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BARITE, HEMATITE AND CINNABAR ORE DEPOSITS IN THE DUSINA AREA, MID-BOSNIAN SCHIST MOUNTAINS

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Key-words. Dusina area (Bosnia), Palaeozoic, Hematite, barite, cinnabar ore deposits, Paragenetic and geochemical characteristics, Post-Variscan metallogeny.

In the Dusina area, which is built up of Lower Palaeozoic metasediments, Devonian carbonate complex and Upper Palaeozoic metarhyolites unconformably overlain by Upper Permian sediments, numerous ore occurrences have been investigated: (a) "stratabound" metamorphic hematite deposits in the pre-Devonian metasediments; (b) epigenetic veins and pipes of barite (\pm calcite) with accessory Hg-tetrahedrite and low-manganese hematite vein occurrences \pm cinnabar in Devonian limestones and dolomites; (c) "Alpine-type" veins with uraninite or Cu-minerals; (d) alluvial and glacial resistates.

On the basis of SrSO_4 content in barites, isotopic composition of sulphide and sulphate sulphur, oxygen and carbon, as well as on the basis of fluid inclusion data author attributes barite deposits, low-manganese hematite deposits and Alpine-type veins to the post-Variscan metallogeny.

Ključne riječi: Područje Dusina (Bosna), Paleozoik, Ležišta hematita, barita, cinabarita, Paragenetske, geokemijske karakteristike, Post-varisicijska metalogenija.

U području Dusine, koje je izgrađeno od donjopaleozojskih metasedimenata, devonskog karbonatnog kompleksa i gornjopaleozojskih metariolita diskordantno prekrivenih gornjopermskim sedimentima, istražene su brojne rudne pojave: (a) "stratabound" metamorfna hematitna ležišta, u preddevonskim metasedimentima; (b) epigenetske žice i trupci barita (\pm kalcit) s akcesornim Hg-tetraedritom te niskomanganske hematitne žične pojave \pm cinabarit u devonskim vapnencima i dolomitima; (c) "alpske žice" s uraninitom ili Cu mineralima; (d) aluvijalni i glacijalni rezistati.

Na osnovi distribucije sadržaja SrSO_4 u baritima, vrijednosti izotopnih analiza sulfidnog i sulfatnog sumpora, kisika i ugljika te rezultata studije fluidnih inkluzija autor smatra da su baritna i nisko-manganska hematitna ležišta te "alpske žice" rudne pojave post-varisicijske metalogeneze.

Introduction

The biggest and the most promising barite deposits found in the Mid-Bosnian Schist (Ore) Mountains are located within the zone, about 22 km long and 2 to 4 km wide, which extends in the east from Toplica on the River Lepenica to Zečeva Glava and Smiljeva Kosa in the west. This zone runs east-northeast-west-southwest in its western part and east-west in its eastern part.

Tectonically, this zone represents a syncline with Devonian carbonate rocks in its core and Silurian (?) schist in its flanks; the axis dips toward the southeast (Sofilj et al., 1980).

From about 250 registered barite occurrences and deposits the greatest number is related to Devonian dolomites, whereas the barite found in another rocks is of a less economic significance. Morphologic and paragenetic characteristics of the mineralization from the western half of this area which is the subject of this study, are very similar or identical to ones found in the eastern half of the mentioned Palaeozoic syncline which were described in detail in earlier papers (Jurković, 1986, 1987, 1988a, 1988b).

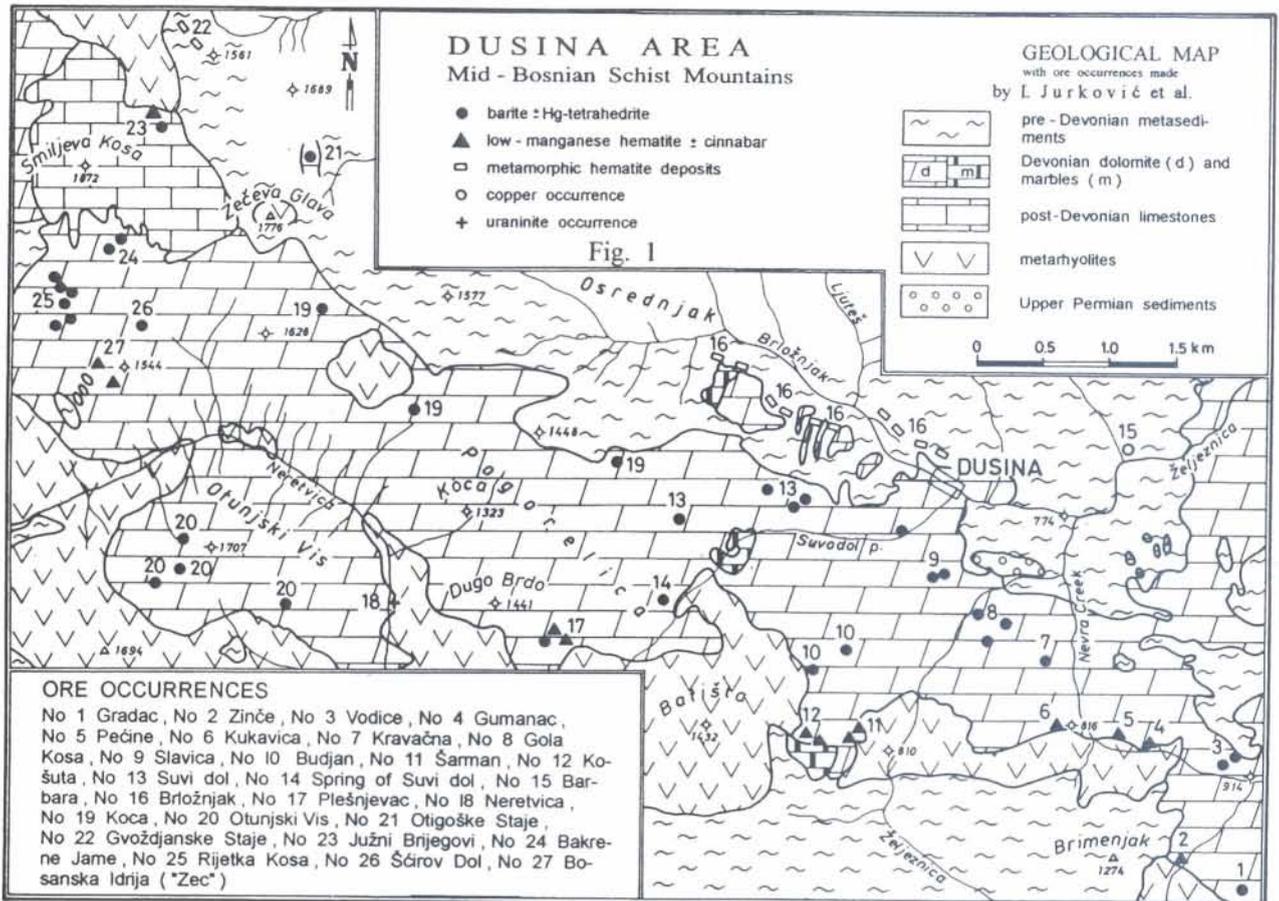
The area under research covers the surface of about 50 km² (12,5 x 4 km) and stretches from Smiljeva Kosa (+1872 m), Zečeva Glava (+1766m), Otunjski Vis (+1707 m), Dugo Brdo (+1441 m), Batišta (+1432 m), Brimenjak (+1766 m) to the river basins of upper course of the Neretva River (Dugi

Potok) and further in the area of Brložnjak Creek and its tributaries, upper course of the Željeznica River and Nevra Creek. This area comprises the west- southwestern part of the Vitreuška-Kreševo syncline (fig.1, geological map made by I. Jurković in collaboration with A. Ferenčić, S. Gregor, M. Jakovljević, A. Kučar and B. Tribuson, 1951).

Basic geological data

The oldest rocks are sericite-chlorite-quartz schists with intercalations of quartzites (the Kruščica and Visočica Mountains) which grade into metasandstones. This series is overlain by zoogene reef massive, rarely bedded limestones, secondary dolomites, locally with marbles. Lower parts of the carbonate sequence belong to the early Devonian (Emsian), whereas upper parts belong to the Middle Devonian, mostly to the Eifelian and to a lesser extent to the Givetian (Živanović, 1979). Upper Devonian formations, which belong to the Frasnian, contain Conodont *Ancyrodella?* ooids (Živanović, 1972), registered only at the Dusina village.

The Devonian carbonate complex is about 400 m thick. Dolomites from the Mts. Vitreuška, Smiljeva Kosa and Otunjski Vis are grayish and creamy, massive and only locally bedded rocks which are fissured and pervaded by veinlets, nests and networks of barite with some calcite. Rare are tabular barite barite veins or irregular bodies. The dolomites



contain only poorly preserved relics of Corals and spicules of Crinoids. In the studied area Lower Carboniferous sedimentary rocks were not registered.

Concerning the magmatic activity Trubelja (1978) and Sofilj et al. (1980) presented the opinion that metarhyolites intruded as intrusives and extrusives rocks during the Carboniferous and early Permian. They considered that quartz keratophyres might be partly of Triassic age. Živanović (1979) and Jovanović et al. (1977) presented the opinion on two-stage character of the magmatism: 1) the older stage gave porphyrite sills found in Silurian muscovite-chlorite schists (¹Pz) and quartz-sericite schists (³Pz) and 2) the younger one which took place in the Carboniferous-Permian and gave quartz porphyries penetrating Silurian and Devonian rocks and thus caused contact metamorphic changes on carbonate rocks. They considered that quartz keratophyres are partly Carboniferous-Permian and partly Triassic in age. Based on the findings of schistose metarhyolites and barite pebbles in Upper Permian breccias and conglomerates, Jeremić (1963) presented the opinion that metarhyolites are of early Permian age.

Older Palaeozoic formations are unconformably overlain by Upper Permian formations which lie directly under Scythian sedimentary rocks. Reddish breccias, conglomeratic breccias, locally with

gypsum-anhydrite formations belong to the Upper Permian. Lower parts are mostly built up of coarse-grained clastics, whereas the upper parts are more fine-grained indicating the deepening of the sedimentary basin.

Ore occurrences

On the fig.1 are presented the locations of all ore occurrences of the studied area. **1. Monomineralic barite occurrences with very little Hg-tetrahedrite**, the Kreševo-type represent the most common and, economically, the most significant type. This type occurs almost exclusively in Devonian dolomites.

2. Barite-calcite or rather calcite-barite veins and pipes in Devonian dolomites in which are predominant either barite or calcite, the Smiljeva Kosa-type.

3. Hydrothermal low-manganese hematite deposits of the Šarman- Košuta-type. They occur in Devonian dolomites close to or along contact with metarhyolites or schists in form of discontinuous short irregular veins or smaller bodies. Hematite is associated with cinnabar, more commonly in the roof.

4. Stratabound metamorphic hematite deposits of the Dusina- Brložnjak type. These deposits are related to a certain stratigraphic horizon within Silurian-Devonian metamorphic rocks. The series of smaller or bigger lensoid bodies are conformably

inserted in host-rocks. The quality of ore is weak with the low economic value.

5. **Siderite-chalcopyrite** occurrence of the Barbara-Vrtla is only of a mineralogical interest.

6. **Metamorphogenic small occurrence of uraninite** with albite of the "alpine-vein" type, found in the upper course of Neretvica River.

7. **Resistates:** (a) barite resistates; (b) moraine (glacier) resistates both on the Smiljeva Kosa.

8. **Pyrophyllite schists** are found in the Mts. Krušćica and Pogorelica.

Description of ore occurrences

Gradac (No 1) On the northern slope of Gradac Hill (1337 m), occurrences of irregularly shaped **barite** bodies are found within Devonian dolomites. Barite is major mineral (>95%), whereas tetrahydroxide and its weathering products are rare.

Zinče (No 2). On the left bank of Zinče Creek, 1 km SSW of Deževica village, in Devonian limestones, close to contact with metarhyolites, old explorations works on **cinnabar** can be seen (Barić, 1942; Jurković, 1956).

Vodice (No 3) A **barite** vein, almost vertical, stretching N55°E is found in Devonian dolomites immediately west of Deževica village, (Jurković, 1989). The barite is a major mineral (more than 95 wt.% BaSO₄). Mercurian tetrahydroxide is rare and almost completely weathered.

Gumanac (No 4) (Gunjani). The **hematite-cinnabar** occurrence is found on the left, northern bank of Nevra Creek. Walter (1887) and Kater (1907) describe exploration works carried out in 1878. in dolomites close to contact with metarhyolites. In dolomite there is 30 to 80 cm wide joint, stretching WNW-ESE with the dip 75-80° at NNE. It is filled partly with breccia-like mass of fragments of country rocks and partly with fault gouge in which cinnabar strings and nests are found. In karst cavities of dolomites, partly filled with sand and clay, flaky and fine-crystalline hematite and impregnated cinnabar are found. About 10 m upstream, in limonitized dolomite about 10-20 cm thick hematite vein, stretching E-W with impregnation of cinnabar and "brownspat" was explored by adit. Jurković (1956) writes that in dolomites along contacts with quartz porphyry there are 1-10 cm wide joints, filled with fragments of the schistose porphyry impregnated by cinnabar and hematite (with 46-52 wt% Fe). In surrounding dolomites there are **barite** veins. Ramović (1979) presented the result of analyses as follows: 0.65 wt% Hg (25 cm); 0.53 wt% Hg (72 cm); 0.14 wt% Hg (30 cm); 0.95 wt% (88 cm). In brackets are lengths of sampled channels.

Pećine (No 5). About 250 m downstream from the Gumanac locality, in Nevra Creek, a **hematite** vein stretching N 60° W with **cinnabar** impregnation is

found. The vein was explored by adit and by several smaller trenches (Jurković, 1956). Mineralization is located along contact between metarhyolite and dolomite in which veinlets of **barite** with chalcedony occur.

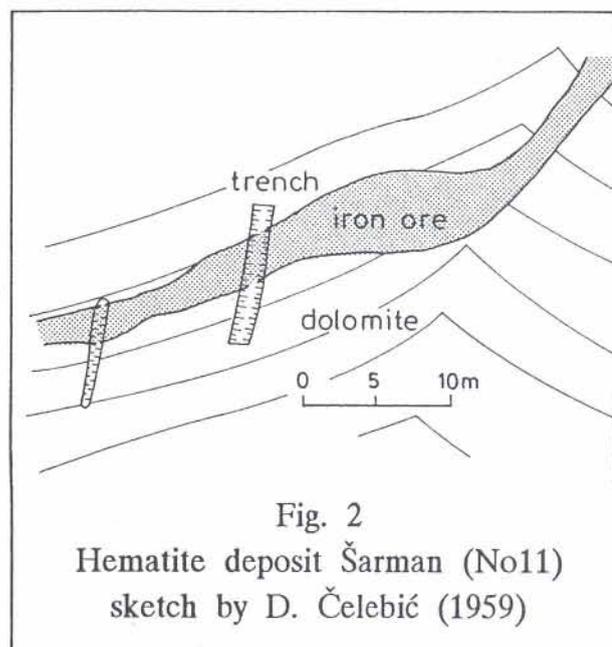
Kukavica (No 6). This locality is found west of the peak elevation +816 m in the bed of Nevra Creek. First data have been presented by Bonkowski (1918) who described mining works: an adit in which separate nests and **cinnabar** strips were detected. An average analysis gave: 0.06 wt% Cu and 1.05 wt% Hg. More reliable data come from Turina (1920) who described 0.7 m thick and 3m long zone of cinnabar vein which contained 0.8-1.6 wt% Hg, but locally up to 4-5 wt%. Mundorfer (1933) published four ore analyses which yielded 4.92; 4.97; 5.28 and 15.26 wt% Hg. On the left bank of Nevra Creek, Pašković (1940) registered on the length of 200 m a row of old exploration adits and shorter trenches in limestones with impregnations and 0.5-2 mm thick veinlets and some small nests of cinnabar. In the deepest adit **hematite** was also found. According to Jurković (1956) the mineralization occurs in limonitized and crushable Devonian dolomites along contact with metarhyolite. In its lower parts the mineralization is represented by hematite vein with complex network of cinnabar veinlets. In its upper parts cinnabar nests and impregnations are found. Ramović (1979) states that two sampled channels carried out in parts locally enriched by cinnabar impregnations yielded 2.31 and 3.76 wt% Hg.

Kravačna (No 7). This occurrence is located 1.5 km south-southeast of Dusina village. In Devonian limestones irregular **barite** bodies containing more than 90 wt% BaSO₄ are found. The paragenesis contains some calcite and tetrahydroxide and hypergene minerals (Jurković, 1956).

Gola Kosa (No 8). This occurrence is found on the western slopes of Arambašev Kamen on the right bank of Željeznica River. Jojić (1948) quoted the existence of a branched **barite** vein with a little tetrahydroxide. From this vein 150 t barite was mined in 1947. About 300-400 m further uphill, in the NE direction, barite vein was explored by three adits in three horizons. The vein was about 60 m long with the dip NW-SE; Jurković (1956) discovered several other smaller barite veins stretching NW-SE which contain some weathered mercurian tetrahydroxide.

Slavica (No 9). On the Slavica ridge, in the middle between the river Željeznica in the east and Suvodol Creek in the west, smaller barite bodies are found in Devonian dolomites (Jurković, 1956).

Budjan (No 10). In the Budjan forest, 1 km SW of the Slavica occurrence, and 1 km NE of the Batišta Peak (+1432 m), on the plateau composed of Devonian dolomites two **barite** occurrences are found (Jurković, 1956).



Šarman (No 11). Northwest of the peak elevation +816 m, on steep left bank of river Željeznica, 250 m above its bedded hematite occurrences are found (fig. 2) which were first described by Walter (1887) and later by Kutzer (1910). The Šarman hematite small nests and veins occur in limestones close to contact or directly along contact with metarhyolites. Ore is composed of coarse grained or more commonly of flaky, steel- grayish to dark-violet hematite with subordinate siderite and "Eisenglimmer" which grades into microcrystalline hematite dust permeating the host-rock. The ore is of high quality but due to the shallow dip, the reserves are restricted. Turina (1920) writes that the rich ore contains 40.87 wt% Fe and 0.17 wt% Hg, whereas poor ore contains 18.76 wt% Fe and 0.08 wt% Hg or 11.20 wt% Fe and 0.15 wt% Hg. Čelebić (1959) quoted chemical analyses performed in the Ilijaš iron-foundry: 48.01 wt% Fe, 0.57 wt% Mn, 12.96 wt% SiO₂, 0.07 wt% S, 0.094 wt% P and 55.35 wt% Fe, 0.45 wt% Mn, 11.23 wt% SiO₂, 0.275 wt% S and 0.26 wt% P, respectively. Jovanović (1979) describes two hematite bodies from Šarman. The bodies are 0.5 to 5 m thick and represented by the series of bedded lenses which consist of hematite, Mn-oxides, pyrite, quartz, sericite and limonite, with the reserves estimated to 20.000 t. Two ore varieties can be distinguished: a) dark-blueish higher-quality ore with 49.5 wt% Fe, 0.16 wt% Mn and 12.20 wt% SiO₂ and b) light-blueish lower- quality ore with 27.3 wt% Fe, 0.15 wt% Mn and 25.7 wt% SiO₂.

Košuta (No 12) is located west of Šarman and 0.7 km east of Batišta (+1432 m). Hauser (1884) first mentioned cinnabar impregnation in yellow Košuta "marl". Walter (1887), Kutzer (1910, 1925) and Jurović (1956, 1957) described a hematite

occurrence which is found in Devonian dolomites, close to contact with metarhyolites and marbles, very similar to those of Šarman area.

Suvi Dol (No 13). Barite occurrences are found on right (northern) flanks of the lower course of Suvodol Creek. West of peak elevation +1065 m, are found two barite occurrences; the first one strikes N 25°W and the second one strikes N10°W. The ore contains more than 95 wt% BaSO₄ with some tetrahedrite and rare quartz and calcite (Jurović, 1956). One kilometre west of it, one more barite occurrence was registered (Ramović, 1979).

Spring of Suvodol Creek (No 14). About 0.5 km downwards of the Suvodol Creek spring a small barite occurrence in Devonian limestones was found (Jurović, 1956).

Barbara (No 15) occurrence is located about 1.5 km east of Dusina before hamlet Vrtla on the left bank of river Željeznica. A short information gave Turina (1920); the ore contains 2.16 wt% Cu and 35.90 wt% SiO₂. Jurović (1956) described the Vrtla occurrence as short veinlets of siderite with chalcopyrite found in Palaeozoic phyllites. It was explored by trenches and by adit. Detected bornite exsolutions along (111) plane in chalcopyrite indicate comparatively higher temperature of formation.

Brložnjak-Dusina (No 16). Great number of old works and slags found in all surrounding creeks indicate mining activity. Conrad (1870) and Walter (1887) gave first data on these works which are described in details and later on reviewed by Kutzer (1910, 1925). Series of discontinuous hematite lenses conformably inserted in the phyllites form certain stratigraphic horizon. On the left bank of Brložnjak Creek, close to village Dusina, the mineralized formations stretch NW-SE with deviations towards the NNW and WNW and with the dip 25°-35° towards the NE. Before the mouth of Ljuteš Creek into Brložnjak, the series moves on the right bank of Brložnjak and plunges very steeply towards the SW and S. The exploration and exploitation of the iron ore was carried out by inclines and shafts and in places with greater quantity of underground waters, by adits performed at the bottom of the creek valley. The mineralized zone is about 2 km long. There had been greater number of mining pits: on the northern flank Dobra Voda, Sipatljevica, and Ovrline, and on the southern one Osoje, Bukovac, Ljuteš and Jasike. It was mined on the slopes of both banks of Brložnjak Creek, about 40 to 60 m above the valley bottom. Only high-quality ore was mined. Some parts of the ore are compact, partly schistose, grading into oligist or are imbedded by it. Locally, hematite is grained or alternates with "Eisenglimmer". Ore cavities are often filled with earthy mass of chlorite, sericite and other silicates or in the ore calcite and quartz veinlets are scattered. The average sample, taken from at that time newly open Osoje pit, contained 44.33 wt% Fe,

1.10 wt% S, 0.08 wt% P, and 16.35 wt% SiO₂. Turina (1920) describes the Brložnjak deposit as 2.5 km long zone of hematite ore, 1.6 to 2.2 m thick, striking E-W with the steep dip, hosted by Dusina phyllites; the ore contains 52.64 wt% Fe and 0.12 wt% Hg. Jurković (1956) carried out microscopic analyses of iron ores from the Brložnjak area which contain flaky and fine-grained hematite, quartz, chlorite, calcite and several silicate minerals which could not be identified. He considered that the Brložnjak deposit was originally a sedimentary iron deposit which was regionally metamorphosed. The mineralization is located in tectonically disturbed crestal parts of the local anticline, the axis of which is parallel to the flow of Brložnjak Creek.

Plešnjevac (No 17). This occurrence is found 0.5 km SE of the Dugo Brdo (+1441 m). According to Walter (1887) the Plešnjevac cinnabar occurrence is located in dolomites. Katzner (1907, 1925) describes the occurrences of cinnabar veinlets on the surface of 30x100 m² found in bedded and cavernous ferruginous dolomites. Besides cinnabar, hematite, calcite and tetrahedrite traces are present; Hg-content varies from 1 to 2 wt%. The mineralization is shallow, only a few metre thick and disappears in fresh and firm dolomites. Ramović (1979) states that Hg-content varies from 0.4 to more than 1 wt%; he also writes about hematite occurrences on the

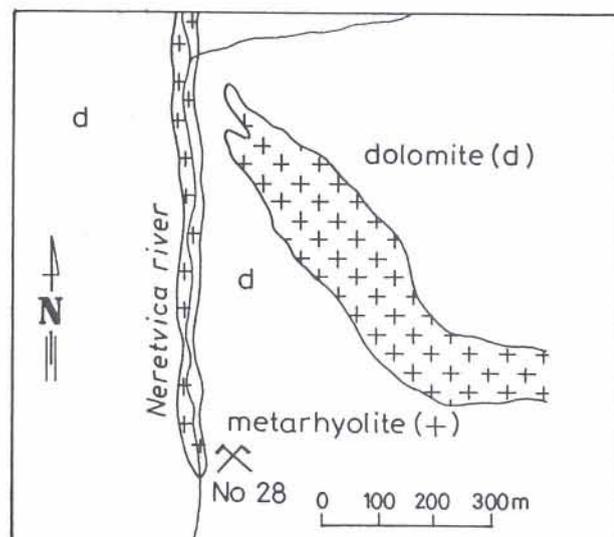


Fig. 3

Uraninite occurrence Neretvica (No 18)
made by M. Ristić (1964/65)

southern slopes of Dugo Brdo. Ramović (1954) described a lensoid barite vein found in the southeastern hollow of Dugo Brdo which was explored up to the depth of 3 m by 3 pits and its lensoid widening by shaft.

Neretvica (No 18). Ristić (1964/1965) investigated the radioactive geophysical anomaly on Mt. Pogorelica which occurs in the bed of the Neretvica left tributary in Devonian dolomites, close to contact with quartz porphyry. This is quartz-feldspar vein which contains a nest composed of tetrahedrite, pyrite, chalcocopyrite with uraninite inclusions (fig.3). Radušinović (1978) established the following paragenesis: uraninite, chalcocopyrite, pyrite, tetrahedrite, bornite, idaite, covellite, chalcocite, malachite, azurite, limonite, and albite, quartz, calcite and dolomite as gauge minerals. Ramović (1979) states the existence of numerous radioactive anomalies located in terrigenous psammite-conglomeratic facies, limestones, schists, red sandstones and conglomerates with graded bedding of the Mt. Pogorelica. Besides uranium, these rocks also contain vanadium, barium, zirconium, thorium (3-15-27 g/t), yttrium, scandium, lanthanum, calcium and tin.

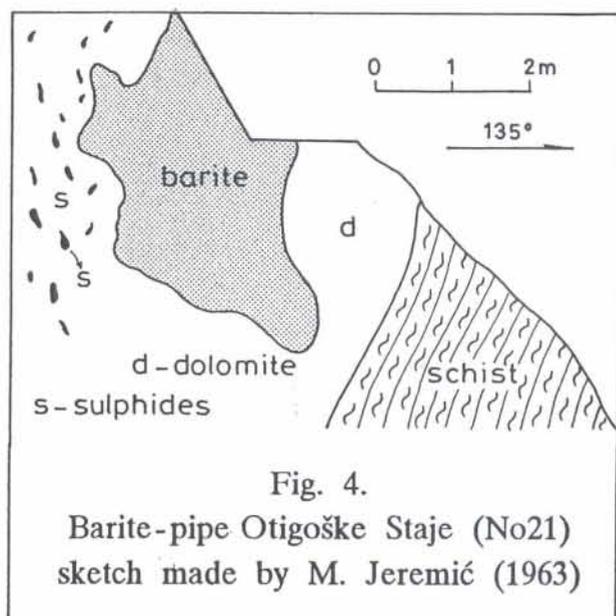
Koca (No 19). On the plateau (+1300 m) which stretches from the peak elevation +1448 m towards the southeast, several unexplored nests, irregular bodies and veins of barite with some tetrahedrite stretching in NNW-SSE direction were found. The tetrahedrite forms a complex network of veinlets and small nests; only rare impregnation of pyrite can be noticed (Ramović, 1956; Jurković, 1956). On the northern slopes of Mt. Koca (+1323 m), between altitude + 1448 m and the spring area of right tributaries of Brložnjak Creek, two occurrences of barite with some tetrahedrite are found (Ramović, 1954; Jurković, 1956).

Otunjski Vis (No 20). Barite occurrences located in Devonian limestones of Otunjski Vis (+1707 m), in the northern parts of Mt. Kruščica, contain some tetrahedrite. They are associated with smaller hematite occurrences (Jurković, 1956; Jeremić, 1963, and Ramović, 1979).

Otiško Staje (No 21) represents shepherd lodgings which occurs 1 km NE of Zečeva Glava (+1766 m). On the half way between them is the locality Pod Vranicom (Jurković, 1956; Ramović et al., 1956). Within a narrow belt made of Devonian dolomites confined with older phyllites in the east and with younger overlying limestones of undefined age in the west, crops out barite body 9 x 5 m in diameter (fig.4) It was explored up to the depth of 10 m; in its neighbourhood two barite veins, each of them 0.5 m thick, also occur.

Gvoždanske Staje (No 22). At the shepherd lodging of the same name, a little bit towards the NW of the peak elevation +1561 m, in phyllite, are found small hematite occurrences similar to those in Brložnjak (No.16), (Ramović et al., 1954 and Jurković, 1956).

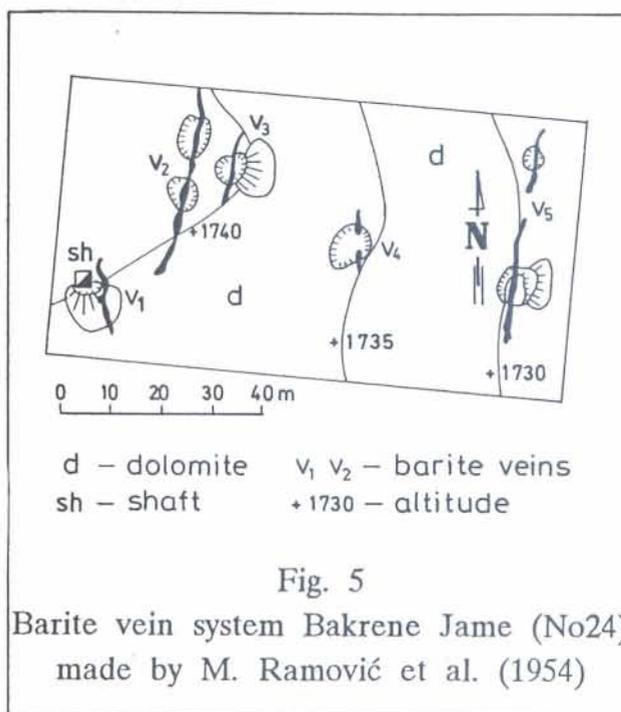
Južni Brijegovi (No 23). This locality is found about 0.6 km ENE of the Smiljeva Kosa (+1872 m),



on altitude of cca +1700 m. All area is composed of limestones which as a younger formation overlie Devonian dolomites which crop out in several places as tectonic windows. In some of the tectonic windows relics of old mining works from Middle Age and Austrian time on mercury and iron ores can be found. In the pits outcrops of **barite** veins 0.4 to 0.6 m thick, but with **hematite** bodies can be seen. **Cinnabar** was mined which originated either by weathering of quite subordinate amount of Hg-tetrahedrite in barite or which occurred as primary mineral close to hematite bodies (R a m o v i ć et al., 1954, 1956; J u r k o v i ć, 1956).

Bakrene Jame(No 24). This locality is found 0.5 km SSE of the peak elevation +1872 m. The mineralization is located in Devonian dolomites close to contact with overlying limestones on altitudes of +1730 to 1740 m. Five subparallel **barite** veins crop out which stretch mostly in the N-S direction (Fig.5). The ore bodies underthrust below overlying light-grayish, schistose and karstified limestones. Karstified dolomite contains scattered veins of calcite and iron hydroxyde and cavities in which onyx (chalcedony) is common. The average thickness of veins is about 1 m (from 0.6 to 1.2 m) and they were explored up to the depth of 8 m (R a m o v i ć et al., 1954). The thickness of veins varies and is shown in local thickening and narrowing. Major mineral is barite with enough calcite in the thickened parts. Hg- tetrahedrite is major ore mineral but in some places galena nests can be recognized. J u r k o v i ć (1956) called attention to the fact that ore occurrences are found only in dolomites and that they are not present in overlying limestones even in the cases when the occurrences underthrust below the limestones. Occurrences from Bakrene Jame are also briefly mentioned in papers published by R a m o v i ć et al. (1956), J e r e m i ć (1963) and R a m o v i ć (1976, 1979).

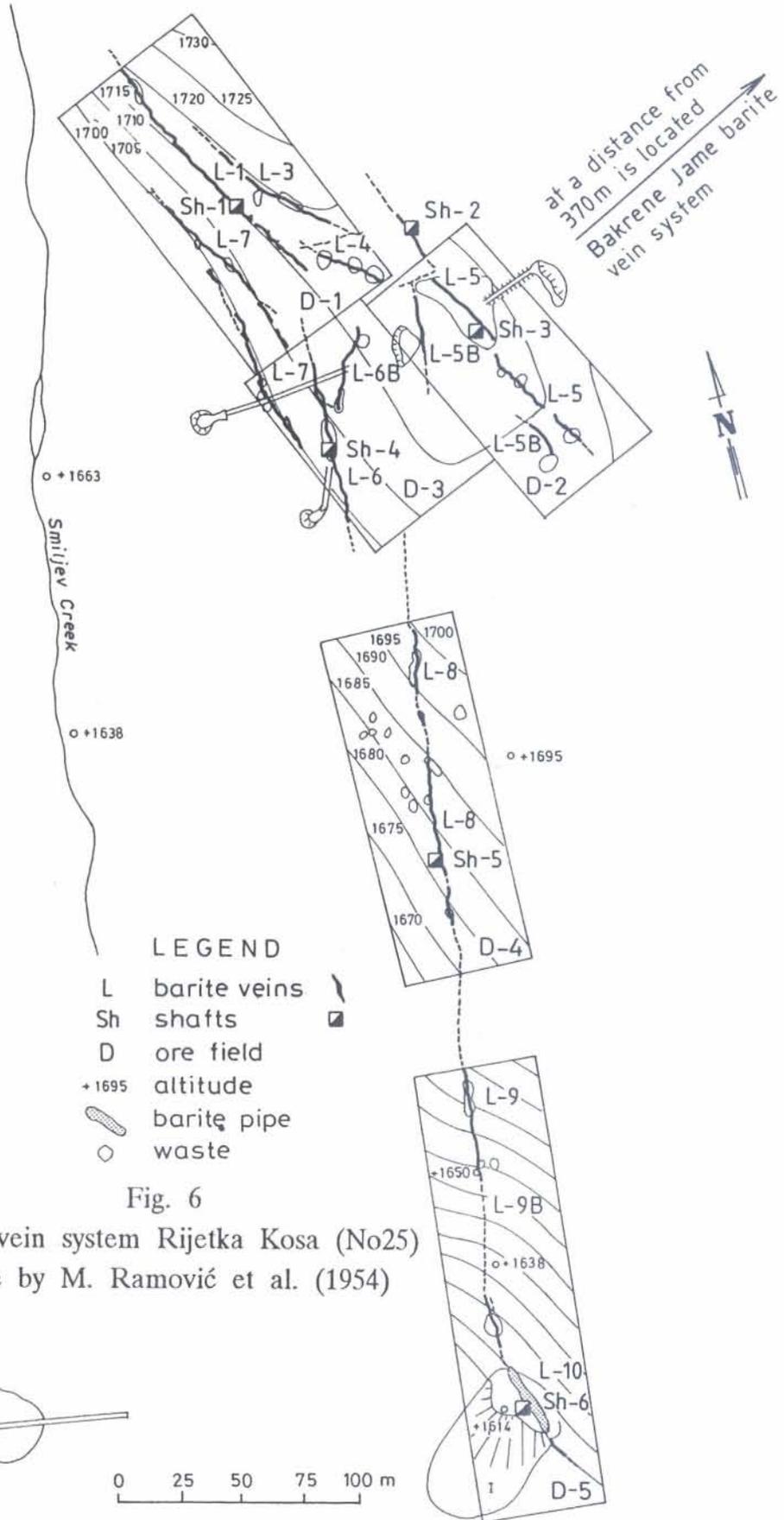
Rijetka Kosa(No 25). "The Kreševo barite mines" organized in 1953 first recent geologic-mining exploration works on **cinnabar**, **Hg- tetrahedrite** and **iron ores with cinnabar** in the area of Smiljeva Kosa, Mt. Zec, Otunjski Vis, Otigoške Staje and Gvoždanske Staje. They found remnants of very ramified Middle Age (Saxon), works of Austrian time as well as the works organized by "Bosnia" and Bosanska Idrija" companies: seven old shafts, some of them up to the depth of 50 m, with numerous underground workings, 30 wastes each of them with 10-40 t of barite and barite residual deposits. Two systems of barite veins in the area of Rijetka Kosa and Bakrene Jame were mined; the veins running north-south are in total 300 m long and 1.5 to 3 m thick with estimated reserves of about 150.000t of barite (fig.5,6).

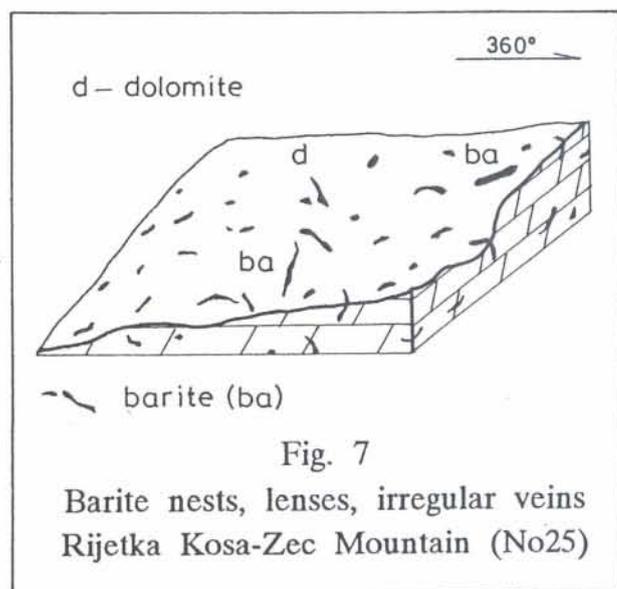


R a m o v i ć et al. (1954) prepared the geological map scaled 1:1000 of the area of Rijetka Kosa and Bakrene Jame (fig.6). They subdivided the mineralization in four groups:

(1) **Barite veins and lenses** with maximally a few percentage of Hg-tetrahedrite. The veins vary in thickness and depths. There are in some places swarms of minute barite and calcite veinlets up to several centimetres thick which intersect dolomites in different directions (fig.7).

(2) **Barite bodies (pipes)**, irregular in shape, which mainly originated on the intersection of fissures in dolomites. The biggest body (pipe) "Meded" occurs in the section D-6 22.5 x 16.5 in diameter with the explored depth of 38 m.(fig.6) In the area of Otigoške Staje the barite body had a dimension of 9x5x16 m, (fig.5) and the L-10 body was 35x5x15 m in size





(fig.6) These deposits contained also a little tetrahedrite.

(3) **Barite-calcite veins and lensoid bodies** in which the calcite nearly equals the barite in quantity.

(4) **Barite-calcite pipes (bodies)**. On outcrops the calcite predominates over the barite. In deeper parts, in the calcite body are scattered irregular barite veins and lenses several decimetre thick. Middle of the body contain more barite than the marginal ones.

In the next paper R a m o v i ć et al. (1956) estimated barite reserves for the localities Rijetka Kosa, Bakrene Jame, Otigoške Staje, Pridvorci and Južni Brijegovi which amounts 138.940 t. R a m o v i ć (1976, 1979) and J e r e m i ć (1960, 1963) quoted mainly data published in earlier papers.

J u r k o v i ć (1956) gave first microscopic study of barite ore. Major mineral is barite (>95wt% BaSO₄), whereas rhombohedral calcite and fine-grained quartz are subordinate. Ankerite (siderite) occurs very rarely. Major opaque mineral is Hg- tetrahedrite which makes veinlets, small nests and fine-grained aggregates in barite. Fine-grained pyrite I is impregnated in tetrahedrite and quartz; galena occurs rarely in form of smaller or bigger agglomerations. Malachite, azurite, goethite and lepidocrocite originated by weathering of sulphides and sulphosalts in the oxydization zone and smaller quantities of chalcocite and covellite in the cementation zone.

Šćirov Dol (No 26). On altitude +1644 m on the southern slopes of Smiljeva Kosa, about 1.5 km south of the peak +1872 m (Smiljeva Kosa) two **barite** veins 0.5 to 1 m thick are found in Devonian dolomites. In outcrops they are followed on the distance of 25 m. Old shaft cut the veins at the depth of 11 m. Mineral paragenesis is same as in barite occurrence at Rijetka Kosa (R a m o v i ć et al., 1954;

R a m o v i ć et al., 1956). The reserves of 2200 t of barite were calculated.

Bosanska Idrija ("Zec") (No 27) In the area of Mt. Zec mercurian silver-bearing tetrahedrite from the barite (Nos. 25 and 26) and hematite ±cinnabar bodies were explored during the Middle Age. M i k o l j i (1969) presented data on the mining activity during the Illyrian and Roman time.

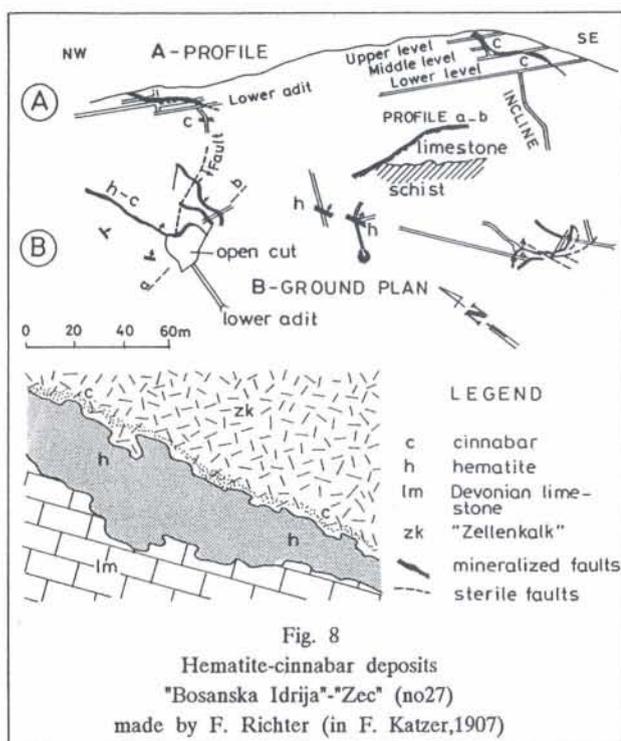
After the occupation of Bosnia and Hercegovina in 1878, Austrian Government began in 1879. the exploration of cinnabar in the area of the Mts. Pogorelica and Inač that was carried out by geologist F. Herbich and 22 miners from the Idrija mercury mine. H e r b i c h (1880) describes results of the exploration carried out in 1879. up to February 1880. During the period February-March in 1880 the exploration was organized by V o g t (1880) who found tetrahedrite occurrences in 67 localities. Starting with May 1880. the exploration was organized by B. Walter, in 1880 through the Austrian Government, from 1881. through the company "Bosnia" and from 1885/86. through the company "Bosanska Idrija" which focused its exploration in the area of Mt. Zec. The Austrian Government took over these works and finished the mercury ore production during the period 1889-1892. W a l t e r (1887), F o u l l o n (1899), R ü c k e r (1896) described results of the exploration in the area of the Mts. Zec, Pogorelica and Inač; the most valuable occurrences are in Mt. Zec.

K a t z e r's (1907, 1910, 1925) descriptions are based mostly on the data of W a l t e r (1887) and oral communications and drawings of F. Richter who organized the exploration.

The most extensive exploration was organized on the location "Zec" around the peak elevation +1644 m on the southeastern flanks of Smiljeva Kosa (+1872 m). **Figure 8** drawn by F. Richter, illustrates that two mining pits existed on the distance of 150 m along the NW-SE strike. Two **hematite** bodies located along irregularly dipping and striking fissures, on the boundary between a firm and massive limestone (dolomite) in the foot and cavernous, weathered "Zellenkalk-type" limestones in the roof, were explored. In the eastern pit this contact was very steep and in the western one it dips under the small angle. The thickness of hematite varied from 0.4 to more than 1 m and in the tickened parts even more than 1.5 m. Along the strike, the eastern body was explored for 30 m and the western one for 50 m after which the fissures closed. **Cinnabar** ore, found in the direct roof of hematite bodies in the lowest parts of "Zellenkalk", extended along the narrowed fissures even after the wedging of hematite (**fig. 8a**). The cinnabar from the overlying limestones occurred in form of more or less enriched impregnations, small nests or networks of veinlets. Locally, in the cinnabar zone, nests with 25 - 30 wt% Hg were registered. In

the newly open pits and underground works, opened in 1886, the analysis of samples taken in shafts and inclines gave: 0.02, 1.70, 6.70, 10.30 and 15.8 wt % Hg, and in overlying limestones: 0.55 wt% Hg and taken in waste: 5.50 wt% Hg.

The transversal fissures in both pits, presumed as supplying channels, were investigated by inclines. However, except one modest enrichment in the western pit the obtained results were negative. The exploration of two hematite outcrops located between the two pits as well as numerous hematite



outcrops stretching in the NW direction towards Smiljeva Kosa were also negative. Thus was proved that the two hematite bodies are the largest in the whole area of Mt. Zec and the further exploration was abandoned. The reserves of the two hematite bodies were up to 10.000 t and cinnabar was mined and distilled to mercury. It was produced in 1890/91 103.5 t of mercury ore with 5.97 wt% Hg which gave 6.1 t of mercury.

These hematite deposits were described also by M a k u c (1941), R a m o v i ć et al. (1954 and 1956) and R a m o v i ć (1976, 1979). Ore microscopic work was carried out by J u r k o v i ć (1956) who found out that the hematite is fine-grained in texture. Minute hematite crystals, several microns in size, form complex networks and, locally, also 0.3 to 0.5 mm long flakes, interstices of which are filled with transparent or cloudy neocalcite or with hematite dust (microlites).

Pyrophyllites (No 28). R a m o v i ć (1976) states that in Palaeozoic terrains of the spring area of the Neretvica River and in the neighbourhood of village

Dusina occur **pyrophyllite schists** which can be used as a raw material in the abrasive industry. Locally, these rocks grade into metapsammities and quartz-sericite schists and shales.

Barite resistates (No 29). In the area of Smiljeva Kosa **barite residual deposits** originated. The movement of barite masses along steep slopes gave rise to a certain roundness of barite blocks and fragments and size sorting (R a m o v i ć, 1976).

Glacial resistates (No 30). K a t z e r (1907) considered that materials which fill up caves, dolinen and hollows in limestones and dolomites of the area of Smiljeva Kosa and Zečeva Glava represent **moraine material** which was transported in the karstified parts of the terrane. The material consists of fragments of schists, metarhyolites, carbonate rocks embedded in sand and white clay which are frequently cemented by **hematite ± cinnabar**.

Unknown locations

I Occurrences of hematite iron ores: Gvoždanuša, Brezje and Koca (K a t z e r, 1910)

II Occurrences of limonite ores: Raskršće (1 km north of village Dusina) was explored by trenches; the ore contained: 35-41 wt% Fe, up to 1 wt% Mn, 1.8-11.0 wt% SiO₂ and 0.18 wt% P (J o v a n o v i ć, 1979).

III Barite occurrences: Šaške Jame (Dusina) (R a m o v i ć & M i l a d i n o v i ć, 1953; R a m o v i ć, 1954), Jarčište and barite stock "Dusina" (R a m o v i ć, 1954); Oborište, Lazine, Marina Stijena, Boina, Gornja Pogorelica (J e r e m i ć, 1963); Neretvica, Kotlov Dol (R a m o v i ć, 1979).

IV Galena occurrences: found in barites of the area of the Nevra Creek and Jarčište (B a r i ć, 1942).

Laboratory examination

I Determination of SrSO₄ content in barites. (table 1)

Eight analyses were performed by Dr. Dubravko Šiftar through our project financed by the Ministry for Science and Technology of the Republic Croatia. Samples were taken by author during his prospection in 1951: B-141, B-79, B-71 and B-152 from barite deposits Rijetka Kosa, sample B-74 from Šćirov Dol, sample B-72 from Mount Zec and samples B-110 and B-94 from Mount Pogorelica.

Table 1

Contents of SrSO₄ in barites (in wt%)

	B-141	B-79	B-71	B-152	B-74	B-72	B-110	B-94
SrSO ₄	6.5	5.1	6.2	5.7	4.9	3.1	2.3	0.5

II Isotopic composition of sulphate sulphur in barite

The examination was carried out in the geochemical laboratory of the Institute "Jože Štefan" in Ljubljana through the above mentioned project. Three samples were analysed on which previously SrSO₄ was determined. Data are presented in table 2.

Sample B-72 is from Mount Zec; B-54 and B-110 are from Mount Pogorelica.

Table 2

Isotopic composition of sulphate sulphur in barites

Barite sample	B-72	B-110	B-94
$\delta^{34}\text{S}\text{‰}$	+12.53	+10.94	+9.56

III Isotopic composition of sulphide sulphur in Hg-tetrahedrite

Sulphide sulphur isotopic composition measured on one Hg-tetrahedrite sample from Smiljeva Kosa (B-141) gave: $\delta^{34}\text{S} = -13.74\text{‰}$

IV Oxygen and carbon isotopic composition of calcite from barite deposits

Measurements on calcite sample B-115 from Mt. Pogorelica gave the values as follow: $\delta^{18}\text{O}_{\text{PDB}} = -6.66\text{‰}$ and $\delta^{18}\text{O}_{\text{SMOW}} = +23.50\text{‰}$; $\delta^{13}\text{C}_{\text{PDB}} = +1.20\text{‰}$

Geochemical characteristics of studied ore deposits

1. Barite and 2. Barite-calcite deposits

1. They represent the most common and economically the most significant mineralizations. Monomineralic and bimineralic occurrences can be distinguished. More common are the monomineralic barite types which contain more than 95 wt% barite, with very small admixtures of **calcite**, **quartz**, and **ferrodolomite**. **Mercury tetrahedrite** characterizes a sulphide phase of the mineralization. It is rarely present in quantities of a few percent, most commonly in quantities less than 1-2 wt% or is hardly noticeable. **Chalcopyrite** is scarce and **enargite** is very rare both of them associated with tetrahedrite. Mostly along wall rocks, fine-grained **pyrite** accompanied by quartz can be noticed. In the area of Bakrene Jame, Rijetka Kosa and Nevra Valley, **galena** is found in form of small nests. In bimineralic paragenetic types of deposits, proportions of barite and coarse-grained rhombohedral calcite show very great variations or are equal or with predominance one of them. The bimineralic parageneses are found in the Smiljeva Kosa Mt. ore occurrences where they are particularly common in larger barite pipes. Other part of the paragenesis is similar or identical to the monomineralic barite-type. Weathering of sulphide minerals gave hypergene minerals originated mostly under the positive redox-state: **goethite**, **lepidocrocite**, **azurite**, **malachite**, **cinnabar**, **melanomane**, and **electrum** and to a lesser extent minerals originated under the negative redox-state: **covellite**, **chalcocite** etc. In the area of Smiljeva Kosa **onyx** occurrences are common with rare **aragonite**.

Forms of ore occurrences. Simple tabular veins originated along crack or fissure zones or along fault planes in Devonian dolomites are the most common forms of barite deposits. They originated by the

simple filling of the open fissures and, rarely, they involve replacement along carbonate permeable fractures. Complex veins originated when a multiple filling took place along the same reopened structure. Pinch- and swell-types formed by filling of various hollows found along reversed or normal faults, i.e. the irregular fault surface causing thinnings or thickenings. Some parts of longer discontinuous tabular veins are characterized by branching. Much less common are ore pipes and brecciated pipes (Smiljeva Kosa) originated at the intersection of faults, joints, and fissures. The biggest body with dimensions 22m x 16.5m x 38m gave 55.000 t crude ore.

SrSO₄ contents of barites. Jurković (1986, 1995), Šiftar (1988; 1990) and Jurković et al. (1994) published data on SrSO₄ content of barites from 13 barite areas studied in the Mid-Bosnian Schist Mountains. In this paper are presented SrSO₄ contents from the last fourteenth Dusina-Mt. Zec area.

The average SrSO₄ content in barites of Mid-Bosnian Schists Mountains (on the basis of 108 analyses) gave 4.22 wt% varying from 2.47 wt% to 6.21 wt%.

Although at least three generations of barites to date were quite positively established, the analyzed barite samples have not been sampled on these criteria due to comparatively their small numbers. By all means, this is a deficiency because the determination of SrSO₄ contents on substantially greater number of barite samples, taken on habitus criteria, would made possible the systematization of mineralization processes and the establishment of mutual relations of barite deposits found in separate barite-bearing areas of Mid-Bosnian Schist Mts. Classical are papers of Hofmann and Schürerberg (1979) for barites from Germany. Based on 1851 carefully selected analyses on SrSO₄ content of the barite samples, these authors established the existence of six successive barite generation and their succession of formation in each separate barite-bearing area in Germany. The variation range is 1.4 to 5.6 wt% SrSO₄, averaging 3.7 wt% SrSO₄. It is obvious that the span from 2.5 to 6.2 wt% SrSO₄ obtained in Mid-Bosnian Schist Mts. is very close to this range in the German barites. Such span of SrSO₄ values indicate obviously on the existence of some barite generations and their different participation in separate barite areas.

It is also interesting to correlate SrSO₄ contents in barites from the other areas in which Hg-tetrahedrite (schwarzite) is either only (Brixlegg-Austria) or major (Rudnany-Slovakia) ore mineral. Barites from the Rudnany siderite mines contain 1.24 wt% SrSO₄ (n=99 analyses) - Čambel-Jarkovský et al. (1985), whereas the Brixlegg barite deposits found in Devonian carbonate rocks contain 7.50 wt% SrSO₄

(Weber, 1986) and 2.14 wt% SrSO₄ (Frimmel and Papesch, 1990), respectively.

$\delta^{34}\text{S}$ in barites. Three barite samples from the Mt. Pogorelica and Zec barite deposits gave $\delta^{34}\text{S}$ range from +9.56 to +12.53 ‰ averaging +11.01 ‰. This average value is close to the average $\delta^{34}\text{S}$ value +11.53 ‰ obtained of 74 barite samples taken in all 14 barite-bearing areas of Mid-Bosnian Schist Mts.; the values range from +6.28 to +17.19 ‰ (Jurković, 1986; Šiftar, 1988, 1990; Jurković et al., 1994; Palinkaš & Jurković, 1993).

Barites from the Rudnany deposits in Slovakia show very similar variations in $\delta^{34}\text{S}$ values from +9.8 to 18.2 ‰ averaging +15.10 ‰ (Cambel, Jarkovský et al., 1985). On the contrary, barites from Brixlegg in Austria have $\delta^{34}\text{S} = +23.50$ ‰ (n=2) (Schulz, 1972; Schroll and Pak, 1980) identical to the isotopic value of the Devonian sea water sulphate.

$\delta^{34}\text{S}$ in tetrahedrite from sample B-141, taken from the Smiljeva Kosa barite deposit amounting $\delta^{34}\text{S} = -13.74$ ‰ fits for itself quite well in the range of $\delta^{34}\text{S}$ from -5.50 to -15.40 ‰. This range characterizes all 18 analyzed tetrahedrite samples from 14 barite-bearing areas of Mid-Bosnian Schist Mountains (Jurković, 1986, 1995; Šiftar, 1988, 1990; Jurković et al., 1994). The analysed tetrahedrite samples were taken in barite deposits hosted in Silurian/Devonian schists, metasandstones and shales, Upper Palaeozoic metarhyolites, Upper Permian clastics and amphibolites. Three pyrite samples from barite deposits in the area Točak, Raštelica and Ljetovik yielded $\delta^{34}\text{S}$ values ranging from -0.70 to -9.86 ‰.

These distinctly negative values of $\delta^{34}\text{S}$ in sulphides of barite deposits of Mid-Bosnian Schist Mts. can be explained by a partial isotopic equilibration of two sulphur-bearing sources: H₂S derived from deep seated ascending fluids heated over 250⁰ to 350⁰C and descending SO₄₋₂ formational waters derived from Upper Permian evaporites (Jurković and Šiftar, 1995). The same assumption has been published by Žak et al. (1991) for negative values of $\delta^{34}\text{S}$ for Hg-tetrahedrites (range -0.90 to -9.60 ‰ averaging -4.93 ‰) and chalcopyrites (≤ 0.0 ‰ to -8.2 ‰) obtained for the Rudnany siderite-barite vein system. Cambel, Jarkovský et al. (1985) presumed that these negative $\delta^{34}\text{S}$ values were caused by the influence of mobilized isotopically light sulphur from a hypothetical, still unknown bacteriogenic sulphide accumulations from the adjacent rocks.

3. Low-manganese hematite deposits \pm cinnabar

Hematite occurrences represent a continuation of the same type found in the area of Deževica (Jurković, 1988a) and Duboki Vaganj (Kreševo) - Jurković (1988b).

The occurrences are found in Devonian carbonate complex very close to contact with metarhyolites or along the contact. Hematite ore fills decametre long joints which are irregular in strike (generally NW-SE) and have in rule the steep dip. The widths of the joints are on average of decimetre size, however, centimetre narrowings or several widenings of a few metre size are common. The biggest bodies (Šćirov Dol) gave several thousand tons of high-quality hematite ore that was significant only for the Middle Age mining activity.

Parageneses are very simple, almost monomineralic. Besides predominant **low-manganese hematite** (<1wt% Mn), subordinate **calcite**, **quartz (chalcedony)** and, rarely, **siderite** or **ankerite** occur. Some occurrences include a little **barite**.

In the direct roof of some occurrences, a narrow zone of **cinnabar** impregnations and smaller or bigger nest-like aggregates are found. Enriched parts of the zone were exploited in the Middle Age for the mercury production.

Structurally, two hematite types are most common: a) compact or loose, enormously fine-grained masses, partly mixed with calcite and/or chalcedony and b) specular hematite in form of basal plates and small flakes (small leaves, thinsheets, foils).

We are of the opinion that the low-manganese hematite deposits \pm cinnabar represent products of autonomous, independent hydrothermal phases in the succession of genesis of the Mid-Bosnian barite deposits. Quiring (1931) and El-Hinawi & Hofmann (1968) gave the same interpretation for the adequate hematite-types in Germany. This conclusion is supported by the facts as follows:

- 1) Hematite deposits can be traced for over 15 km long zone: Duboki Vagan-Opogor-Fratarske Lopate-Dusina-Mt.Zec. In this zone barite deposits are predominant; they contain a little Hg- tetrahedrite, whereas other sulphides are quite accessory constituents. The generation of hematite, practically in the absence of sulphides indicates high redox state during the metallogenic evolution of this area. The same opinion used Žak et al. (1991) for the hematite coprecipitation in barite deposits of the Bohemian Massif.
- 2) Hematite occurrences are related to separate fairly pronounced tectonic phase as indicated by the occurrence of ore breccias.
- 3) Hematite deposits are younger than the Mačkara-type siderite-barite-tetrahedrite deposits (Jurković et al., 1993) and the Duboki Vagan-type (Jurković, 1988b). The siderites of these deposits, which are high-manganese (2.5-2.6 wt% MnCO₃), were affected by ascendent "rejuvenation" and thus caused the partial transformation of siderite in so called "red spar" (Rotspat). Sample E-92/1 of rhombohedral "red-spar" crystals from the Mačkara Mine, which was analyzed by dr. D.

Šiftar, gave 7.14 wt% Fe₂O₃. Under the microscope, on polished thin sections of the same sample, hematitization in form of dense dissemination of minute hematite grains of microne size was noticed. This rejuvenation phase could be contemporaneous with the formation of hematite deposits. Such occurrences were noticed on the German barite and siderite - barite deposits described by Schneiderhöhn (1949), Sherp & Stadler (1973), and others.

Hofmann & Schürenberg (1979) and Hofmann (1979) published data of investigations obtained on numerous hematite occurrences from the series of barite-bearing areas in south and central Germany. The German hematite belong to three generations. Early Variscan hematite I, genetically related to the sulphide phase, is radioactive and characterized by the presence of tungsten (up to 0.3 wt%). The second generation is so called "Brekzienverheiler or breccia-healer" hematite II ("glimmerartige Hämatit"), the most widespread type in the German barite-bearing areas, appearing at the end of the fourth barite phase (healing often breccias), is characterized by high Ni content (up to 120 ppm) and less Bi, Cu and Mn. This hematite, which is the most representative type, is related to strong tectonic events. Hematite III, which occurs within the fifth barite phase, contains comparatively high germanium (up to 300 ppm), molybdenum (up to 250 ppm) as well as Sb, As and Mn. Baumann & Krs (1967), using paleomagnetic method, indicated Cretaceous-Tertiary age of the German hematites II and III.

In the paper on the German barite deposits, Hofmann (1979) presented the opinion that a very strong tectonic phase occurred between the third and fourth barite phases for which is also related the raise of fluids with Bi, Cu, Ni, Co and Hg. In Mid-Bosnian Schist Mountains the formation of the main barite phase ± tetrahedrite - Cu (Hg, Fe, Zn, Ag)₁₂-Sb(As, Bi)₄S₁₃ - tetrahedrites may be equivalent to this tectonic phase. Ni-bearing "breccia-healer" hematite II originated by the end of this phase. The low-manganese Mid-Bosnian hematite occurrences can be equivalent to "brecciahealer" hematite. Within the fifth barite phase are included formation of Ge-bearing hematite III and within products of the sixth phase, formation of carbonate mineralization with calcite and dolomite with significant Hg traces, last phase PbS and Ni-Co minerals occur again. This phase corresponds to the formation of rhombohedral calcite and galena nests in Mid-Bosnian Schist Mts.

The presented data indicate that the Mid-Bosnian barite and hematite deposits show significant conformities in the position of mercurian tetrahedrite and larger calcite masses of the mineralization succession with the German deposits.

4. Late Alpine mineralization

An uraninite occurrence from the upper courses of the Neretvica River, described by Ristić (1964/65) and Radušinović (1978), belongs to a later phase of the Alpine cycle (18 Ma). The Alpine-type veins are composed of quartz and albite with some calcite and dolomite and contain uraninite, chalcopyrite, pyrite, tetrahedrite, bornite and idaite and their weathering minerals: covellite, chalcocite, malachite, azurite, goethite and lepidocrocite. This occurrence is evidence that a multiple remobilization of hydrothermal fluids from Permian (late Variscan) to Neodic (late-Alpine) time took place in Mid-Bosnian Schist Mts. In the Zagrlski Creek nearby Busovača, a similar process took place and it gave alpine-type quartz hyalophane veins (Bermanec, 1992; Jurković et al., 1993).

5. Resistates

(a) Kater (1903, 1925) was first to present the idea on the glacial activity in the Mt. Vranica area. Sofilj et al. (1980) presumed that Mt. Vranica glaciers were generated during the Pleistocene (Wurm period). Jurković et al. (1994) described in detail some moraines investigated in 1951. and their mineral debris pushed ahead of the glacier front.

In the area of Mt. Zec and Smiljeva Kosa, a part of the karstified surface of dolomites and limestones are filled by moraine material which contains fragments of various rocks, clay and sand and, besides that, hematite and cinnabar.

(b) Due to very high altitude position, the karstification of carbonate rocks of the Mts Zec, Smiljeva Kosa and Pogorelica was of significant intensity. Barite deposits were also affected by erosion and barite resistates were generated (Ramović, 1976).

6. Metamorphic hematite deposits of the Brložnjak-type

These deposits are insufficiently known because the former Middle Age exploration and exploitation mining works, and one adit from the Austrian time are blocked and thus not available. The oldest published descriptions are very scanty and incredible. According to our opinion, these deposits, primarily of sedimentary origin, were subsequently metamorphosed. The deposits probably belong to an older, Lower Palaeozoic metallogenic epoch.

Discussion and conclusion

A. *Basic characteristics of Variscan and post-Variscan barite deposits of Central Europe* (Southern Poland, Central and Southern Germany, Bohemian Massif, Gemericum, Eastern Alps and Northern Italy) were obtained from numerous geochemical studies summarized by Behr et al. (1987); Behr & Gerler, (1987), Pohl & Belocky (1994); Baumann, 1994; Dill, 1994; Klém,

1994. According to these authors hydrothermal solutions in the Variscan and post-Variscan mineralization cycle are characterized by strongly different chemical composition.

The Variscan mineralization formed by Na-K-Cl-H₂O type solutions with variable degree of salinity (less than 10 wt% NaCl equ.). These solutions derived probably from post-granitic alteration fluids which were continuously modified during the Variscan cycle by altered heated meteoric waters under varying local P-T conditions, especially before the beginning of the post-Variscan cycle.

Post-Variscan solutions represent Na-Ca-Cl-H₂O fluid system, characterized by high salinity ranging from 10 wt% to 30 wt% NaCl equ., with Th=250⁰ to 300⁰C. This type of fluid system is very uniform over large areas.

The post-Variscan period started in the late Permian or in the Scythian and lasted intermittently up to the late Tertiary.

B. Basic characteristics of the Mid-Bosnian Schist Mts. barite occurrences

Barite occurrences can be divided into three main groups.

First group: Barite is an accessory (locally, even absent) mineral originated in the last phase of mineralization of the polymetallic sulphide vein deposits: quartz-sphalerite-stibnite-wolframite(Čemernica); quartz-siderite-albite-pyrrhotite-sphalerite, cassiterite-stannite-molybdenite (Vrtlasce, Donje Selo); quartz-siderite-gold-bearing pyrite (Bakovići) paragenetic types. These late Variscan deposits are believed to be related to penecontemporaneous rhyolite granite magmatism.

Second group: Barite is more or less important subordinate gangue mineral occurring in metasomatic ore bodies located in Upper Silurian-Lower Devonian carbonate rocks. Gold-bearing pyrite, chalcopryrite, and gold-silver bearing Sb-tetrahedrite (mercury only in traces) are the main sulphide minerals; siderite and barite are present in very variable mutual proportion as the main gangue minerals. Their most significant characteristics are positive $\delta^{34}\text{S}$ values of sulphide sulphur. The values for tetrahedrite are $\delta^{34}\text{S} = +3.28\text{‰}$ and $+3.73\text{‰}$. This type of deposit belongs probably to the beginning of post-Variscan mineralization, is still characterized by features of the same sulphur source as the previous first group.

Third group: Barite occurs in the deposits characterized by the mercurian Sb-Cu-tetrahedrite as the only or the major sulphide mineral. These tetrahedrites contain 0.3 to 16 wt% Hg, 0.08-0.21 wt% Ag, 20-50 g/t Au, 0.3-4.2 wt% Zn; 0.03-0.33 wt% Bi; 1.1-8.1 wt% Fe. The most characteristic feature of all investigated 18 tetrahedrite samples are distinctly negative values of $\delta^{34}\text{S}$ which vary from -5.50 to -15.40 ‰ in tetrahedrites and between -4.61 ‰ and

-9.86 ‰ in pyrite. Barite is characterized by high strontium content, varying from 2.47 wt% to 6.21 wt% SrSO₄ in each of fourteen barite areas. Next fundamental geochemical characteristics of these barites as well as of associated gangue minerals (quartz, calcite and fluorite) are data obtained by detailed fluid inclusion study (P a l i n k a š & J u r k o v i ć, 1993). This study revealed: Th= 200⁰ to 310⁰C; NaCl-CaCl₂(±MgCl₂)-H₂O fluid system; very high salinity (24-26 wt% NaCl equiv), high positive sulphate sulphide $\delta^{34}\text{S}$ values of barite. Such a fluid system is widespread very uniformly by over 3000 km² large area of Mid-Bosnian Schist Mts. in the triangle Jajce- Gornji Vakuf-Kreševo. The presented data fit the post-Variscan fluid systems in the barite and barite-fluorite deposits of the Central Europe (see paragraph A).

Third barite group can be divided in the two subgroups:

(a) The first subgroup is hosted by Silurian-Lower Carboniferous schists, shales and metasandstones. The main representative is Mačkara vein. Siderite ("red-spar" type) is the major gangue mineral; quartz and barite are main subordinate gangue minerals; Au-Ag-bearing mercurian tetrahedrite with proportions from 10 to 40 wt% in crude ore is nearly the only sulphide mineral, whereas pyrite and chalcopryrite are accessories. Second representative is the Cvrče-Borova Ravan vein in which barite is dominant gangue mineral with very subordinate siderite and quartz, whereas Hg- tetrahedrite is dominant sulphide mineral but present only in a few crude ore.

(b) To the second subgroup belong monomineralic barite veins and irregular bodies hosted by Devonian carbonate rocks. They contain over 95 wt% BaSO₄ (some of them are characterized by the presence of great quantities of rhombohedral calcite). Hg-tetrahedrite is main, very often hardly visible sulphide, present in amount less than 1 wt%, rarely, more.

C. Conclusion

Comparing the basic characteristics of the Central European barite deposits with those from the Mid-Bosnian Schist Mountains we can emphasize the following conclusions.

The first group of barite occurrences belongs obviously to the last Late Variscan phase of mineralization, the timing position of the second group is ambiguous, whereas the third group of barite deposits (mercurian-bearing-tetrahedrite deposits) is undoubtedly post-Variscan in age. Since the paragenesis of this third group consists of more barite generations (multistadial process) most of it probably originated between the late Permian and Middle Triassic, whereas some of reactivated phases lasted up to the late Tertiary (very long-lasting process). Comparatively high positive isotopic composition of

sulphate sulphur in barites and distinctly negative values of $\delta^{34}\text{S}$ of sulphide sulphur in mercurian tetrahedrites and pyrites over a large area of Mid-Bosnian Schist Mts., as well as very high salinity of the fluid system indicate the formation of post-Variscan deposits from a mixed fluid system. The participation of the Upper Permian saline formation waters in these solutions is obvious.

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REFERENCES

- Barić, Lj. (1942): Mineraloško-petrografska istraživanja bosanskog rudogorja.- *Vjesnik hr. geol. zavoda*, I, 39-45, Zagreb.
- Baumann, L. (1994): Ore parageneses of the Erzgebirge history, results and problems.- *Monogr. Series on Mineral Deposits 31, 25-46: Mineral Deposits of the Erzgebirge /Krušne hory (Germany/Czech Republic)*.- Edited by K. von Gehlen and D.D. Klemm, Gebrüder Borntraeger Berlin- Stuttgart.
- Baumann, L. & Krs, M. (1967): Paläomagnetische Altersbestimmungen an einigen Mineralparagenesen des Freiburger Lagerstättenbezirks.- *Geologie*, 16, 765-780, Berlin.
- Behr, H.-J. & Gerler, J. (1987): Inclusions of sedimentary brines in post-Variscan mineralizations in the Federal Republic of Germany - A study by neutron activation analysis.- In: E.E. Horn and H.J. Behr (Eds.), *Current Research on Fluid Inclusions*, ECRFI, Göttingen, April 10-13, 1985.- *Chem. Geology*, 61, 65-77, Amsterdam.
- Behr, H.-J., Horn, E. E., Fentzel-Beume, K. and Reutel, Chr. (1987): Fluid inclusion characteristics of the Variscan and post-Variscan mineralizing fluids in the Federal Republic of Germany.- *Chem. Geology*, 61, 273-285, Amsterdam.
- Bermanc, V. (1992): Kristalokemijske karakteristike minerala iz asocijacije koje sadrže barijeve silikate (in Croatian).- *Ph. D. Thesis*. University of Zagreb, Croatia.
- Bonkowski, F. (1918): Bericht über die Kupfererzorkommen um die Stadt Kreševo (Bosnien).- *Archiv Inst. Geol. istraž.*, Zagreb.
- Cambel, B. & Jarkovsky, J. et al. (1985): Rudnianske rudne pole-geochemicko-metalogeneticka charakteristika. (The Rudnany ore field-geochemical-metallogenetic characteristics).- *Slovenska akademia vied*, 363 pp. Bratislava.
- Conrad, A. (1870): Bosnien mit Bezug auf seine Mineralschätze.- *Mitteil. s. k. k. geograph. Gesell.* in Wien, 219.
- Čelebić, D. J. (1959): Program istraživanja željeznih ruda u BiH za 1960.- *Geoinženjering*, Sarajevo.
- Dill, H. (1994): Facies Variation and Mineralization in Central Europe from the Late Paleozoic through the Cenozoic.- *Econ. Geology*, 89, 268-287.
- El-Hinnawi, E. & Hofmann, R. (1968): Ueber den Germaniumgehalt verschiedener mitteleuropäischer oxidischer Eisenerze.- *Chemie d. Erde*, 27, 91-99, Jena.
- Foullon, V. H. (1899): Das Bergbaugebiet von Fojnica und Kreševo in Bosnien, Wien.
- Frimmell, H. E. & Papesch, W. (1990): Sr, O, and C Isotope Study of the Brixlegg Barite Deposits, Tyrol (Austria).- *Econ. Geology*, 85, 1162-1171.
- Hauer, F. (1884): Erze und Mineralien aus Bosnien. *Jhrb. d. Geol. Reichsanstalt*, B-34, 753.
- Herbich, R. (1880): Erhebungen und Vorstudien über den Metallbergbau in Bosnien.- *Neues Jahrbuch f. Mineralogie*, 94.
- Hofmann, R. (1979): Die Entwicklung der Abscheidungen in den gangförmiger Barytvorkommen in Deutschland.- *Monograph Series No 17, 1-80*. Zur Minerogenie des hydrothermalen Baryts in Deutschland, Gebrüder Borntraeger Berlin-Stuttgart.
- Hofmann, R. & Schürenberg, H. (1979): Geochemische Untersuchungen gangförmiger Barytvorkommen in Deutschland.- *Monograph Series No 17, 1-80*; Zur Minerogenie des Hydrothermalen Baryts in Deutschland, Gebrüder Borntraeger Berlin-Stuttgart.
- Jeremić, M. (1960): Intenzitet i ekstenzitet bosanske hidrotermalne baritizacije.- *Rud.-met. zbornik*, 2, 125-132, Ljubljana.
- Jeremić, M. (1963): Metalogenija paleozojskih ležišta barita Bosne.- *Arhiv za tehnologiju (Technologica Acta)*, god. I, v. I, br. 1-2, 1-61, Tuzla.
- Jojić, D. (1948) Pregled ležišta barita NR BiH.- *Arhiv "Geoinženjering"*, Sarajevo.
- Jovanović, R. (1979): Područje Raduša planina- Jajce-Mrkonjić grad.- U *"Mineralne sirovine Bosne i Hercegovine"*, II Tom: Ležišta crnih metala, 263-265, Sarajevo.
- Jovanović, R., Mojičević, M., Tokić, S. and Rokić, Lj. (1977): Osnovna geološka karta 1:100.000, list Sarajevo s tumačem (52 str.), Beograd.
- Jurković, I. (1956): Mineralne parageneze Srednjobosanskog Rudogorja s osobitim osvrtom na tetrahedrite.- *Disertacija 306 p.*, University of Zagreb.
- Jurković, I. (1957): The basic characteristics of the metallogenic region of the Mid-Bosnian Ore Mountains.- *Zbornik (Proceedings) II Kongresa geologa FNR*, 504-519, Sarajevo.
- Jurković, I. (1960): Quecksilberfahlerz vom Mačkaragang bei Gornji Vakuf in Bosnien (Jugoslawien).- *Neues Jahrbuch f. Miner.* 94, Festband Paul Ramdohr, I Hälfte, 539-558, Stuttgart.
- Jurković, I. (1986): Quantitative chemical and optical investigations of the tetrahedrite from barite-bearing deposit Vidici on the northern slopes of the Mountain Medjuvršje south of the town of Kreševo, Bosnia.- *Geol. vjesnik*, 39, 187-214, Zagreb.
- Jurković, I. (1987): Barite deposits on Mount Medjuvršje south and south-east of the town of Kreševo, Bosnia.- *Geol. vjesnik* 40, 313-336, Zagreb.
- Jurković, I. (1988a): Ore deposits in the Duboki Vagan region south and south-west of the town of Kreševo, Bosnia.- *Geol. vjesnik* 41, 355-367, Zagreb.
- Jurković, I. (1988b): Rudne pojave između Kreševa i Deževica u Srednjobosanskom Rudogorju.- *Zemaljski muzej Bosne i Hercegovine. Zbornik naučnog skupa "Minerali, stijene izumrla i živi svijet BiH"*, 19-35, Sarajevo.
- Jurković, I. (1991): Gold- and silver-bearing Hg tetrahedrite deposits in Central Bosnia, Yugoslavia.- *EUG VI, Strasbourg. TERRA Abstract 3 no 1*, 411.
- Jurković, I. (1995): Bakovići, the biggest gold deposit of Bosnia and Herzegovina.- *Rud.-geol.naft. zb.* 7, 1-15, Zagreb.
- Jurković, I., Slovenec, D. and Namjesnik, K. (1993): An uncommon metamorphic Cr-Ba-Fe-Cu deposit from the Busovača district, Central Bosnia.- *Bull. of the Geol. Soc. of Greece*, v. 28, no 3, 677-690, Athens.
- Jurković, I., Pezdich, J. and Šiftar, D. (1994): Geology and geochemistry of the mineralization from the Gornji Vakuf area, Bosnia.- *Rud.-geol.-naft. zb.* 6, 19-37, Zagreb.
- Jurković, I. & Šiftar, D. (1995): Sulphate isotope composition of evaporites in the Western Dinarides.- In J. Pašava, B. Kribek and K. Žak (eds.) *"Mineral Deposits: From Their Origin to their Environmental Impacts"*, 581-584, A.A. Balkema Rotterdam.
- Katzer, F. (1903): Geologischer Führer durch Bosnien und die Herzegovina.- 280 p.p. Sarajevo.
- Katzer, F. (1907): Die Fahlerz-Quecksilberlagerstätten Bosniens und Herzegovina.- 121 p.p. Wien.
- Katzer, F. (1910): Die Eisenerzlagerstätten Bosniens und der Herzegovina.- Sonderabdruck aus dem *Berg- und Hüttenmännischen Hochschulen in Leoben und Příbram*, 58 Bd, 343, Wien.
- Katzer, F. (1925): Geologie von Bosnien und Herzegovina.- 527 p.p. Sarajevo.
- Klemm, W. (1994): Chemical evolution of hydrothermal solutions during Variscan and post-Variscan mineralization in the Erzgebirge, Germany.- In R. Seltman, H. Kämpf and P. Möller (eds) *Metallogeny of Collisional Orogens*, 150-158, Czech Republic Survey, Prague.
- Makuc, N. (1941): Nalazišta žive i sinjavca na Zec planini i u oko-

- lici Kreševa.- Arhiv Inst. Geol. Istr., Zagreb.
- Mikolji, V. (1969): Povijest željeza i željeznog obrta u Bosni. Izdanje Metalurškog instituta "Hasan Brkić", 155 p.p. Zenica.
- Mundorfer, J. (1933): Analize živinih ruda.- Arhiv Inst. geol. istr., Zagreb.
- Pak, E. (1978): Schwefelisotopenuntersuchungen am Institut für Radiumforschung und Kernphysik II.- *Anz. Oesterr. Akad. d. Wissenschaft. math.-nat.*, 6-22, Wien.
- Palinkaš, L. & Jurković, I. (1993): Lanthanide geochemistry and fluid inclusion peculiarities of the fluorite from the barite deposits south of Kreševo, Bosnia.- *Geologia croatica*, 47/1, 103-115, Zagreb.
- Paskiević, K. (1940): Preliminarni izvještaj o rudištima rajona Kreševo i Tmor (od 28.0.9.1940).- Arhiv Inst. geol. istr., Zagreb.
- Pohl, W. & Belocky, R. (1994): Alpidic Metamorphic Fluids and Metallogenesis in the Eastern Alps.- *Mitteil. Oesterr. Gesell.* 86(1993), 141-152, Wien.
- Quiring, H. (1931): Verbreitung und Entstehungszeit der Eisen-glanz-Gänge im rheinischen Schiefergebirge.- *Z. Berg- und Hütten- und Salinenwesen im preuss. Staate*, 79, 176-184, Berlin.
- Radusinović, D. (1978): Bakarno-uranska mineralizacija u Neretvici.- *Zbornik radova IX kongresa geol. Jugoslavije*, 735-741, Sarajevo.
- Ramović, M. (1954): Kratak osvrt na ekonomski značaj i proizvodnju barita u svijetu.- Arhiv "Geostrazivanja" Sarajevo.
- Ramović, M. (1956): Kraći pregled baritnih ležišta Bosne i Hercegovine.- *Geol. glasnik* 2, 67-82, Sarajevo.
- Ramović, M. (1976): Barit.- U "Mineralne sirovine Bosne i Hercegovine", knj. II, Ležišta nemetalnih sirovina, 358-379, Sarajevo.
- Ramović, M. (1979): Cinabarit i hematit.- U "Mineralne sirovine Bosne i Hercegovine", knj. III, p. 91, Sarajevo.
- Ramović, M. & Miladinović, J. (1953): Terenski izvještaj iz kolovoza 1953: Bariti u Kolovojama, Smiljevoj Kosi i Zecu.- Arhiv "Geoinženjering", Sarajevo.
- Ramović, M., Jeremić, M., Mioč, P. and Kubat, I. (1954): Izvještaj o geološko-rudarskim istražnim radovima tokom 1954. god. na ispitivanju starih radova na Zec planini (srez Kiseljak NR BiH): Smiljeva Kosa, Bakarne Jame, Zečeva Glava, Otigoške i Gvoždanske Staje (tetraedrit, bariti, cinabarit, željezne rude sa niskim sadržajem mangana).- Geoinženjering, Sarajevo.
- Ramović, M., Čelebić, Dj. and Rančić, B. (1956): Elaborat o rezervama, kvalitetu i načinu pojavljivanja (tipovi ležišta) barita u Bosni i Hercegovini.- Arhiv "Geoinženjering", Sarajevo.
- Ristić, N. (1964/1965): Pojave i ležišta uranijuma u Jugoslaviji.- *Disertacija*. University of Beograd.
- Rücker, A. (1896): Einiges über das Goldvorkommen in Bosnien.- Monographische Skizze, 191 p.p. Wien.
- Schneiderhöhn, H. (1949): Schwerspatgänge und pseudomorphe Quarzgänge in Westdeutschland.- *N. Jb. Min., Mh* 1949, 47-89, Stuttgart.
- Schroll, E. & Pak, E. (1980): Schwefelisotopenzusammensetzung von Baryten aus den Ost- und Südalpen. *TMPM*, 79-91, Wien.
- Schulz, O. (1972): Unterdevonische Baryt-Fahlerz-Mineralization und ihre steilachsige Verformung im Grosskopf bei Brixlegg (Tirol).- *TMPM* 18, 114-128, Wien.
- Sherp, A. & Stadler, G. (1973): Aspekte der Erzbildung im Siegerland.- *Z. deutsch. Geol. gesell.*, 124, 51-59, Hannover.
- Sofilj, J., Živanović, M., and Pamić, J. (1980): Osnovna geološka karta 1:100.000, list Prozor s tumačem, Beograd.
- Šiftar, D. (1988): Kemijske značajke barita iz nekih ležišta u Bosni.- *Rud. met. zbornik*, 35(1-4), 75-89, Ljubljana.
- Šiftar, D. (1990): Usporedba kemizma barita iz područja Raštelice i Kreševa u Srednjobosanskom rudogorju (The chemism of barite from Raštelica in Kreševo region in Mid-Bosnian ore Mountains- a comparison).- *Geol. vjesnik*, 43, 109-112, Zagreb.
- Trubelja, F. (1978): Paleozojski magmatiti srednjobosanskih škriljavih planina.- U "Geologija Bosne i Hercegovine", knj. IV. Magmatizam i metalogenija, 11-19, Sarajevo.
- Turina, I. (1920): Izvještaj o rudnim pojavama područja Dusine. Arhiv Inst. Geol. istraživanja. Zagreb.
- Vogt, F. (1880): Nachtrag I zu den zitierten Erhebungen und Vorstudien, Wien.
- Walter, B. (1887): Beitrag zur Kenntniss der Erzlagertstätten Bosniens, 182 pp. Wien.
- Weber, Z. (1986): The barite deposits of the Eastern Alps (Austria): Genesis and economic importance.- In S. Janković (ed.), *Mineral Deposits of the Tethyan Eurasian Metallogenic Belt between the Alps and Pamirs*, 69-80, Beograd.
- Žak, M. Radvanec, M., Bartalsky, B. and Grečula, P. (1991): Izotopy S, C, O, Sr a metamorfo-hydrotermalni model žilne mineralizacije Gemerika. *Mineralia slovacica*, 23, 95-103.
- Živanović, M. (1972): Geološki sastav i tektonski sklop oblasti Vranice u Centralnoj Bosni.- *Disertacija*, University of Beograd.
- Živanović, M. (1979): Naslage Centralno-bosanskog paleozoika (Vranica). U "Geologija Bosne i Hercegovine", knj. I. Paleozojske naslage, 55-68, Sarajevo.