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Geochemical characteristics of barite occurrences in the Palaeozoic complex of South-eastern Bosnia and their relationship to the barite deposits of the Mid-Bosnian Schist Mountains

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ABSTRACT

In Palaeozoic rocks of South-eastern Bosnia (SEB) there are numerous, but very small vein and replacement barite ore deposits containing up to 10% Pb-Zn-Fe-Cu sulphides. Their geochemical characteristics are compared with large barite monosulphide (Hg-tetrahedrite) ore deposits in Mid-Bosnian Schist Mountains (MBSM). The $^{87}Sr/^{86}Sr$ isotope ratios in the barites of both areas are very similar, (0.710972 and 0.714170 in SEB, 0.711764 and 0.712548 in MBSM), and indicate the epigenetic hydrothermal origin of the barite ore deposits. This conclusion is supported by the elevated Sr content in barites of both areas (0.48 to 2.83% in SEB, 1.44% in MBSM) and the $\delta^{13}C$ and $\delta^{18}O$ values in calcite and siderite of barite ore deposits which are shifted toward lower values relative to typical values occurring in the Devonian host rock. The $\delta^{18}O$ values in barites from SEB (+14.2‰ to +15.6‰) are remarkably lower than those from MBSM (+15.8‰ to +22.4‰). This can be explained by the lower temperature and lower salinity of mineralisation fluids in barite ore deposits of SEB. The $\delta^{34}S$ values in barites of SEB are positive (+11.6‰ to 17.7‰), and enriched in heavy sulphur isotopes in comparison with sulphides of SEB (–0.41 to +4.26‰), whereas those in tetrahedrites are negative (–4.95 in SEB, –5.50 to –15.40‰ in MBSM) indicating two remarkably different sulphur sources and times of formation. Barite ore deposits of both areas, SEB and MBSM, have been genetically linked to fluids that originated during Late Variscan S-type magmatism and metamorphism of Upper Proterozoic and Lower Palaeozoic rock complexes. However, later Post Variscan/Eoalpine heating processes affected significant parts of barite ore deposits in MBSM. They caused fluidization of sulphides in barite deposits, ascension of subcrustal deep-seated fluids enriched in H_2S and mercury (± fluorine), which passed through Upper Proterozoic and Caledonian ore deposits amalgamating their Au and Ag content leading to formation of a new mineral, Hg-tetrahedrite rich in Au (10–50 g/t) and Ag (1000 do 3000g/t).

Keywords: Palaeozoic complexes of South-eastern Bosnia and Mid-Bosnian Schist Mountains, barite ore deposits, trace elements, isotopic composition of sulphur, oxygen and strontium in barite, Pb-Zn-Fe-Cu-Sb sulphides, Hg-tetrahedrite

1. INTRODUCTION

The biggest barite ore deposits in the whole Dinarides are located in the Mid-Bosnian Schist Mountains (MBSM). This Palaeozoic complex consists mostly of Lower Palaeozoic (Ordovician$_{(?)}$–Silurian-Devonian) rocks and subordinately of Lower–Middle Carboniferous and Upper Permian rocks. These deposits are, regarding their mineral paragenesis, unique even on a global scale. The main mineral in the mineral paragenesis, in addition to barite and locally siderite, is Hg-Ag-Au-rich antimony tetrahedrite, named schwazite after the Schwaz locality, in Austria. Schneiderhöhn (1942) grouped this type of paragenesis as a separate genetic type.

Barite occurrences in the Palaeozoic complex of South-eastern Bosnia (SEB) represent the most South-eastern outcrops of numerous mineable barite deposits in the Dinarides (Fig. 1). Compared to numerous geochemical data of barites from MBSM only a few geochemical analyses of barites from SEB (PEZDIČ et al., 1977/1979; KUBAT et al., 1979/1980) have been performed.

The aim of this study is to present the more comprehensive geochemical data on barite occurrences in SEB and compare them with those in the MBSM area. A model for the origin of the barite has been developed on the basis of trace elements, $^{87}Sr/^{86}Sr$ ratios, isotope composition of sulphur and oxygen in barites, carbon and oxygen in neocarbonates (neocalcite, neodolomite, neosiderite), and sulphur isotope composition in associated Pb, Zn, Cu, Sb and Fe sulphides.

Research history of the barite occurrences in South-eastern Bosnia

Initial data concerning the barite occurrences in South-eastern Bosnia were described by JOJIĆ (1947), RAMOVIĆ, M. (1954) and JEREMIĆ (1958). In the barite belt of Renovica--Prača-Omrke, which has a general NNE-SSW trend, RAMOVIĆ, M. (1956, 1957) discovered three different paragenetic types of barite bodies (Fig. 2a). JEREMIĆ (1963) registered 52 barite occurrences in Palaeozoic rocks of SEB (Figs. 2b, 2c, 2d). Most barite veins strike at 340°, dip more than 12° to NE, are very small (100 tons to a few thousand tons), and the total production from 1954–1966 was 24.000 tons of barite (RAMOVIĆ, M. et al., 1976; RAMOVIĆ, M. et al., 1979).

KUBAT et al. (1979/1980) produced the first isotopic sulphur analyses for Pb and Fe sulphides, barite, and 1 Pb isotopic analysis for galena (PEZDIČ et al., 1977/1979). RAMOVŠ & KULENOVIĆ (1982) determined the stratigraphic position of mineralisation in sideritised limestones in the areas of Šarulje-Mastilove Stijene, the Kamenička River and Milotina as being primarily Lower Devonian and to a lesser extent Middle Devonian. JANJIĆ & ĐORĐEVIĆ (1985) published results of isotopic analyses in minerals of ore deposits Potkozara (Kratina) and Oglečevski potok (Kordići). KULENOVIĆ (1987) produced a brief overview of barite occurrences in SEB, stating that deposits occur in a 15 km long and 3 to 6 km wide belt extending from Fočanska Jabuka in the South-west across Borovac, Klek and Prača to Renovica in the Northeast (Figs. 2e, 2f, 2g, 2h). RAMOVIĆ, E. (1991) published the project investigation of BLEČIĆ (1983) on fluid inclusions in sphalerite and barite in the Ranoprge deposit, fluid inclusions in quartz and $\delta^{34}S$ of antimonite in Kratina and Kordići (Goražđe). Most researchers of SEB consider that barite deposits originated in the Hercynian metallogenic epoch probably associated with quartz-porphyry being similar that quartz-porphyry in the MBSM (RAMOVIĆ, M., 1957; JEREMIĆ, 1963; ŽIVANOVIĆ, 1972; RAMOVIĆ, M. et al., 1976; RAMOVIĆ, M. et al., 1979). KULENOVIĆ (1986, 1987) and ČIČIĆ (2002) proposed a hypothesis suggesting the existence of more than one metallogenic epoch in the Palaeozoic of SEB indicating the probable existence of a Caledonian metallogenic epoch (in the Upper Silurian and Lower Devonian).

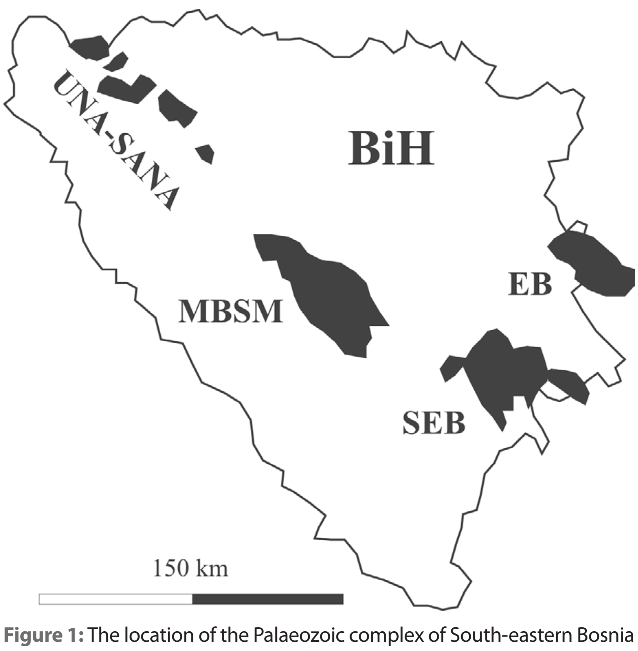

Figure 1: The location of the Palaeozoic complex of South-eastern Bosnia (SEB) in relation to Palaeozoic complexes of the Mid-Bosnian Schist Mountains (MBSM), Eastern Bosnia (EB) and the Una-Sana area in Bosnia and Herzegovina.

2. GEOLOGICAL SETTING

The Palaeozoic of SEB is elaborated by KATZER (1926), KOSTIĆ–PODGORSKA (1958), ŽIVANOVIĆ (1962), DIMITRIJEVIĆ, N.M. & DIMITRIJEVIĆ, D.M. (1972), BUZALJKO & PAMIĆ (1982), VUJNOVIĆ (1983), RAMOVŠ & KULENOVIĆ (1982), KULENOVIĆ (1986), KRSTIĆ et al. (1988), ČIČIĆ (2002) & HRVATOVIĆ (2006), and RAMOVŠ et al. (1984).

The most detailed research resulting in many new palaeontological data was carried out by KULENOVIĆ (1986), and produced evidence for Upper Silurian (S_3), Lower Devonian (D_1), Middle Devonian (D_2), Upper Devonian (D_3), Lower Carboniferous (C_1) and Upper Permian (P_3) deposits (Fig. 3).

Upper Silurian (S_3) deposits, being <100 m thick, were found near Prača and Ustikolina, but the upper and lower boundaries are uncertain. They consist of silicic, clastic and

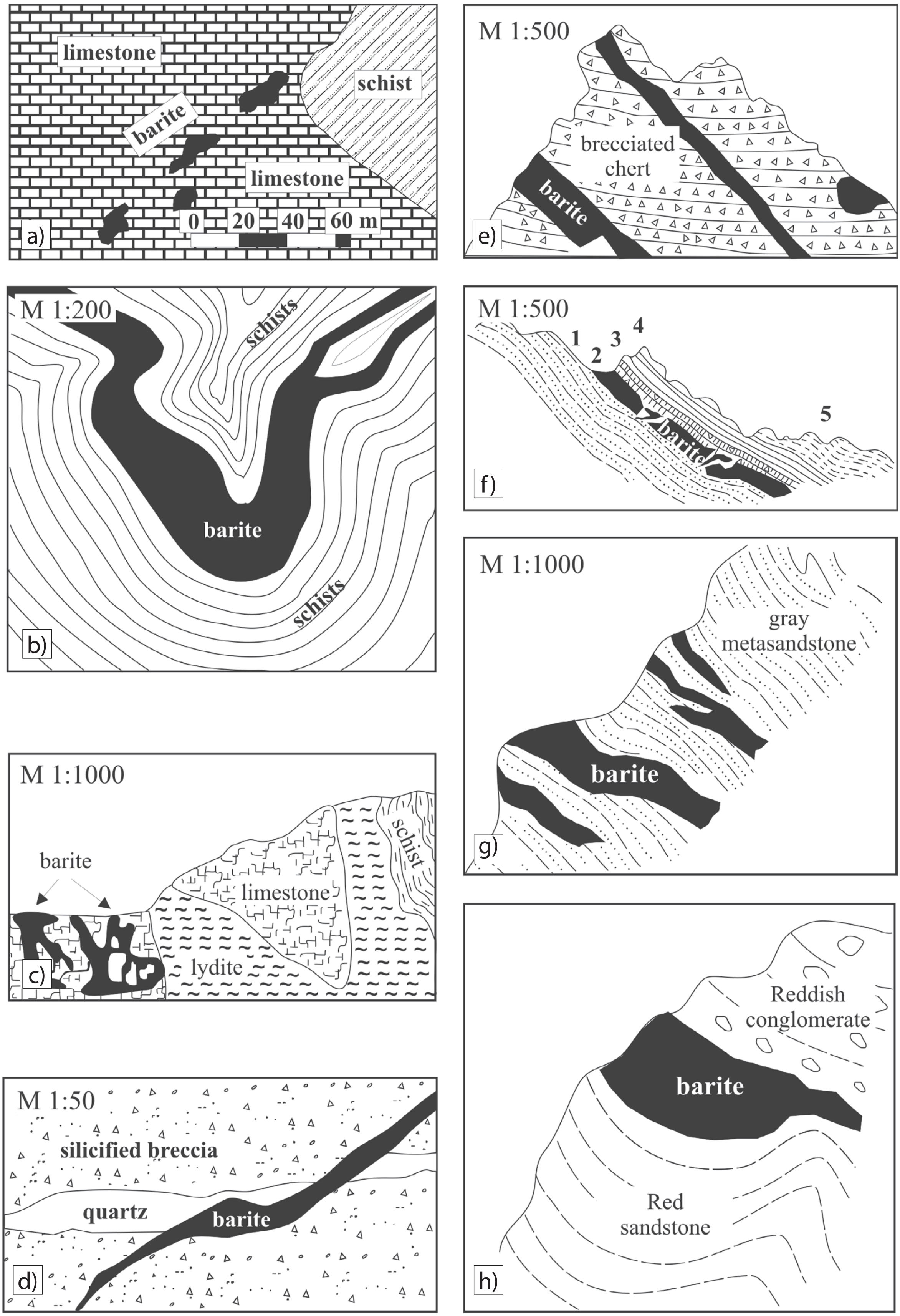

Figure 2: Barite occurrences in Palaeozoic rocks of SEB: a) Lensoid barite bodies in limestone of Kurjača, near Prača (RAMOVIĆ, M. 1957); b) Folded barite vein in schists of Badnjevi, near Prača (JEREMIĆ, 1963); c) Brecciated barite body in limestone of Debeljak, near Prača (JEREMIĆ, 1963); d) Crossed quartz and barite veins in silicified breccia of Ravne Njive, near Prača (JEREMIĆ, 1963); e) Barite bodies in Palaeozoic brecciated chert of Gradina, in SEB (KULENOVIĆ, 1987); f) Barite bodies in Palaeozoic rocks of Homar Klek, in SEB (KULENOVIĆ, 1987) where 1 = gray metasandstone, 2 = barite bodies, 3 = brecciated barite, 4 = alevrolite, 5 = red sandstone; g) Barite bodies in Palaeozoic gray metasandstone of Rasoha-Jasik, in SEB (KULENOVIĆ, 1987); h) Barite body in Palaeozoic rocks of Šušnjata Glava in SEB (KULENOVIĆ, 1987).

dolomitic limestone rock with conodonts. Sedimentation from the Upper Silurian continued into the Lower Devonian, but transitional deposits (S_3–D_1) could not be separated. Sequences are composed of alevrolites, cherts, argilloschists, metasandstones, tuffites and marbleized limestone (KULENOVIĆ, 1986).

The Lower Devonian consists of alevrolites with chert (either independent small masses or intercalations in alevrolites), layered and bank limestones. This lower part of the Lower Devonian is overlain by sequences composed of cherts, diverse argilloschists, metasandstones and limestones among which very fossiliferous bank limestones occur. Chert breccias, metadiabases, schistose spilites, diabases and some red clastites are locally developed. According to KULENOVIĆ (1986) granitoides occurring in the Odska River and Osanica, intruded between Lower and Upper Devonian or in the Upper Devonian.

The Upper Devonian is composed of limestone schists, cherts, chert breccias, ferrous sandstone and marbleized limestones. Tabular sericite-quartz schists mark the lower part of the Lower Carboniferous. They are overlain by phyllite schists with intercalations or lenses of schistose sandstones containing fossil flora of Lower Visean age. Fossiliferous Lower Carboniferous phyllites with black lydite intercalations are the next deposits in the sequence (KULENOVIĆ, 1986).

The uppermost, unfossiliferous part of the phyllite schists represents, the transition from the Lower to Middle Carboniferous according to KULENOVIĆ (1986). These are discordantly overlain by deposits of Upper Permian sandstones, schists, conglomerates and fossil-rich Bellerophone limestones. KRSTIĆ et al. (1988) discovered olistoliths and olistostromes composed of limestones and clastics in the "Culm flysch" in the Prača area. They stated that olistostrome formation is associated with very active tectonic zones, which caused the shearing and movement of large blocks such as Vlaška Stijena, Kiseljak, Klek and some others. ČIČIĆ (2002) and HRVATOVIĆ (2006) presented short overviews of the stratigraphic development of quartz-porphyry in SEB.

The most widespread rocks of the Mid-Bosnian Schist Mountains (MBSM) are pre–Devonian metamorphic rocks (SOFILJ et al., 1980). MAJER et al. (1991) determined that they were formed by low grade metamorphism at 350°–

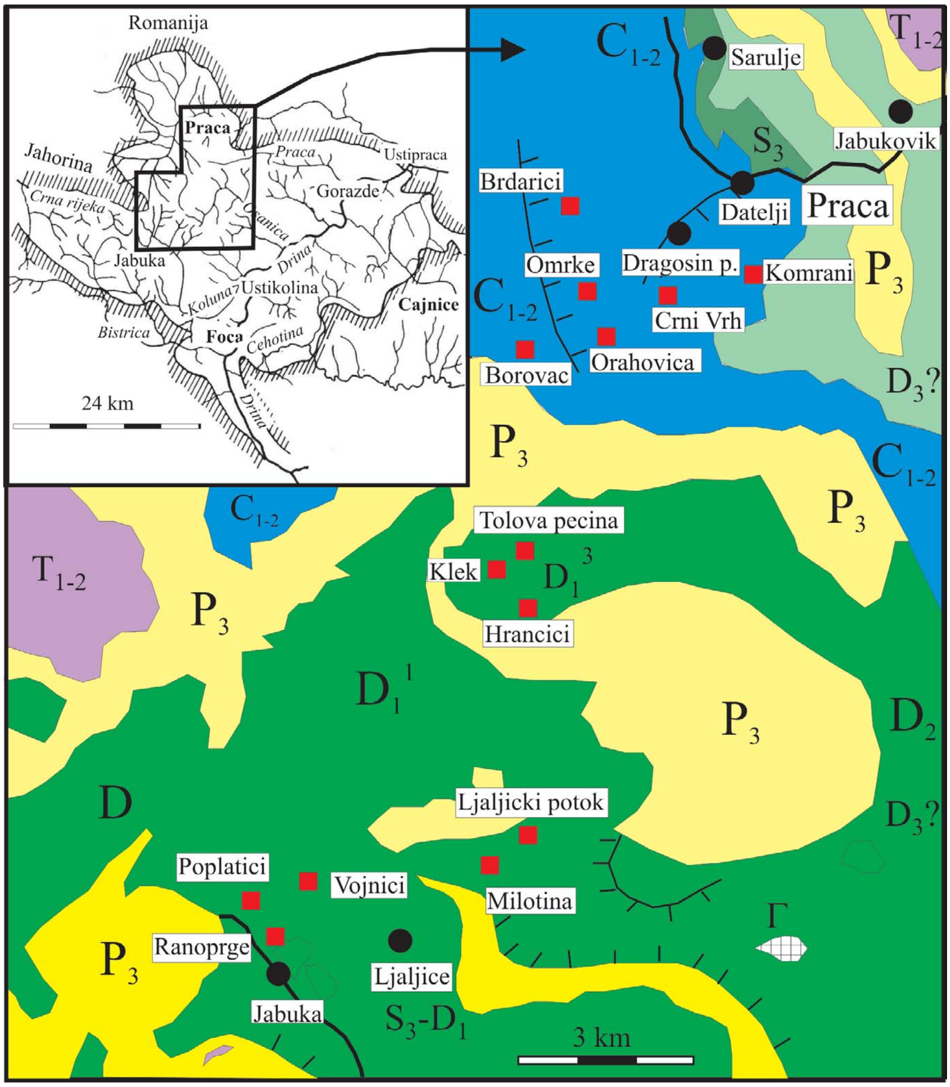

Figure 3: Geological map of the area between Fočanska Jabuka and Prača (after KULENOVIĆ, 1986). Circles denote the locations of barite samples analyzed here, whereas rectangles represent locations, which are undergoing analysis. T_{1-2} = Lower-Middle Triassic; P_3 = Upper Permian; C_{1-2} = Lower-Middle Carboniferous; D_3 = Upper Devonian; D_2 = Middle Devonian; D_1 = Lower Devonian; S_3–D_1 = Upper Silurian-Lower Devonian; S_3 = Upper Silurian; Γ = Granitoid.

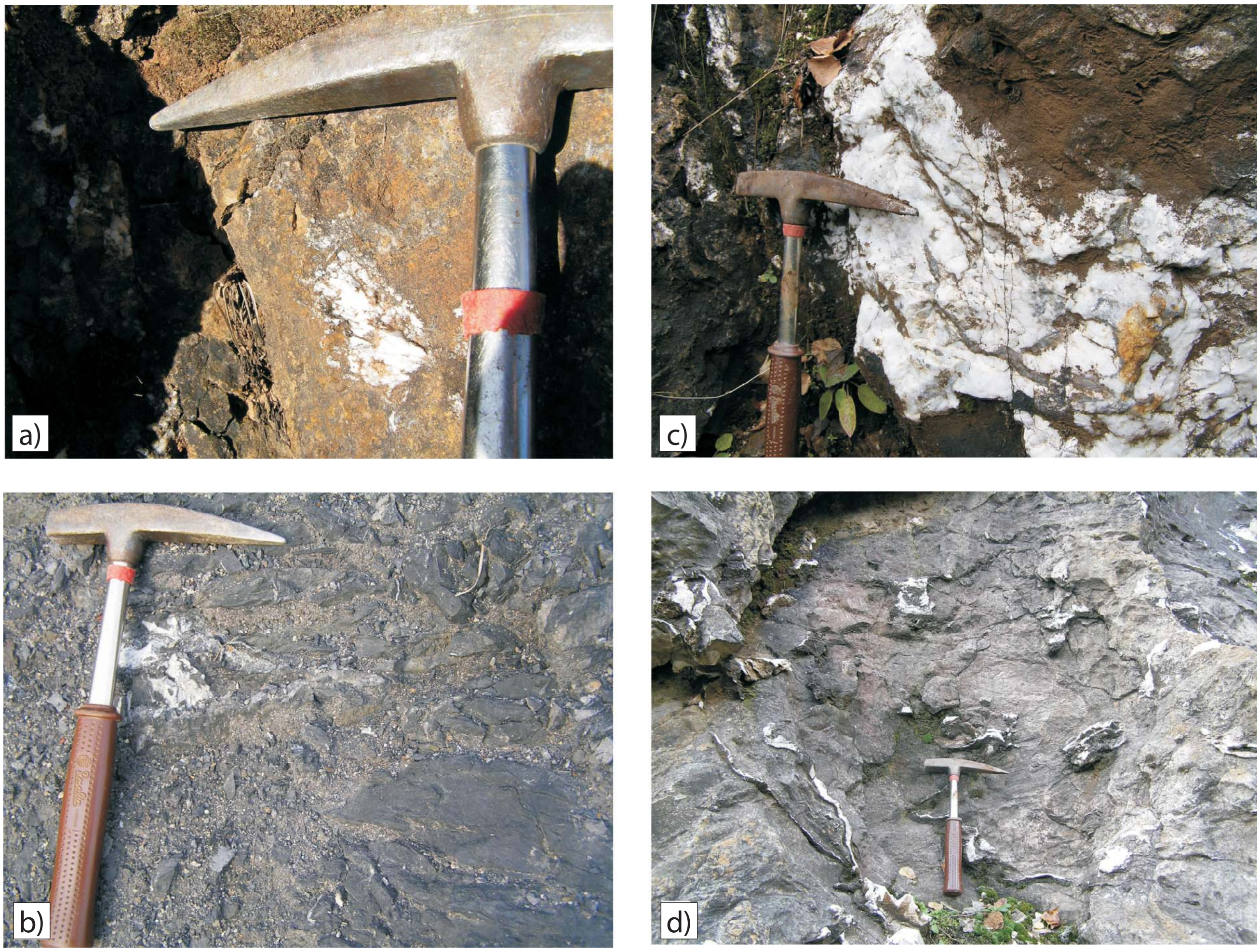

Figure 4: Photographs of white barite occurrences: a) in Permian limestone of Datelji; b) in Carboniferous schists of Pale; c) in Devonian limestone of the Glumac deposit (Kreševo); d) in Devonian limestone of the Dubrave deposit (Kreševo). Note hammer for the scale.

400°C and a pressure of 3–5 kbars. Their crystallization age, obtained by K–Ar dating is 343 ± 13 Ma (PALINKAŠ et al., 1996). Fossiliferous Devonian carbonate rocks overlie this metamorphic complex (ŽIVANOVIĆ, 1972). The uplift of this area is related to the Hercynian orogeny and extrusions of rhyolites. Upper Permian continental and lagoonal deposits that unconformably overlie older Palaeozoic rocks, grade into Lower and Middle Triassic sediments.

Mineralization in the SEB Palaeozoic complex comprises small, but numerous barite deposits. They occur as irregular metasomatic barite bodies and epigenetic veins in the carbonate rocks, and contain traces or accessory amounts of Pb, Zn, and subordinantly Cu and Fe sulphides (Fig 4). Additionally, they occur as epigenetic barite veins located in metaclastites but enriched in sulphides (up to 10%). All sulphides have positive $\delta^{34}S$ values (0 to +5‰). The rare younger Hg–Ag tetrahedrite is characterized by a negative $\delta^{34}S$ value (–4.95‰).

The Hg–Ag–Au tetrahedrite deposits in the MBSM represent a peculiar and unique phenomenon in the whole Dinarides (KATZER, 1907; JURKOVIĆ, 1956). The Mačkara vein type is observed in pre–Devonian metamorphic rocks of the Gornji Vakuf area (JURKOVIĆ, 1960; JURKOVIĆ et al., 1994). The Kreševo vein and metasomatic irregular bodies are very widespread in the area composed of Devonian dolomites and limestones (JURKOVIĆ, 1996).

The Trošnik metasomatic type that occurs in the Fojnica–Bakovići area represents, at present, a unique exception among tetrahedrite-bearing barite deposits in MBSM. Its tetrahedrite is neither the main nor the unique sulphide mineral rich in mercury, but is subordinate to pyrite and chalcopyrite and characterized by traces of mercury and positive $\delta^{34}S_{CDT}$ values (JURKOVIĆ, 1958).

3. ANALYTICAL METHODS

Ore samples were collected from seven outcrops in SEB and ten outcrops in MBSM. Barites were hand-picked under binocular microscope and then crushed and powdered for chemical analyses in an agate mortar.

Trace elements were analysed by inductively coupled plasma (ICP) mass spectrometry in Acme Analytical Laboratories (Vancouver) Ltd in Canada. In order to use X-ray powder diffractometry (XRD), barite samples were powdered in an agate mortar. Diffractograms were recorded by a Philips diffractometer with counter and Cu-K_α radiation at U =40 kV and I = 20 mA at the Institute of mineralogy, petrology and mineral resources at Faculty for Mining, Geology

Table 1: Trace element contents of barites from SEB and MBSM.

Sample	MBSM K ppm	SEB D ppm	SEB S ppm	SEB DP ppm	SEB J ppm	SEB P ppm	SEB **FC** ppm	MBSM ppm	SEB **range** ppm
Ba	>50000	>50000	>50000	>50000	>50000	>50000	>50000		
Be	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		
Co	0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2		
Cs	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Ga	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5		
Hf	0.5	0.4	0.3	0.3	0.3	0.7	0.6	0.5	0.3–0.7
Nb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Rb	0.4	0.3	0.1	0.2	0.2	0.2	<0.1	0.4	<0.1–0.3
Sn	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		
Sr	14354	12201	4846	6158	18888	7650	28292	14354	4846–28992
Ta	1.4	0.9	0.8	0.8	0.9	1.7	1.7	1.4	0.8–1.7
Th	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2		
U	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
V	13	10	<8.0	<8.0	<8.0	<8.0	<8.0	13	<8–10
W	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5		
Zr	1.6	0.4	<0.1	<0.1	0.2	0.2	1.4	1.6	<0.1–1.4
Y	1.0	0.7	0.9	0.5	0.6	1.2	1.3	1.0	0.5–1.3
La	2.4	1.6	1.4	1.8	1.7	1.1	3.5	2.4	1.1–3.5
Ce	0.9	0.3	0.2	0.2	0.3	0.2	0.7	0.9	0.2–0.7
Pr	0.10	0.04	0.03	0.04	0.04	0.03	0.06	0.10	0.03–0.06
Nd	0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3		
Sm	0.45	0.33	0.35	0.25	0.30	0.58	0.67	0.45	<0.25–0.67
Eu	0.85	<0.02	0.04	0.24	<0.02	1.03	1.00	0.85	<0.02–2.03
Gd	1.02	0.80	0.81	0.70	0.68	1.44	1.62	1.02	0.68–1.62
Tb	0.08	0.06	0.06	0.05	0.05	0.10	0.10	0.08	0.05–0.10
Dy	2.78	2.20	2.09	1.76	1.74	3.80	4.05	2.78	1.74–4.05
Ho	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02		
Er	0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03		
Tm	0.02	0.11	0.01	<0.01	<0.01	0.03	0.03	0.02	0.01–0.11
Yb	0.07	<0.05	0.06	<0.05	<0.05	0.06	0.08	0.07	<0.05–0.08
Lu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		
Mo	0.20	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Cu	3.90	1.40	1.60	0.30	2.30	18.10	0.80	3.90	0.3–18.1
Pb	2.40	1.20	4.50	11.20	4.30	0.40	0.50	2.40	0.4–11.2
Zn	6.00	1.00	1.00	<1	2.00	1.00	<1	6.00	<1–2
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Ni	0.90	0.20	0.30	0.10	0.20	<0.1	<0.1	0.90	<0.01–0.3
As	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5		
Au	<0.0005	<0.0005	0.00120	<0.0005	<0.0005	<0.0005	<0.0005		
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Sb	0.30	0.10	0.10	1.20	0.10	0.90	0.20	0.30	0.1–0.2
Bi	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Hg	0.19	0.09	1.66	0.42	0.63	0.22	0.03	0.19	0.03–1.66
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Se	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5		
Ca	300.00	500.00	1.31	0.01	<0.1	<0.1	<0.1	300.00	<0.01–13100
ΣREE	9.03	5.87	5.41	5.46	5.25	8.73	12.17		
La_N/Yb_N	24.59	22.95	16.74	25.82	24.39	13.15	31.38		
Eu/Eu*	19.08	0.46	0.91	5.97	0.45	24.17	23.04		
Ce/Ce*	0.47	0.12	0.08	0.08	0.12	0.09	0.24		

and Petroleum Engineering at the University of Zagreb. Carbon, sulphur and oxygen isotopes were determined at the Stable Isotope Laboratory of the University of Lausanne using the Finnigan Mat facility. Strontium isotopic ratios were determined by thermal ionisation mass spectrometry (TIMS) in the Activation Laboratory Ltd in Anchaster (Ontario).

4. RESULTS

4.1. Trace element composition of barite samples

Trace elements were analysed in six samples of pure barite from the Prača-Foča area in SEB and in one sample of pure barite from the Glumac deposit in the Kreševo area (K) in MBSM. Barite samples in SEB were collected in the Šarulje (Š), Jabukovik (J), Pale (P), Datelji (D), Dragosin Potok (DP) and Fočanska Jabuka (FJ) barite deposits.

The trace element contents of the analysed barites are listed in Table 1. They are generally present in very low concentrations. The values of 15 trace elements (Be, Ga, Nb, Sn, Th, U, W, Ho, Lu, Ag, As, Cd, Bi, Ti, Se) are below the detection limits of the analytical method in both areas. Five trace elements (Cs, Co, Nd, Mo, Er) only occur in the Glumac deposit (MBSM), whereas Au (1.2 ppm) is only detected in the Šarulje deposit (SEB). Of the 24 trace elements detected in the barites of both areas, 16 show similar values in both SEB and MBSM, 6 are slightly higher in MBSM and 2 trace elements (Zn and Ni) are significantly higher in MBSM (Table 1). REEs are present in very low concentrations. Maximum total REE contents range from 5.25 to 12.17 ppm. (Table 1). The chondrite normalized (SUN & MCDONOUGH, 1989) REE patterns of all analysed barites are shown in Fig. 5. The REE patterns are characterized by an enrichment of the LREE against the HREE such as Ho, Er, Tm, Yb and Lu (minimal La_N/Yb_N = 13.15 to 31.38). The Tm values in all barite deposits excluding Jabukovik and Dragosin Potok deposits are an exception to this statement. The REE patterns of all barite samples display a negative Ce anomaly (Ce/Ce* = 0.08 to 0.47). Significant difference in the REE patterns of studied barites is visible only in Eu anomaly. Barites of the Jabukovik, Datelji and Šarulje deposits are characterised by a negative Eu anomaly (Eu/Eu* = 0.45; 0.46 and 0.91 respectively), whereas those of the Dragosin Potok, Pale, Fočanska Jabuka and Kreševo deposits show positive anomaly (Eu/Eu* = 5.97; 24.17; 23.04; 19.08 respectively).

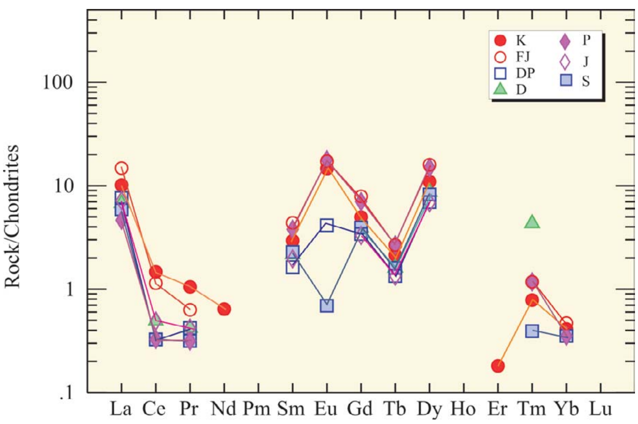

Figure 5: Plot of rare-earth elements normalized to C1 chondrites (SUN & MCDONOUGH, 1989). Legend: Šarulje (S), Jabukovik (J), Pale (P), Datelji (D), Dragosin Potok (DP), Fočanska Jabuka (FJ) and Kreševo (K).

4.2. Ca content in barites

Minor substitution of Ca for Ba in the crystal lattice of barite is often observed. In the studied barites, the highest Ca content is found in the barite from the Šarulje deposit (1.31 %). The barite from the Datelji deposit contains 0.05 % Ca, in Kreševo area 0.03 % Ca and the barite from Dragosin Potok only 0.01 % Ca. Other studied barites are characterized by a Ca content which is below the detection limits of 0.01 % (Table 1). The X-ray analyses of the barites from Šarulje, Datelji and the Kreševo area reveal the presence of calcite as individual phase only in the barite from the Šarulje deposit (3.24 % $CaCO_3$). The Ca content in other Ca bearing barites is most probably substituted for Ba in the crystal lattice. Consequently, the barite from the Datelji deposit contains 0.17 % $CaSO_4$, 0.10% in the Kreševo area and the barite from Dragosin Potok has 0.03 % $CaSO_4$ component.

4.3. Sr content in barites

In comparison to other foreign elements in the crystal lattice of barite, Sr is evidently enriched in all the studied barite. Its content varies from 0.48 to 2.83 % in the barites of SEB and in the barite from MBSM it is 1.44 % (Table 2). The Sr content of barites in Table 2 is additionally expressed as a $SrSO_4$ component. The obtained Sr value for barite of MBSM is in agreement with Sr values for 22 barite samples already published by Jurković et al. (1997), which range from 0.48 to 3.15% Sr (average 2.0%). The X-ray analyses of the barites revealed that their Sr content is the lowest in Šarulje deposit, the middle in Kreševo area and the highest in Fočanska Jabuka deposit, and demonstrated that strontianite ($SrCO_3$) as an individual phase does not exist in the barites. Accordingly, the presence of Sr in the barites could be explained by its substitution for Ba in the crystal lattice, and expressed as a $SrSO_4$ component.

Such a relatively high Sr content is typical for an ascending hydrothermal type of mineralization, whereas a low Sr content characterizes the volcano-sedimentary type of barite deposits.

Table 2: Content of Sr and $SrSO_4$ in barite.

Sample	Sr (%)	$SrSO_4$ (%)
K	1.44	3.03
D	1.22	2.56
S	0.48	1.03
DP	0.62	1.30
J	1.89	3.96
P	0.77	1.60
FC	2.83	5.93

4.4. Isotopic composition of sulphur (as sulphate) and oxygen in barites

The isotopes are analysed not only in the barites of previously mentioned localities in SEB and Kreševo area, but also in some other barite deposits in MBSM (Table 3).

Sulphur isotope data in Table 3 are expressed relative to Canon Diablo troilite and oxygen isotope data relative to Vienna Standard Mean Ocean Water.

The sulphur isotopes ($\delta^{34}S$) in the barites from SEB span a narrow range, from +11.6‰ to +17.7‰ (mean +14.4‰). The only available $\delta^{34}S$ analysis of the barite from the Šarulje deposit (PEZDIČ et al., 1977/1979; KUBAT et al., 1979, 1980) has a value of 12.4‰ and fits very well into the range determined here. Barites from MBSM also display a narrow range of $\delta^{34}S$ values, varying between +10.1‰ and +16.8‰ (mean value = +11.8‰). This data is in accordance with the earlier published $\delta^{34}S$ values from 22 barite samples from MBSM (JURKOVIĆ et al., 1997), which vary from +8.05‰ to +18.48‰ (mean value = +11.5‰). Regarding only the mean values, the barites from MBSM are characterized by a slight enrichment of the light sulphur isotope compared to the barites from SEB.

The oxygen isotope values ($\delta^{18}O$) shown in Table 3 represent the first $\delta^{18}O$ data for selected barites in the Dinarides. The barites from SEB have $\delta^{18}O$ values within a narrow range, from +14.2‰ to +15.6‰ (mean +14.7‰). The barite samples from MBSM reveal remarkably higher $\delta^{18}O$ values ranging from +15.8‰ to +22.4‰ (mean +18.47‰). The sulphur and the oxygen isotope data of the barites investigated in this study are summarized in Fig. 6.

Table 3: Sulphur and oxygen isotope data in the barites from SEB and MBSM.

	Sample		$\delta^{34}S_{CDT}$	$\delta^{34}S_{std}$	$\delta^{18}O_{VSMOW}$	$\delta^{18}O_{std}$
	Locality	Sign				
SEB	Datelji	D	13.1	0.0	14.8	0.1
	Ljaljice	Lj-1	17.6	0.2	15.6	<0.5
	Jabukovik	J	16.7	0.2	15.3	0.3
	Fočanska J.	FC	17.7	0.2	15.1	0.1
	Šarulje	S	14.4	0.5	14.4	0.2
	Dragosin P.	DP	11.6	0.0	15.3	0.2
	Pale	P	12.2	0.3	14.2	0.0
	Šarulje, Glav.*		12.4			
MBSM	Mačkara 1	MC-1	11.6	<0.3	17.6	<0.5
	Kreševo	K	10.8	0.2	19.7	0.2
	Rijetka Kosa	RIK	11.4	<0.3	21.7	<0.5
	Otunjski Vis	OTV	10.1	<0.3	16.3	<0.5
	Sabiljine P.	SBP	11.2	0.15	15.8	<0.5
	Vrelo-1	VRL-1	11.7	<0.3	18.0	<0.5
	Selakova K.	SEK	16.8	0.18	16.1	<0.5
	Medenik-1	MED-1	10.8	<0.3	22.4	<0.5
	Medenik 2	MED-2	12.1	<0.3	21.2	<0.5
	Mačkara-2	MAC	11.7	<0.3	16.1	<0.5

Šarulje, Glav.*= $\delta^{34}S$ analyse made by PEZDIČ et al. (1977/1979)

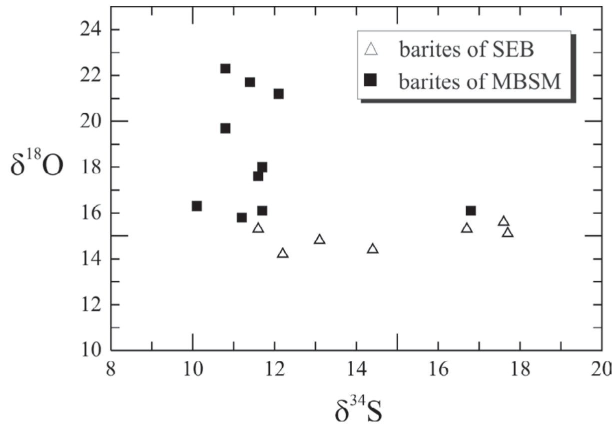

Figure 6: Comparison of sulphur and oxygen isotope data in the barites from SEB and MBSM.

4.5. Isotopic composition of carbon and oxygen in neominerals from SEB

The carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope ratios in the neominerals of the barite deposits from SEB are represented in Table 4.

The $\delta^{13}C$ values are expressed relative to the Vienna Peedee Belemnite Standard (VPDB) and the $\delta^{18}O$ values relative to both the Vienna Peedee Belemnite Standard (VPDB) and the Vienna Standard Mean Ocean Water (SMOW).

The values of $\delta^{13}C$ measured in the microcrystalline siderite from Šarulje deposit and in the "red spar" siderite from Ljaljice (Fočanska Jabuka) deposit are –7.60‰ and –3.22‰ respectively. The coarse crystallised calcite from the Dragosin potok deposit has a positive $\delta^{13}C$ value (+0.19‰). The $\delta^{18}O_{VPDB}$ values are negative for all examined minerals and range from –6.5‰ to –9.90‰ (Table 4).

The data are in agreement with previously published $\delta^{13}C$ and $\delta^{18}O$ values for neominerals occurring in the Devonian host rock of other deposits in Bosnia. For the purpose of comparison, data published by JANJIĆ & ĐORĐEVIĆ (1985) and JURKOVIĆ et al. (1997) are listed in Table 4.

4.6. Strontium isotope ratios in the barites and the metarhyolite

The strontium isotope ratios ($^{87}Sr/^{86}Sr$) in the barites are listed in Table 5. The $^{87}Sr/^{86}Sr$ values in the barites of SEB are 0.710972 and 0.714170 and are very similar to those in the barites from MBSM (0.711764 and 0.712548). Such Sr ratios in the barites from both areas are more radiogenic, when compared to the values between 0.70680 and 0.70925, which characterize coeval seawater, rocks and fossils from Lower Cambrian to Upper Permian (GRADSTEIN et al., 2006).

The $^{87}Sr/^{86}Sr$ value of the metarhyolite from the Vranica Mountain in MBSM is extremely high (0.776995).

Table 4: Isotopic composition of carbon and oxygen in the neominerals from SEB and their comparation with already published analyses of the same type in SEB and MBSM.

	Sample		Type of	Mineral/	$\delta^{13}C_{VPDB}$	$\delta^{13}C_{std}$	$\delta^{18}O_{VPDB}$	$\delta^{18}O_{VSMOW}$	$\delta^{18}O_{std}$
	Locality	Sign	**deposit**	**rock**	**‰**		**‰**	**‰**	
SEB	Dragosin P.	DP	barite	calcite	+0.19	0.06	–6.50	+24.2	0.12
	Šarulje	S	barite	siderite	–7.60	0.04	–6.83	+23.9	0.05
	Ljajice	LJ	barite	siderite	–3.22	0.10	–9.90	+20.7	0.12
SEB*	Kratina		stibnite	dolosparite	–1.10 to –2.02				
	Kordići			microsparite	–0.66 to –1.53		–11.60 to –12.73		
MBSM**	Gornji V. Zec Mountain		barite/ tetrahedrite	calcite	–2.62 to +1.20		–8.32 to –6.66		
	Deževica Kreševo			siderite	–5.55 to +1.01		–8.82 to –10.33		

* analyses published by JANJIĆ & ĐORĐEVIĆ, 1985.
**analyses published by JURKOVIĆ et al., 1997.

Table 5: Strontium isotope analyses in the barites from SEB and MBSM and metarhyolite.

	Sample		Mineral/rock	$^{87}Sr/^{86}Sr$	
	Locality	Sign		Value	+/– 2s
SEB	Šarulje	Š	barite	0.710972	6
	Ljajice	LJ-1	barite	0.714170	5
MBSM	Kreševo	K	barite	0.712548	8
	Mačkara	MAC	barite	0.711764	4
	Vranica	D1	metarhyolite	0.776995	5

5. DISCUSSION

The discussion is focused on conclusions of the newly obtained geochemical data on barite and those previously published by numerous authors (PALINKAŠ & JURKOVIĆ, 1994; JURKOVIĆ et al., 1997; STRMIĆ et al., 2000; PALINKAŠ et al., 2001; JURKOVIĆ & PALINKAŠ, 2002; PALINKAŠ et al., 2008).

Typical Devonian barite deposits with Pb, Zn, and Fe sulphides in the Palaeozoic area of Graz (Austria) belong to the synsedimentary volcanogenic type of barite deposit and were used here as geochemical parameter to distinguish syngenetic from hydrothermal-epigenetic type of barite deposits.

Additionally, the comparison is related to the geochemical investigations of the Brixlegg ore deposit, Tyrol, Austria (SCHULZ, 1972; GSTREIN, 1979; SCHROLL & PAK, 1980; FRIMMEL & PAPESCH, 1990; EBNER et al., 1999), and the Rudnany ore deposit, Gemericum unit, Slovakia (CAMBELL et al., 1985; ŽAK et al., 1991; RADVANEC et. al., 2004). Besides the Bosnian tetrahedrite occurrences, these represent the most important European Hg-Ag-Sb tetrahedrite ore deposits, and are included into the discussion.

5.1. REE

The low total REE concentrations, light REE enriched chondrite normalized REE patterns and negative Ce anomaly determined in the barites are usually interpreted as an indication of a hydrothermally influenced seawater fluid component in the barite origin (GUICHARD et al., 1979; MURRAY et al., 1990).

The most significant difference in the shape of REE patterns is expressed in the Eu-anomaly that is positive for barites from Dragosin Potok, Pale, Fočanska Jabuka and Kreševo area, and negative for the barites from the Šarulje, Datelji and Jabukovik deposits. This indicates the presence of two different sources of hydrothermal fluids.

Spatially large (up to 1 km long) but poor barite ore deposits associated with siderite and Fe-, Cu-, Pb-, Zn- and Sb-sulphides in the area of Šarulje, Mastilove Stijene, Kamenička River and Milotina, are especially interesting from the genetic point of view. According to KULENOVIĆ (1987), these are stratabound types of deposits. The $^{87}Sr/^{86}Sr$ ratio of barite from Šarulje (Table 5) indicates an epigenetic type of formation. The investigation will try to resolve the ambiguity based on more precious REE analyses and $^{87}Sr/^{86}Sr$ ratios in barite and host rock (Devonian dolomite).

5.2. $^{87}Sr/^{86}Sr$ ratio

The Rb/Sr ratios in the investigated barites from both the, SEB and MBSM, are very low (Table 1). Accordingly, the initial $^{87}Sr/^{86}Sr$ ratios of the barites have not significantly increased since the time of crystallization and reflect the composition of the host fluids.

The significantly higher $^{87}Sr/^{86}Sr$ ratios of the barites from SEB and MBSM (0.710972 to 0.714170) relative to those of contemporaneous seawater, rocks and fossils from Lower Cambrian to Upper Permian (0.70680 and 0.70925, after GRADSTEIN et al., 2006), suggest hydrothermal fluids and an epigenetic origin of Bosnian barites. The higher recorded $^{87}Sr/^{86}Sr$ ratios of the rocks through which hydrothermal fluids have circulated suggest an evolved crustal source for Ba, Sr and Rb. An extremly high $^{87}Sr/^{86}Sr$ ratio of metarhyolite (0.776995) indicates a crustal source for the rhyolite magma (S-type of granitoid magma).

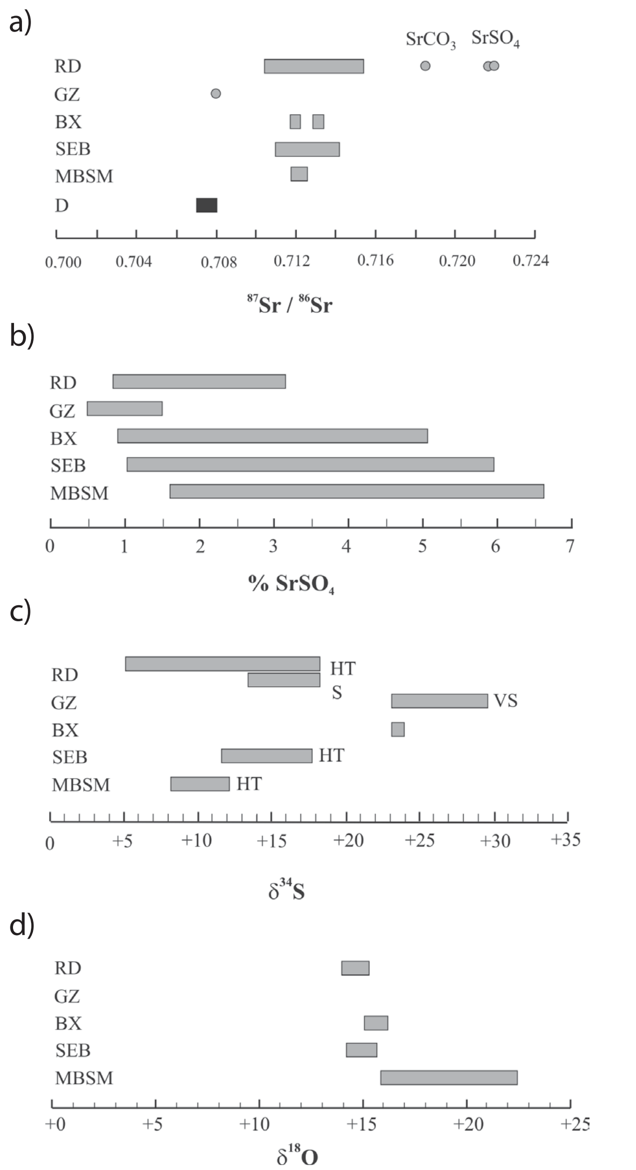

Figure 7: Comparison of $^{87}Sr/^{86}Sr$ ratio, $SrSO_4$ %, $\delta^{34}S$ and $\delta^{18}O$ values in barites from SEB and MBSM and those from Brixlegg (BX), Graz (GZ) and Rudnany deposits (RD): a) besides $^{87}Sr/^{86}Sr$ ratio in barites, typical values of $^{87}Sr/^{86}Sr$ ratio in Devonian dolomite (D) and in strontianite ($SrCO_3$) and in celestine ($SrSO_4$) of Rudnany deposit are shown too; b) the $SrSO_4$ content in barites; c) measured $\delta^{34}S$ values in barites where HT = hydrothermal barite; S = sedimentary barite, VS = volcanogenic-sedimentary barite; d) measured $\delta^{18}O$ values in barite.

The comparison of $^{87}Sr/^{86}Sr$ ratio in barites from SEB and MBSM and those from the Brixlegg, Graz and Rudnany deposits are shown in Fig. 7a.

5.3. $SrSO_4$ content in barite

The relationhips between the $SrSO_4$ content in barites of Bosnia and some other worldwide known barite deposits are shown in Fig. 7b. The $SrSO_4$ content in barites depends significantly on the genetic type of barite deposit. For instance, the Palaeozoic barites from Graz (Austria) belong to the synsedimentary volcanogenic type of barite deposit and have low $SrSO_4$ contents (0.6 to 1.6 wt%). Devonian barites of the same genetic type in Meggen and Rammelsberg deposits, also have low $SrSO_4$ contents (0.23–0.59 wt%). In contrast, barites of Bosnia and also those of the Brixlegg (BX) deposit in Austria and the Rudnany (RD) deposit in Slovakia are characterized by considerably higher $SrSO_4$ contents (0.9 to 5.01 wt% and 0.8 to 3.2 wt%, respectively), which are typical for hydrothermal epigenetic deposits. Extended ranges of $SrSO_4$ contents could be the result of partial remobilization processes during the Hercynian and Alpine orogeny.

5.4. $\delta^{13}C$ and $\delta^{18}O_{VPDB}$ of the main host-rock and neominerals

The $\delta^{13}C$ and $\delta^{18}O_{VPDB}$ values determined in neominerals of Devonian rocks hosting different barite deposits in Bosnia, have been compared with those being typical for primary Devonian dolomite, and are shown in Figs. 8a and 8b. In primary Devonian dolomite the typical $\delta^{13}C$ values range from +0.5‰ to +3‰ and the $\delta^{18}O_{VPDB}$ values between –3.5‰ and –7.0‰ (GRADSTEIN et al., 2006). Carbon and oxygen isotope values of all neominerals in the Devonian dolomites are shifted relative to these typical values toward lower values as clearly demonstrated in Fig. 8. This indicates a change in the isotopic characteristics of Devonian host rocks during mineralization and points to the epigenetic origin of barite deposits. The isotopic data of carbon and oxygen of previous investigators, (presented in Table 4), also suggests the same conclusion. The comparison of $\delta^{13}C$ and $\delta^{18}O_{SMOW}$ ratio in siderites from SEB and MBSM and those from the Brixlegg, Graz and Rudnany deposits are shown in Figs. 9a and 9b.

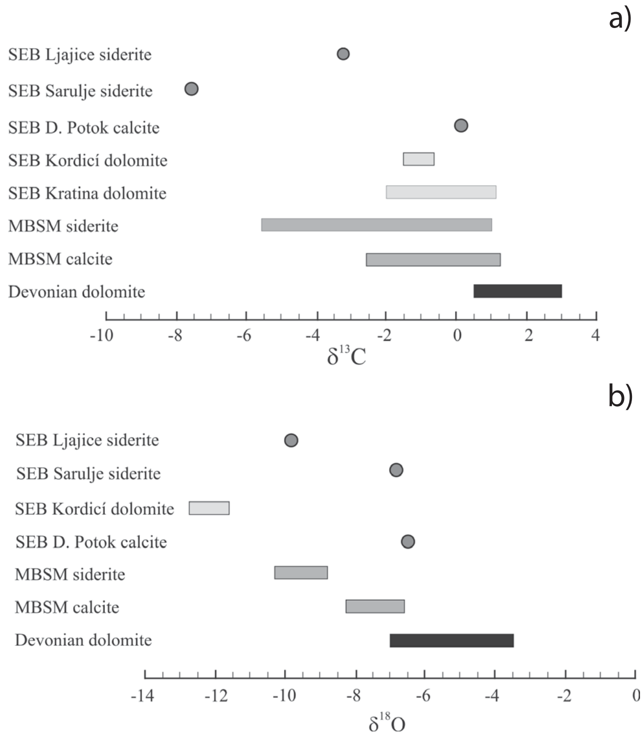

Figure 8: Comparison of $\delta^{13}C$ (a) and $\delta^{18}O_{VPDB}$ (b) values of neominerals in Devonian rocks hosting different barite deposits in Bosnia and those being typical for primary Devonian dolomite.

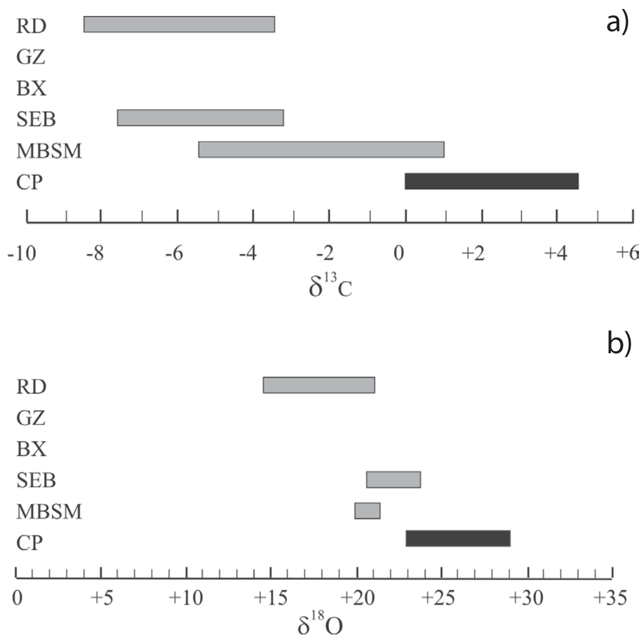

Figure 9: Comparison of $\delta^{13}C$ (a) and $\delta^{18}O_{SMOW}$ (b) values in siderites from SEB and MBSM and those from the Brixlegg, Graz and Rudnany deposits where CP = Typical Carboniferous-Permian values.

5.5. $\delta^{34}S$ in barites and sulphides

Most barite deposits in MBSM contain tetrahedrite as the sole ore mineral. Measured $\delta^{34}S$ values in 18 samples of Hg tetrahedrite in MBSM range from –5.50‰ to –15.40‰ (mean values –10.49‰). The $\delta^{34}S$ values in 3 pyrite samples from the same deposits are –0.7‰, –4.6‰ and –9.86‰ (ŠIFTAR, 1988, 1990). Distinctively, the tetrahedrite from the Trošnik (Fojnica) deposit, which has a minimal content of Hg, gave positive $\delta^{34}S$ values (+3.28‰ and +3.73‰), as did another sulphide mineral in this deposit (KUBAT et al., 1979/1980). The measurements of $\delta^{34}S$ values in antimonite in the Čemernica deposit gave +3.48‰, +2.12‰ and +2.21‰ and in sphalerite +3.71‰ (KUBAT et al., 1979/1980). Obviously, two different sulphur sources were included in the genesis of sulphide minerals in MBSM. The $\delta^{34}S$ values in barites are characterized relative to these sulphides by a significant enrichment of the heavy sulphur isotope (+10.1‰ to +16.8‰).

Hg-tetrahedrite also occurs in the barite deposits in SEB, but as a minor component. Its $\delta^{34}S$ values are also negative (–4.95%, Fočanska Jabuka). The main ore minerals are galena, sphalerite and pyrite, and chalcopyrite is subordinate. According to KUBAT et al. (1979/1980) the $\delta^{34}S$ values of these sulphides range from –0.5 to +4.5‰ (Table 6). Compared to these data, the $\delta^{34}S$ values in barites are enriched by heavy sulphur isotope (as in the barite deposits in MBSM).

Two isotopically different types of sulphide also occur in the Rudnany deposit. The main ore minerals are Hg-tetrahedrite and chalcopyrite, which have markedly negative $\delta^{34}S$ values (Fig. 10). In contrast, pyrite and cinnabar have positive $\delta^{34}S$ values (CAMBELL et al., 1985). According to ŽAK et al. (1991) and GRECULA et al. (1991) negative $\delta^{34}S$ values in tetrahedrite and chalcopyrite are consequences of isotope fractionation between H_2S, (derived from deep-seated fluids) and SO_4^{2-}, (derived from the Permian sea water).

In Palaeozoic strata of Graz, galena, sphalerite and pyrite occur, and they exhibit relatively high positive $\delta^{34}S$ values ranging from +2.5‰ to +13.2‰ (PAK et al., 1980). Data are not available for the Brixlegg deposit where Hg-tetrahedrite is the sole ore mineral and other sulphides only occur as accessory minerals $\delta^{34}S$. Analysis of tetrahedrite from Schwaz, Tyrol (obtained from Professor PROHASKA (Leoben) revealed a negative $\delta^{34}S$ value (–1.60‰).

Comparison of the sulphur isotopic composition in sulphide minerals from different barite deposits in SEB, MBSM, Graz and Rudnany is shown in Figs. 10a and 10b. Positive $\delta^{34}S$ values in sulphides of both barite deposits from SEB (Table 6) and polymetallic sulphide deposits from MBSM (KUBAT et al., 1979/1980), and also positive $\delta^{34}S$ values in barites from barite deposits in SEB and MBSM indicate that one of the sources of the sulphur in these deposits could be older Lower Palaeozoic stratiform volcano-sedimentary sulphide deposits. Studies of such a type of sulphide deposit were undertaken on the Lower Palaeozoic series of Gemericum in Slovakia. They revealed $\delta^{34}S$ values ranging between +2‰ to +15‰ (KANTOR & RYBAY, 1970; RADVANEC et al., 1992). There are still no measurements of $\delta^{34}S$ values in Lower Palaeozoic stratiform volcano-sedimentary sulphide deposits in the Dinarides.

Variscan metamorphism caused the circulation of hydrothermal fluids that remobilized sulphur from the Lower Palaeozoic and older stratiform volcano-sedimentary sulphide deposits and led to the formation of the younger sulphide deposits. The obvious enrichment of heavy sulphur isotopes in barites compared with those in sulphides in the barite deposits of both, SEB and MBSM, indicates retrograde Variscan metamorphism and influence of the sulphate derived sulphur from the Permian sea.

5.6. $\delta^{18}O_{VPDB, SMOW}$ in barites and fluid inclusions

The $\delta^{18}O$ values in barites in SEB (+14.2‰ to +15.6‰) are very similar to those in the Brixlegg and Rudnany barite de-

Table 6: Sulphur isotope data for sulphides in barite deposits of SEB (KUBAT et al.,1979/80)

Locality	Mineral	$\delta^{34}S$ (‰)
Ranoprge	galena	+3.04
	chalcopyrite	+2.49
	pyrite	+2.80
Kurjača	galena	+0.34
Šarulje	galena	+0.53
Kopilovo	galena	–0.41
	pyrite	+1.44
Goražde	stibnite	+1.21
	stibnite	+2.29
	stibnite	+4.26

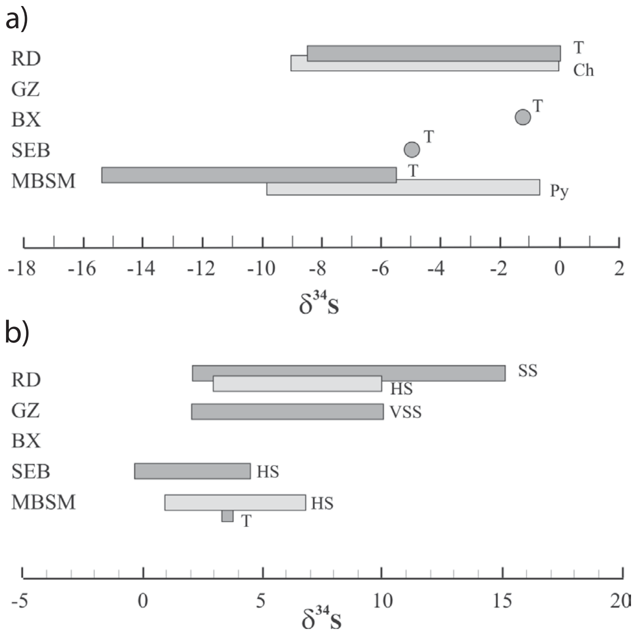

Figure 10: Comparison of $\delta^{34}S$ values in tetrahedrites and other sulphides from SEB, MBSM and those from the Brixlegg, Graz and Rudnany deposits where T = tetrahedrite, Ch = chalcopyrite, Py = pyrite, SS = sedimentary sulphides, HS = hydrothermal sulphides, VSS = volcanogenic-sedimentary sulphides.

posits (Fig. 7). Remarkably higher $\delta^{18}O$ values occur in barite samples from MBSM (+15.8‰ to +22.4‰). According to RAMOVIĆ E. (1991) the only fluid inclusion study in barite deposits in SEB was that of BLEČIĆ (1983), who discovered primary fluid inclusions in the barite in the Pb-Zn deposit in Ranoprge (Fočanska Jabuka) and determined T_h between +110ºC and +140ºC and a salinity of 10 wt% NaCl equ.

In the last 15 years, numerous fluid inclusion studies were carried out in ore deposits (mostly barite deposits) of Palaeozoic complexes in MBSM (PALINKAŠ & JURKOVIĆ, 1994; JURKOVIĆ & PALINKAŠ, 1999; STRMIĆ et al., 2000; PALINKAŠ et al., 2001; JURKOVIĆ & PALINKAŠ, 2002; PALINKAŠ et al., 2008). The results of all these studies demonstrated higher salinity 24.2 do 26.3 wt% NaCl equ. in Kreševo and 32.6 to 32.9 wt% NaCl equ. in Raštelica. Analyses of fluid inclusions of these authors in barites of barite deposits in MBSM revealed higher homogenisation temperatures (+210ºC to +310ºC in Kreševo area, +230ºC to 270ºC and 320º to +350ºC in the Raštelica deposit. There is a clear correlation between lower $\delta^{18}O$ values and lower T_h of fluid inclusions in barite deposits from SEB relative to higher $\delta^{18}O$ values and higher T_h of fluid inclusions in barite deposits from the MBSM. This is in agreement with the statement of HOEFS (1997) who stated that mineralisation fluids of higher temperature are characterized by higher salinity and higher $\delta^{18}O$ values. The process of barite mineralisation in the Brixlegg deposit took place at temperatures ranging from +70ºC to 130ºC (FRIMMEL, 1991). In Rudnany, (a vein ore deposit consisting of siderite, barite, tetrahedrite and chalcopyrite), the study of fluid inclusions determined T_h varying between +150ºC and +300ºC (RADVANEC et al., 2004).

5.7. Origin of the barium-strontium bearing hydrothermal fluids

The $^{87}Sr/^{86}Sr$ ratios determined in the barites (0.710972 to 0.714170) from both SEB and MBSM are high. The high Ba content and high $^{87}Sr/^{86}Sr$ ratio in the mineralisation fluid could be achieved by hydrothermal leaching of Rb-rich altered felsic rock. According to FRIMMEL & PAPESCH (1990) the high $^{87}Sr/^{86}Sr$ ratios are typical for fluids being connected to S-type magmatism and/or being crustal contaminated by circulation through Rb-rich clastites and extrusive magmatic rocks.

Until 1969 or 1972 respectively it was believed that the carbonate sequences of Jezero (Jajce) and Vranica Mountain were of Upper Carboniferous to Lower Permian age (KATZER, 1926). Rhyolitic magmatism occurred in the Middle and Upper Permian and partly in the Triassic (KATZER, 1926). JURKOVIĆ & MAJER (1954) found signs of contact metamorphism at the contact between the rhyolite and these carbonate rocks on the Vranica Mountain and Sinjakovo, concluding that the rhyolite is of Upper Carboniferous to Middle Permian age. MUDRENOVIĆ et al. (1969) however, found Silurian-Devonian conodonts in limestones in the Jezero area (Jajce). Based on Devonian fossils on the Vranica Mountain, however, the age boundary of rhyolite to Middle-Upper Carboniferous-Lower Permian has been revised (ŽIVANOVIĆ, 1972). According to HRVATOVIĆ (1996, 2006) rhyolites are the product of two stage volcanic activity. Most of them are synsedimentary with metasediments of presumed Silurian age. Some hypabyssal rhyolites intruded into Late Silurian and Early Devonian limestones, which also occur as xenoliths within the volcanic bodies. HRVATOVIĆ marked the Upper Permian as the upper boundary of rhyolite age, while he observed a large quantity of quartz-porphyry pebbles in basal breccias and conglomerates of discordant Upper Permian Formation of Kruščica Mt. The basal discordant breccias, with quartz-porphyry fragments, were previously observed by JEREMIĆ (1963). Petrological studies of the rhyolites of Sinjakovo and Vranica Mt. were undertaken by JURKOVIĆ & MAJER (1954) and MAJER & GARAŠIĆ (2001). JURKOVIĆ & MAJER (1954) determined the leucogranite or albite granitic character of the rhyolite magma. MAJER & GARAŠIĆ (2001) identified the peraluminous character of the rhyolite of Vranica Mountain (PI = 1.9–4.1). The low content of compatible trace elements and high contents of incompatible trace elements indicate a crustal magmatic origin. Additionally, the authors concluded that relationships between Rb, Y and Nb suggest a syncollisional origin of the rhyolite magma.

In the same sample of metarhyolite being studied by MAJER & GARAŠIĆ (2001) we determined an extremely high $^{87}Sr/^{86}Sr$ ratio (0.776995 ±2s), confirming the hypothesis of a crustal origin of the rhyolite magma. In Slavonian S-granites (Psunj, Papuk and Krndija Mountain), LANPHERE & PAMIĆ (1992) discovered that the $^{87}Sr/^{86}Sr$ ratio corresponds to a value of 0.72539±17, while in the Moslavačka Mountain it is 0.74302±5. An unusual spectrum of paragenetic types of ore deposits (JURKOVIĆ, 1956) supports the presence of an S-type granite in MBSM. Ore deposits of Ba and subordinately of Fe (barite, siderite, ankerite, pyrite and stibnite) dominate. All other ore deposits of Cu, Pb, Zn and As are very small and their minerals are subordinate to barite and siderite ore deposits. Metals, typical for I-type magma (Sn, W, Mo, F, B, Li) occur very rarely, only as occurrences of mineralogical importance.

5.8. Genetic model for the formation of the barite-sulphide deposits in the Palaeozoic complexes of MBSM and SEB

On the basis of geological and geochemical data comprising former investigations and data determined in this study, it can be concluded that barite ore deposits in SEB and MBSM had been formed by hydrothermal fluids,linked to magmatic and metamorphic processes and influenced by Permian seawater.

The following phases of hydrothermal mineralisation have been recognized in the SEB and MBSM area: a) Early Variscan phase which is not the subject of this study; b) Late Variscan phase which is responsible for the origin of barite ore deposits containing Fe-, Cu-, Zn-, Pb- and Sb- (As) sulphides with positive $\delta^{34}S_{CDT}$ values; c) Post-Variscan (Early Eoalpine) phase which affected the existing Late Variscan barite ± siderite ore deposits with mercury-bearing fluids associated with the processes of degassing of the Upper mantle, and leading to formation of Hg-, Ag- and Au-rich tetrahedrites showing negative $\delta^{34}S_{CDT}$ values. Degassing processes were linked to the early phase of the Permo-Triassic intercontinental rifting.

Late Variscan phase. In the whole of the Dinarides, barite ore deposits were formed in the late stage of the Variscan cycle and are located in the Upper Silurian, Devonian, Carboniferous and Permian rocks. Ore mineralisation in the clastites is usually present in the form of veins or impregnations, whereas in carbonate rocks it occurs as irregular bodies or replacement nests. Barite is the dominant mineral, quartz is subordinate and siderite and calcite occur only locally. Sulphides of Fe, Cu, Zn, Pb, Sb and As occur in very variable mutual relationships, ranging from trace amounts up to 10 %, but all have positive $\delta^{34}S$ values. The form of occurrence and geochemical data of the studied barite ore deposits indicate their epigenetic nature and origin, caused by circulation of hydrothermal fluids which were related to late stage Variscan metamorphism and magmatism and influenced by Permian seawater. The bulk of the Late Variscan barite ore deposits were formed most likely in Lower Permian time.

Most of the barite ore deposits in MBSM experienced processes of regeneration and remobilisation in the Post-Variscan stage. Only rare barite deposits have been partly or completely preserved. The Trošnik deposit is a very good example of a preserved type of barite ore deposit, located near Fojnica in the NE part of MBSM. It occurs in a pre-Devonian complex of rocks. The paragenesis of the deposits contain pyrite and chalcopyrite as the main minerals, whereas siderite and quartz occur as gangue minerals. Sb- and Fe-rich tetrahedrite occurs too, but contains only traces of Hg and has positive $\delta^{34}S$ values (+3.23‰ to +3.73‰, KUBAT et al., 1979/1980). A very similar result (+4.0‰) was produced in the current analysis of this tetrahedrite.

Barite ore deposits in SEB, however, have been almost completely preserved in their primary state. They are small but numerous, characterized by Fe-, Cu-, Zn-, Pb- and Sb-sulphides, but do not contain Au, only small amounts of Ag. A post-Variscan overprint characterized by the formation of Au-, Hg-tetrahedrite having negative $\delta^{34}S$ values (–4.95‰) is only locally present (Fočanska Jabuka, Šarulje).

Geochemical differences between barite ore deposits in MBSM and SEB are summarized in Table 7. Monosulphide Hg-tetrahedrite barite ore deposits in MBSM differ from polysulphide barite ore deposits in SEB in having: a) more positive $\delta^{18}O$ values in barites, b) lower $\delta^{34}S$ values in barites, c) pronouncedly negative $\delta^{34}S$ values in Hg-tetrahedrite, d) significantly higher homogenisation temperature and higher salinity in fluid inclusions of barites, quartzes and fluorites.

Regarding the connection of other ore deposits in Dinarides with the Late Variscan phase, it should be emphasized that at the end of the Lower Permian, continental or shallow marine clastic sediments of the Grödener Formation were formed under a warm arid climate. These sediments are widespread in the Dinarides and are according to JURKOVIĆ & PALINKAŠ (1996) bearers of uranium (Žirovski Vrh, Slovenia), copper (Cerkno-Sava Fold, Slovenia; Vitez-Ustiprača, Monte Negro) and low manganese haematite ore deposits (Mokronog-Hrastno, Slovenia; Rude, Croatia; Bukovica, Croatia). These deposits are described by DROVENIK et al. (1980), ŠINKOVEC (1971), ČOP et al. (1998), and KULENOVIĆ (1987). The Middle Permian sediments grade upwards into the Upper Permian shallow marine evaporite and carbonate sediments, (the Bellerophon Formation), or locally into the Sabkha transition zone or continental red beds. An early diagenetic Sabkha type deposit is described by PALINKAŠ et al. (1993). Most of the Upper Permian evaporites occur on tectonic lines along the Una, Sana, Vrbas and Bosna rivers, and in the Mostar, Sinj, Knin and Drniš areas. Upper Permian evaporites are characterized by a mean $\delta^{34}S$ value of + 11‰ (JURKOVIĆ & ŠIFTAR, 1995).

The post-Variscan/ Eoalpine phase. Strong magmatic activity (rhyolites, keratophyres, diabases) took place during the Permian period, especially in the Asslian-Sakmarian stages. PAMIĆ et al. (2004) using K-Ar method determined the age of metadiabase (287.8 ± 11.1 Ma) and ortho-greenschist (268.7 ± 10.2 Ma) at Bradine (Ivan Mt., MBSM) and connected their results to post-Variscan magmatism. Using the same method on the same rock types, the authors determined a cooling phase which lasted until the Triassic (247.0 ± 9.5 Ma; 238.4 ± 9.2 Ma). The results support the heating event during Upper Permian time in the MBSM.

Heating of some parts of the crust in the Dinarides during the Middle/Upper Permian enabled lateral (extensional) movements of the continental crust and the rise of upper mantle fluids. The optimum geotectonic environments in the

Dinarides developed along a Permo-Triassic intracontinental rift. Contemporaneously, former Late Palaeozoic faults, the western Voljevac fault and eastern Busovača fault, as well as a dense framework of faults of lower order between them, had been reactivated. The geotectonic conditions facilitated penetration of mercury (± fluorine)-bearing fluids from deep levels of the Upper mantle to higher levels of the crust. KARAMATA et al. (1995) emphasized that the highest concentration of mercury in former Yugoslavia occurred in the Triassic mineralization of the Dinarides (mercury deposits Idrija, Tršće, Spič, Draževići, Kovač Mt). Independently of this statement, JURKOVIĆ & PALINKAŠ (1996) wrote "Fluorine and mercury bounded to the Hg-tetrahedrite in the MBSM were probably derived at least partially from the uppermost zone of the mantle". On their way to upper levels fluids passed through Upper Proterozoic and Caledonian Au- and Ag- bearing ore deposits, and Hg being present in fluids amalgamated with the Au and Ag. At still higher levels, these fluids reached barite ore deposits being formed in the Late Variscan phase. There, most of the primary sulphides have been fluidized, and a new mineral, Hg- tetrahedrite, rich in Au (10–50 g/t) and Ag (1000 do 3000g/t) was formed.

Results of 183 mercury-bearing minerals analysed from the ore deposits of the Dinarides suggested the conclusion that isomorphic substitution of mercury into the host minerals decreased in the following order: sphalerite → tetrahedrite → gold/silver → pyrite → galena → realgar → antimonite (KARAMATA et al., 1995). This is in agreement with the situation in the MBSM.

Strongly negative $\delta^{34}S$ values of Hg-tetrahedrite in MBSM ore deposits were explained by remobilization of isotopically light sulphur of biogenic origin from the Middle/Upper Permian stratiform U-Cu (±Fe) ore deposits in the Dinarides and/or from older similar genetic types of ore deposits. The role of isotope fractionation between ascending deep-seated H_2S and descending SO_4^{2-} from Permian seawater is not excluded.

The early phase of intracontinental rifting: Controversial opinions exist concerning the beginning of the Alpine cycle. CASSINIS et al. (1975) and WOPFNER (1984) considered that the hiatus between the Lower and Middle Permian sedimentary cycles separates the Variscan cycle from the overlying Alpine cycle. KRAINER (1993) considers the rifting processes during the Middle Triassic as indicating the beginning of the Alpine cycle.

The contemporaneous nature of the early phase of the intracontinental rifting and the beginning of the Alpine cycle in the Dinarides is emphasised here, because the Permian/Triassic boundary (251 Ma) has a well documented suite of

Table 7: Summarized geochemical data from barite ore deposits in SEB and MBSM.

Geochemical data	Ore area	n	Late Variscan	n	Post Variscan/Eoalpine	Authors
T_h (homogenisation temperature)	SEB		+110°C to +140°C			BLEČIĆ (1983)
	MBSM				+190°C to +140°C (Kreševo) +210°C to +250°C ; +320°C to +350°C (Raštelica)	PALINKAŠ & JURKOVIĆ (1994) STRMIĆ et al. (2000)
salinity wt% NaCl equ.	SEB		~ 10 wt%			BLEČIĆ (1983)
	MBSM				24.2 to 32.9 wt%	PALINKAŠ & JURKOVIĆ (1994) STRMIĆ et al. (2000)
% $SrSO_4$ in barites	SEB	6	1.03 to 5.93 (2.73)%			this work
	MBSM			1 23	3.03 % 1.60 to 6.60 (4.22)%	this work JURKOVIĆ et al. (1997)
$\delta^{34}S_{CDT}$ in barites	SEB	7	+11.6 to +17.7 (+14.61) ‰			this work
	MBSM			10	+10.1 to +16.8 (+11.80) ‰	this work
$\delta^{18}O_{VSMOW}$ in barites	SEB	7	+14.2 to 15.6 (+14.7) ‰			this work
	MBSM			10	+15.8 to +22.4 (+18.50) ‰	this work
$\delta^{34}S_{CDT}$ in tetrahedrites	SEB	1	–4.95 ‰			KUBAT et al. (1979/80)
	MBSM			18	–5.5 to –15.4 (–10.49) ‰	JURKOVIĆ et al. (1997)
$\delta^{34}S_{CDT}$ in Fe-Cu-Zn-Pb-Sb sulphides	SEB	10	–0.41 to +4.26 ‰			KUBAT et al. (1979/80)
	MBSM				–4.55 ‰	JURKOVIĆ et al. (1997)
$\delta^{13}C_{VPDB}$ in neocarbonates	SEB	3	–7.60 to +0.19‰			this work
	MBSM				+1.20 to –5.50 (–2.12) ‰	JURKOVIĆ et al. (1997)
$\delta^{18}O_{SMOW}$ in neocarbonates	SEB	3	+20.7 to +24.2 ‰			this work
	MBSM				+23.7 to +29.1 ‰	JURKOVIĆ et al. (1997)
$^{87}Sr/^{86}Sr$ ratio	SEB	2	0.710972 and 0.714170			this work
	MBSM			2	0.711764 and 0.712548	this work

chemical evidence supported by global correlation (GRADSTEIN et al., 2006). The most important are as follows:

a) an extraordinarily fast rise in the $\delta^{34}S$ of sea water sulphate, ranging from +8 up to +12‰ to +20 up to +29‰ between the Middle and Upper Lower Triassic (245 Ma) termed the "Roet event" (NIELSEN, 1965; RICK, 1990);

b) global cooling and the beginning of mass extinction coincide with the remarkable increase in $^{87}Sr/^{86}Sr$ values from 0.7068 to 0.7080 from the end of the Capitanian (260Ma) to the Upper Permian-Lower Triassic boundary (251 Ma) (MARTIN & MACDOUGALL, 1995). KORTE et al. (2003) consider that this event may be a response to increased continental weathering following glacial climates of the early Permian.

c) The end-Permian mass extinction coincides with an abrupt negative shift of 4% in values of carbon isotopes in marine and terrestrial settings, probably caused by decreased marine production and an influx of light carbon from volcanic, soil-carbon or a methanogenic source (SEPHTONE et al, 2002). The Triassic period begins just after this carbon minimum (ERWIN, 1995)

d) large scale global shifts to higher $\delta^{18}O$ values in carbonates indicate a general progressive change from the Late Permian through the Triassic and are interpreted as the result of cooler sea water or a glacial episode suggesting a total cooling of 4°C in tropical seas (WALLMAN, 2001).

6. CONCLUSION

Geochemical investigations of barites revealed:

(1) Trace element compositions in barites from both area (SEB and MBSM) are very similar indicating a unique ore bearing area with the influence of seawater on hydrothermal barite origin.

(2) Barites of both areas show elevated Sr content (0.48 to 2.83% in barites from SEB, 1.44% in barite from MBSM), typical for epigenetic hydrothermal barite ore deposits. The Sr substitues for Ba in the crystal lattice.

(3) The $^{87}Sr/^{86}Sr$ isotope ratios in the barites of both areas are similar (0.710972 and 0.714170 in barites from SEB, 0.711764 and 0.712548 in barites from MBSM) and are more radiogenic in comparison with values which characterize coeval seawater, rocks and fossils from Lower Cambrian to Upper Permian (0.70680 to 0.70925). This also indicates an epigenetic hydrothermal origin of barite ore deposits.

(4) Very high $^{87}Sr/^{86}Sr$ isotope ratio (0.776995) determined in a rhyolite sample from Vranica Mt. (MBSM) confirms the origin of rhyolite magma by crustal anatexis.

(5) The $\delta^{13}C$ and $\delta^{18}O$ values in calcite, dolomite and siderite of barite ore deposits are shifted toward lower values relative to typical values occurring in Devonian host rock, also indicating an epigenetic origin of barite ore deposits.

(6) The $\delta^{18}O$ values in barites in SEB (+14.2‰ to +15.6‰) are remarkably lower than $\delta^{18}O$ values of barite samples from the MBSM (+15.8‰ to +22.4‰). This can be explained by a lower temperature and lower salinity of mineralisation fluids in barite ore deposits of SEB (HOEFS, 1997).

(7) The barite ore deposits of SEB are characterized by $\delta^{34}S$ values which are positive (+11.6‰ to +17.7‰) and enriched in heavy sulphur isotope in barites in comparison with sulphides (–0.41 to +4.26‰), and negative in tetrahedrite (–4.95‰). This indicates three different sulphur sources for barite ore deposits in SEB. The same is true for $\delta^{34}S$ values in barite ore deposits of MBSM (+10.1 to +16.8‰ in barites, –9.86 to –0.71‰ in pyrites, –5.50 to –15.40‰ in tetrahedrites). The source of heavy sulphur isotope in Fe, Cu, Zn, Pb, Sb sulphides and in barites is deep seated, linked to Caledonian, Neoproterozoic and Early Palaeozoic sulphide deposits. The $\delta^{34}S$ values of barites of the Late Variscan deposits have been influenced by Permian sea-water sulphate. This influence was stronger in the barites of the post-Variscan phase. In contrast the very light sulphur isotope in Hg-tetrahedrites is probably of biogenic origin and/or a consequence of isotope fractionation between H_2S derived from deeper seated upper mantle fluids and SO_4^{2-}, derived from the Permian evaporites.

(8) In both ore areas of Bosnia, SEB and MBSM, two paragenetic types of barite ore deposits were determined. The older type originated in the Late Variscan phase (Lower Permian) and the younger one in the Post Variscan/Early Eoalpine phase. The older type of barite ore deposit contains more than 90% barite, small amounts of quartz, locally siderite and calcite, and polysulphides (Fe-, Cu-, Pb-, Zn- and Sb(As)–sulphides), the amount of which depends on the host rock (5–10% in clastites, 1–2% in carbonate rocks). This type dominates in SEB, and very rarely shows signs of the Post-Variscan overpint. In the MBSM area, it only occurs in the Trošnik deposit and partly altered in the Jezero area (Jajce). All other barite ore deposits in MBSM (Kreševo, Kiseljak, Zec and Pogorelica Mt., Gornji Vakuf, Medenik) were overprinted during the Post-Variscan phase and have the genetic characteristics of a younger regenerated type of barite ore deposit. The younger type of barite ore deposit is characterized by monosulphide (Au-, Ag- and Hg-rich tetrahedrite). Other sulphides, mainly Cu-sulphosalts, only occur in trace amounts. This tetrahedrite has been formed by regeneration and fluidization of sulphides of older types of barite ore deposit with a supply of Hg, Au, Ag and F from the mantle and/or amalgamation of Au and Ag from Caledonian and older ore deposits. The younger type of barite ore deposit occurs only sporadically in SEB (Fočanska Jabuka) and then as younger barite veins and nests with Hg tetrahedrite having negative $\delta^{34}S$ (–4.95‰).

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