.40	23.50	19.91	11.93
Ag	0.0095	0.0138	0.0074	0.0035
	Low content of Sb, high content of Ag			
Sb	1.38	1.35	0.99	0.43
Ag	0.0809	0.1637	0.0852	0.0909

silver and vice versa the poor antimonite ore contains high silver content (table 2).

Isotope composition of sulphide sulphur in antimonite and sphalerite

It was determined the isotope composition on 4 samples (table 3).

The obtained values indicate magmatic source of sulphur supplied by hydrothermal solutions. The results correspond with the isotopic values of sulphide sulphur and sulphosalts from the ore deposits in the Busovača-Fojnica-Kreševo area with realgar (+0.99‰) and orpiment (+1.32‰) from the Hrmza arsenic deposit, with

the values of tetrahedrite (+3.28‰ and +3.73‰) from the gold-bearing tetrahedrite deposit Trošnik and with the isotopic composition of pyrite sulphur (+4.78‰ and +6.76‰) from the gold-bearing pyrite deposit Bakovići (Jurković, 1995).

Calculations of ore reserves

The calculated reserves are presented as probable B category, possible C₁ category and geological reserves of C₂ category.

In the B category are inserted those parts of the ore vein which are spatially limited by galleries 874 and 754 and incline 874-754. This category has very low contents of antimony and silver because they represent only remnants of Saxon and Austrian exploitation. In the category C₂ were inserted ore reserves from first 50 m bellow surface and ores situated from 50 to 100 m bellow gallery 752 and 754. All other parts of the vein belong to the category C₁. As cubic weight of compact ore was taken the average value of three measurements: 2.69, 2.95; 2.49=2.71 kg/dm³.

Sample symbol	Mineral	$\delta^{34}\text{S}/\beta^2\text{S}$	$\delta^{34}\text{S}\%$	Authors
5 At 2	antimonite	22.134	+3.48	Kubat et al. (1979/80)
6 ER-A-38	antimonite	22.193	+2.12	
7 ER-S-35	sphalerite	22.138	+3.71	
803	antimonite	22.191	+2.21	

Table 4. Calculation of ore reserves in the Čemernica mine

Class	m ²	thick- ness m	volume m ³	ores t	Zn			Sb			Ag		
					%	%	gr/t	t	t	kg	t	t	kg
B	38968	0.443	17.273	46.637	4.81	1.27	73.68	2244	590	3436.0			
C ₁	72824	0.622	45.271	122.232	6.60	5.63	124.16	8067	6881	15176.9			
C ₂	82298	0.600	50.778	137.101	5.63	3.53	119.3	7719	4836	16361.9			
Σ	194090	0.584	113.322	305.970	5.89	4.02	114.3	18030	12307	34974.8			

In the table 4 are presented ore reserves in tonnes, their average chemical composition and content of zinc, antimony and silver metals.

Ore occurrences in broader neighbourhood of Čemernica

At locations Osoje, Putljovac, Donja Lučica, Povitine and Ledina (fig. 1) occurrences of quartz veins, are found which are thinner and shorter than in the Čemernica area, but contain very similar or identical mineral parageneses (K a t z e r, 1925, J u r k o v i ć, 1956, 1962).

Osoje is located 0.5 km northeastward from Uketovac peak (+1237 m). Several NNW-SSE trending veins dipping towards the SW are composed of xenomorphic and fine-grained **quartz** which is accompanied with **pyrrhotite** mostly decomposed in the crypto-microcrystalline mass of **pyrite** and **marcasite** and locally with abundant **arsenopyrite** and scarce **sphalerite**. Abundant **chalcopyrite** and quite subordinate **enargite** and **antimonite** replace the older sulphide generation or fill quartz hollows. Post-ore tectonics is shown in cataclases and brecciation. **Covellite**, **chalcocite**, **malachite**, **goethite** and **lepidocrocite** are hypergenic ore minerals.

Putljovac occurrence is located 3 km southeastward of Čemernica and 1 km north-northeastward of Fojnica. A quartz vein, a few centimeter to 1 m thick, stretching NNW-SSE with NE dip, is strongly disrupted by strong NNW-trending and weaker NNE-trending faults. Mineral paragenesis comprises **quartz** as main mineral, whereas **antimonite**, **sphalerite**, **pyrite**, **arsenopyrite** and **siderite** are subordinate.

Donja Lučica occurrence is found 15 km eastward of Fojnica. Quartz vein, disturbed by post-ore tectonics, is 0.2–0.3 m, locally 1 m thick, stretches NNW-SSE and dip towards NE. The vein is composed of predominant milky-white, rarely blueish **quartz**. Older sulphides are **pyrite**, frequently cataclased **arsenopyrite** and very scarce **sphalerite**. Younger sulphide generation is represented by abundant **antimonite**, 50–150 micrometres in diameter, frequently deformed as shown by polysynthetic pressure twins and optical anomalies and with recrystallization structure. Scarce **boulangerite** forms network of microscopic needles and together with antimonite fills quartz hollows or replaces older sulphides. **Plagionite** occurs as prismatic or needle-like crystal characterized by reddish internal reflections and strong anisotropy. **Realgar** is scarce. Hypergenic minerals are **valentinite**, **anglesite**, **goethite** and **lepidocrocite**.

Povitine occurrence is located in upper courses of the creek of the same name, 2 km eastward of Čemernica. K a t z e r (1907) described two thin **quartz** veins in which predominant quartz is associated with scarce **siderite**, **sphalerite** and **antimonite**.

Crvenika occurrence is found 2.5 km north-northeastward of Fojnica. Here, iron hat is composed of **quartz** and **limonite** with remnants of unoxidized **pyrite**.

Ledine occurrence is located in the Ledine creek 0.5 km eastward of Crvenika. Mineral paragenesis includes predominant **quartz** and subordinate **pyrite** and **antimonite**, and secondary **goethite** and **lepidocrocite**.

Other wolfram-bearing antimonite deposits in Bosnia and in neighbouring states

Bosnia. In the Tertiary lead-zinc ore district Srebrenica (Eastern Bosnia), related to the dacite-andesite volcanic activity, R a m o v i ć (1961, 1963) found two huebnerite-bearing quartz-antimonite veins, the first one no 59, located 150 m south of the village Čumavići (NW Srebrenica district) contains abundant brown-red-dish huebnerite crystals. Chemical analysis (Gromović) gave (in %) 30.84 SiO₂, 6.14 MnO, 23.96 WO₃ (or Mn_{0.84}Fe_{0.16}WO₄). The second locality is Zmajeva Bare (NE Srebrenica district) with huebnerite in ore fragments. K u b a t (1963) found at Čumavići 2 cm long prismatic and platy huebnerite crystals. Analysis made by Gromović gave (in %) 22.22 SiO₂, 12.55 Fe₂O₃, 10.34 MnO, 40.76 WO₃.

Serbia (Yugoslavia). P e t r o v i ć & M u d r i n i ć (1982) describe the Osanica (Eastern Serbia) antimonite deposit. Eight discontinuous veins, 0.15 up to 0.5–1.0 m thick, and up to 500 m long cut gneisses and leptinoliths, intruded by Hercynian granite-porphyre and rhyolite, and Tertiary dacite. Quartz-chalcedony gangue contains nests, lenses and strips of antimonite and wolframite with scarce pyrite, marcasite and only locally pyrrhotite and arsenopyrite. Ore contains 1–6 % Sb, less than 1% WO₃ and 1–4 g/t Au. Very rare are quartz veins with scheelite or quartz veins with galena, sphalerite, scarce pyrite, pyrrhotite, boulangerite, marcasite, and chalcopyrite. J a n k o v i ć (1990) considers that existence of different paragenetic types point to different types of differentiation of hydrothermal solutions and of a manifold formation.

Greece. M a r i n o s (1982) cites some small antimony occurrences formed along silicified fault zones in schists at Lahanas (Central Macedonia). Ore is composed of

calcite, arsenopyrite, ferberite, pyrite, quartz, antimonite and barite. The second ore occurrence is Filadelfion with antimonite, wolframite, scheelite, pyrite, arsenopyrite, berthierite, quartz. Mineralization is related to the Tertiary rhyolites; wolfram is mobilized from crystalline schists.

Bulgaria. Ribnovo and Krstov Dol are wolfram-bearing antimonite occurrences (Janković, 1982). Ribnovo contains: antimonite, wolframite, pyrite, marcasite, arsenopyrite, sphalerite, galena, boulangerite, tetrahedrite, chalcopryrite, quartz, barite. Krstov Dol: antimonite, scheelite, sphalerite, jamesonite, chalcopryrite, berthierite, realgar, quartz, calcite.

Austria. W-Sb occurrence is found at Arzthal NE of Matrei a. Brenner (Osterreichische geologische Karte, Sheet 148); Cu, Tet. Py, W, Sb occurrence at Knappen Kuchl-Klammalm, Navistal in Lanersbach (ök-149); and at Obertilliach in Obertilliach (ök-196) with Sb, W, Py, Cu (Weber et al., 1997).

Discussion

Antimonite occurs in (a) monometallic antimony deposits formed from completely differentiated hydrothermal solutions; (b) bimetallic deposits (Sb-As±Tl; Sb-W; Sb-Hg; Sb-Fe) formed from partially differentiated hydrothermal solutions and (c) polymetallic deposits (Sb-Pb-Zn; Sb-As-Tl-Hg; Sb-Hg-W, Sb-As-Pb-Zn, Sb-As±Tl±Ni±U±Mo) formed from incompletely differentiated hydrothermal solutions enriched in elements mobilized from host rocks. The most widespread type is Sb-Pb-Zn±As. Transitional type contains antimony dominantly as sulphosalts and scarce antimonite (Janković, 1982).

Wolframite-bearing antimonite deposits are rare in the world. Kempe et al. (1994) consider that such deposits occur in regions with low-grade metamorphism at the margin of old continents, without provable relations to magmatic processes. They are connected with tectonic structures of overthrusting, nappe systems or large faults. Ore minerals are hosted by quartz veins or breccias with argillized and sericitized wall rocks. Ore deposits consist of quartz, sometimes with chalcedony and opal, carbonates and ferberite, scheelite, antimonite and cinnabar as the main ore minerals. Scarce are pyrite, marcasite, arsenopyrite, chalcopryrite, pyrrotite, sphalerite, galena, tetrahedrite and some other minerals. Fluid inclusion study and $\delta^{18}\text{O}$ composition indicate low Th below +200°C and low salinity (3–15 wt% equ NaCl) of ore forming fluids.

Čemernica deposit belongs to the polymetallic deposits. It represents a very uncommon and rare Sb-Zn-Hg-W-Pb-Fe-Ag type of antimonite deposits. It contains also some arsenic, copper, barium and manganese. The most characteristic feature of this deposit is extraordinarily small content of galena in the paragenesis. Most of lead is incorporated into antimony sulphosalts: jamesonite, boulangerite and plagiogonite, associated with antimony-iron sulphosalt berthierite. The Čemernica deposit is characterized with dominant antimonite, subordinate Sb-sulphosalts and lack of galena. Such paragenesis distinguishes the Čemernica vein system from other deposits in which the predominant antimony minerals are Sb-sulphosalts with or without scarce antimonite.

The marked polymetallic character of the Čemernica deposit suggests enrichment either by mobilization from host rocks or during polyphase metamorphism. In order to corroborate this statement fluid inclusion study was carried out of quartz crystals from the Čemernica vein, which

manifested aqueous and aqueous-carbonic fluid systems indicating polyphase mineralization process made by L. Palinkaš, published in Jurković et al., 1999.

Originally ore-forming two phase irregular aqueous inclusions (L+V) were characterized by Th between +150° and +230°C (max. at +190°C), Te -25°C, Tm ice between -16,6° and -11°C, salinity from 14.9 to 20.2 wt % equ. NaCl. Freezing temperature is from -40° to -60°C. Frozen content is clear, colourless, typical for NaCl-KCl-H₂O inclusions.

Some aqueous pseudosecondary or primary solitary inclusions (L+V) show Th +330°C (the highest recorded), Te at -31.2°C (divalent cations), salinity of 16.9 wt % equ. NaCl. These characteristics affiliate them into ore-forming inclusions.

Regular, oval three phase aqueous-carbonic inclusions (NaCl-H₂O-CO₂) freeze in two steps, aqueous part around -60°C, and solid CO₂ at around -120°C. Majority of them melt between -61 and -64°C indicating the presence of CH₄ and of N₂. Tm ice is between -7 to -13°C, Tm Clath is around 3.9 to 5.5°C corresponding to 9.4–10.7 wt % equ. NaCl.

Genesis

Hermann (1942,1947), Petrascheck (1942, 1954), Schumacher et al. (1950); Polić (1951) and Simić (1951) considered the Čemernica antimonite deposit as hydrothermal deposit genetically related to the Tertiary magmatism. Kätzer (1907, 1925), Jurković (1956, 1957, 1962a), Cissarz (1956), Janković (1958, 1967, 1982), Kubat (1978a, 1978b, 1995), Ramović et al. (1979), Sofilj et al. (1980), Ramović (1991), Pamić & Jurković (1997), on the contrary, regarded this deposit related to the Late Palaeozoic rhyolite (granite) magmatism. Recently, Kubat (1982) and Janković (1987, 1990) classified the Čemernica deposit to the Triassic metallogenic epoch.

Fluid inclusion study demonstrated at least three fluid systems in quartz crystal from the Čemernica deposit: (a) aqueous NaCl-KCl-H₂O inclusions, typical residual magmatic fluids, as transitional, to post-granitic alteration fluid according to Behre et al. (1987) and Klemm (1994); (b) aqueous NaCl-CaCl₂(±MgCl₂)-H₂O post-Variscan fluid system; aqueous-carbonic NaCl-H₂O-CO₂ inclusions typical for Late Alpidic fluid system.

The older, primary system is of hydrothermal origin related to the rhyolitic (granitic) Late Paleozoic magmatism. The granite-related origin could also explain the great variations in solution characteristics during this cycle in the surrounding areas between Busovača-Fojnica in the north and Kreševo-Kiseljak in the south of the eastern part of the Mid-Bosnian Schist Mountains. The Hrmza, Trošnik, Bakovići, Čemernica, Donje Selo, Vrtlasce ore deposits from this area are characterized by the presence of Sn, W, Mo, F as typical granitophylite elements.

Admixing of meteoric water and hot saline connate waters greatly changed in the post-Variscan time the character of primary fluid inclusions (temperature, salinity, chemical composition). Such overprint with similar fluid conditions caught hold not only all mentioned deposits, but also some hundred barite deposits in the Gomji Vakuf-Kreševo area (Palinkaš & Jurković, 1994). Connate water originated from the widespread Late Permian gypsum-anhydrite deposits. Sulphate sulphur isotope composition of the gypsum and anhydrite with $\delta^{34}\text{S} = +11.0\text{‰}$ is close to the $\delta^{34}\text{S} = +10.0\text{‰}$ for

barite (Jurković & Šiftar, 1995). During this period the migrating solutions segregated from rock complexes different ore-forming components giving rise to the enrichment of ore parageneses. In this way the Čemernica deposit obtained an uncommon, peculiar mineral assemblage.

The last, Pyrenean orogenic phase was responsible for high CO₂, CH₄ and N₂ contents, generated by younger Alpine metamorphic processes (Pohl, 1992). Mid-Bosnian post-Variscan fluids, with homogenous chemical composition over large distances and their tectonically controlled migration fluids, can be correlated with the similar post-Variscan fluid systems in Germany (Behr & Gerler, 1987; Behret et al., 1987; Klemm, 1994) and in the Bohemian Massif (Šmejkal et al., 1988).

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