

Geochemical characteristics of mercurian tetrahedrite, barite and fluorite from the Duboki Vagan, Glumac and Dubrave-Dugi Dol barite deposits, south of Kreševo, Mid-Bosnian Schist Mts.



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ABSTRACT

The geochemical characteristics of tetrahedrite and barite of the Duboki Vagan barite deposit near the town of Kreševo in the MBSM (Mid-Bosnian Schist Mountains) have been determined and correlated with the results of previously studied barite, from the adjacent Glumac deposit, and fluorite, from the Dubrave-Dugi Dol barite deposits. The studied tetrahedrite is characterized by a high content of Au (39 ppm) and Ag (>300 ppm), the presence of Co (63.5 ppm), Ni (266.2 ppm) and Cd (313.6 ppm) in the crystal lattice and negative $\delta^{34}\text{S}_{\text{CDT}}$ values (–11.80‰). On the plot of its C1 chondrite-normalized REE abundances, a slightly expressed positive Eu anomaly and high HREE concentrations are observed. The high content of SrSO_4 (2.33 to 3.42 wt.%) in the barite crystal lattice indicates hydrothermal parent solutions. The $\delta^{34}\text{S}_{\text{CDT}}$ values of the studied barite are +10.40‰, which is typical for Permian seawater and its $\delta^{18}\text{O}_{\text{SMOW}}$ values range between 15.6 and 17.7‰. A distinct positive Eu anomaly is shown on the plot of the C1 chondrite-normalized REE abundances in barite. Geochemical characteristics of the studied tetrahedrite and barite of Duboki Vagan are very similar to those of previously investigated Glumac and Dubrave-Dugi Dol barite deposits. The fluorite from the Dubrave-Dugi Dol deposits displays a negative Eu anomaly and its Tb/La and Tb/Ca ratios indicate a quite different origin in relation to barite formation. This is all in the accordance with the possible existence of two different paragenetic types of barite deposits in the MBSM and SEB (Southeastern Bosnia), which significantly differ in the $\delta^{18}\text{O}_{\text{SMOW}}$ ranges of their barites and $\delta^{34}\text{S}_{\text{CDT}}$ values of their sulphides. The first type of barite deposits originated in the Late Variscan phase (Lower Permian). It is characterized by numerous Cu, Fe, Zn, Sb, As, Pb sulphides and Cu-Sb-tetrahedrite without mercury, all having positive $\delta^{34}\text{S}_{\text{CDT}}$ values (0 to +5 ‰). Early intercontinental rifting took place between the uppermost Permian and Lower Triassic and enabled, in a great number of barite deposits, (especially in the MBSM), remobilization and partial fluidization of their Fe, Cu, Zn, Sb and Pb sulphides which reacted with ascended mercury, sulphur and fluorine rich mantle fluids and resulted in the formation of Hg-tetrahedrite and octahedral fluorite. These processes caused the occurrence of the second paragenetic type of barite deposit with Hg-tetrahedrite as the main ore mineral, but characterized by strongly negative $\delta^{34}\text{S}_{\text{CDT}}$ values.

Keywords: Paleozoic, Mid-Bosnia, Hg-tetrahedrite, barite, fluorite, stable isotopes (S, C and O), trace elements, REE, genesis

1. INTRODUCTION

In the Mid-Bosnian Schist Mountains (MBSM) and South-eastern Bosnia (SEB) two completely different paragenetic types of barite deposits occur. Small amounts (<10%) of diverse sulphides (pyrite, chalcopyrite, sphalerite, galena, arsenopyrite and tetrahedrite without mercur) occur with barite in the first type. The second type of barite deposit is almost monosulphidic containing only Hg-tetrahedrite. There is a remarkable geochemical difference between the sulphides of these two types of barite deposits. All sulphides of the first type are characterized by positive $\delta^{34}\text{S}_{\text{CDT}}$ values (0 to +5‰), whereas the Hg-tetrahedrite of the second type contains negative $\delta^{34}\text{S}_{\text{CDT}}$ values (−4.95 to −15.40‰). Additionally, JURKOVIĆ et al. (2010), found that the $\delta^{18}\text{O}_{\text{SMOW}}$ values in barite of the first polysulphide type are significantly lower (+14.2‰ to +15.6‰) than the $\delta^{18}\text{O}_{\text{SMOW}}$ values in barite from the second monosulphidic Hg-tetrahedrite type (+15.8‰ to +22.4‰). Such differences can be explained by lower temperature and lower salinity of mineralisation in the first type of barite deposits JURKOVIĆ et al. (2010). These authors state that the first polysulphide paragenetic type of barite deposits originated in Late Variscan phase (Lower Permian). The second one originated in Post Variscan/Early Eoalpine phase due to the exposure of the first barite deposit type to the impact of early intercontinental rifting (JURKOVIĆ et al., 2010).

The aim of this work is to investigate the geochemical characteristics of the tetrahedrite and barite of the Duboki Vagan barite deposit near Kreševo in the MBSM, correlate them with the results of previously studied barite from the adjacent Glumac deposit and fluorite from the Dubrave-Dugi Dol barite deposits. In addition a broad comparison of these results with geochemical characteristics of the other barite deposits in the MBSM and SEB will be made.

2. GEOLOGY AND PARAGENESIS OF THE BARITE DEPOSITS

2.1. Geology

The Duboki Vagan, Glumac and Dubrave-Dugi Dol barite deposits occur in the area which surrounds the town of Kreševo and belongs to the Mid-Bosnian Schist Mountains (MBSM). According to JOVANOVIĆ et al. (1977, 1978), rocks of Palaeozoic and Triassic age have been recognized in this area. The lowermost part of the Palaeozoic sequences includes chlorite and muscovite schists, phyllites and argillaceous schists, quartzites and lidites. The overlying dolomites, dolomitic limestones and marbles are found to be Devonian in age (SOFILJ et al., 1980). Magmatic rocks occur as porphyrites forming sills within chlorite and muscovite schists, and as quartz porphyry and keratophyre extrusions being situated on the verge of the Devonian carbonate complex (JURKOVIĆ, 1987). The youngest Palaeozoic sediments consist of conglomerates, sandstones, phyllites with Permian flora and brecciated limestones (JURKOVIĆ, 1987). The Lower Triassic is represented by sandstones, clay-like

schists, marls and rare limestones, while the Middle Triassic is composed of dolomites and limestones. The lower Ladinian horizons consist of sandstones, hornstones, marls, clay-like schists and rare limestones, whereas limestones dominate in upper Ladinian horizons (JURKOVIĆ, 1987). The geological relationships between the Lower Palaeozoic metamorphic complex and the overlying (<300 m thick) carbonate complex are not clear. The occurrence of barite deposits is exclusively related to the Upper Silurian – Devonian metaclastites and dolomites (Fig. 1).

2.2. Duboki Vagan

The northern border of the Duboki Vagan ore deposit runs 1 km south of the town of Kreševo and its southern limit is 4 km south of Kreševo (Fig. 1). The Duboki Vagan lies at absolute altitudes of +800 to +1000 m. Barite is the main ore mineral (50–75% of the ore mass), while pyrite and Hg-tetrahedrite (2–3%) are subordinate ore minerals. Quartz is the main gangue mineral (25–33% of the ore mass), followed by subordinate siderite (which is strongly oxidized into goethite). Octahedral fluorite is an accessory mineral. The deposit is hosted by the Devonian dolomite, intruded by a large mass of metarhyolite (1–2 km²) which crystallized from an S-type granitoid magma (JURKOVIĆ et al., 2010).

The Duboki Vagan deposit lies in a large, 20 m deep karstified depression. The bottom of the depression is filled with rubble and blocks of siliceous barite which represented gangue from an earlier time. Part of this material comes from mining operations, but part is the residue left by the weathering and leaching out of the ore-bearing Devonian dolomite. The ancient miners removed only cinnabar, which was necessary for the amalgamation of gold from Hg-tetrahedrite, and limonite used in the production of iron.

In recent times the old dumps and elluvial deposits have been worked over and barite recovered. This clearing up has afforded a better view of the morphology of the Duboki Vagan barite deposit. The ore bodies are irregular seams running NW–SE, 1–1.5 m thick, dipping towards the NE, but there are also satellite barite veins. Recently, MIKO performed a quantitative chemical analysis of one Hg-tetrahedrite sample from the Duboki Vagan deposit (JURKOVIĆ & MIKO, 1997) which determined the weight % composition of: 37.53 Cu; 1.09 Fe; 4.69 Zn; **0.129 Ag**; **2.45 Hg**; 1.41 As; 24.25 Sb; 0.20 Bi; 25.03 Ws; 154.50 ppm Au ($\Sigma = 97.70$ wt.%).

2.3. Dubrave-Dugi Dol

Dubrave-Dugi Dol barite deposits are located ~ 1 km south-east of Međuvršje summit (+1195 m) and 3 km southeast of Kreševo. According to JURKOVIĆ & MIKO (1997), the ore is hosted in dolomite of Devonian age and occurs as irregular nests, lense-shaped veins, networks of veinlets or as breccias in tectonically dislocated dolomites. These authors also noted significant allochthonous residual barite deposits on a karstified dolomite relief. A detailed description of the mineral paragenesis was given by JURKOVIĆ (1987). He pointed out that the main mineral is barite, Hg-tetrahedrite is the

most frequent sulphide at 1–5 wt.%, whereas pyrite, chalcocopyrite I and II, and two unidentified copper sulphosalts, colloform pyrite and goethite are accessories. Hg-tetrahedrite replaces barite grains along margins and fine fissures (JURKOVIĆ, 1987). Quartz I and II occur as gangue minerals, as does transparent fluorite, being violet or colourless, and scarce leaves of sericite and rutile (JURKOVIĆ, 1987). Quantitative chemical analyses of the Hg-tetrahedrite sample from the Dubrave-Dugi Dol ore deposits, performed by MIKO (JURKOVIĆ & MIKO, 1997), is expressed (wt%) as: 40.62 Cu; 2.63 Fe; 3.81 Zn; **0.29 Ag**; **0.33 Hg**; 1.98 As; 25.44 Sb; 0.06 Bi; 24.78 S; 8.30 ppm Au ($\Sigma = 99.94$ wt.%).

2.4. Glumac

The Glumac barite deposits are situated at elevations of 800 to 920 metres above sea level on the northern side of Međuvršje mountain and ~1 km south of Kreševo. Ore bodies occur in different forms (nests, veins, irregular bodies, ore breccias), and are usually very irregular (JURKOVIĆ, 1987). The main mineral is barite, whereas calcite, ankerite, fluorite, neodolomite, Hg-tetrahedrite, pyrite and quartz are subordinate (JURKOVIĆ, 1987). Chemical analysis of the Hg-tetrahedrite sample from Glumac–Vidici location, which is a part of Glumac barite occurrences, indicated the following composition (wt%): 40.26 Cu; 4.15 Fe; 1.22 Zn; **0.20 Ag**; **1.83 Hg**; 2.73 As; 24.89 Sb; trace Bi; 24.22 S; 0.20 LOI; 13.40 ppm Au, $\Sigma = 99.70$ wt.% (JURKOVIĆ, 1987).

3. RESEARCH HISTORY

The first data on ore deposits and mining works in the area of Duboki Vagan come from WOLF (1847). These deposits were later investigated by CONRAD (1870), HERBICH (1880, 1880a), VOGT (1880), WALTER (1887), KATZER (1907), JURKOVIĆ et al. (1951), JURKOVIĆ (1956, 1958), JEREMIĆ (1963), MIKOLJI (1969), JOVANOVIĆ et al. (1977), JURKOVIĆ (1987, 1988), JURKOVIĆ et al. (1997) and JURKOVIĆ & MIKO (1997).

JURKOVIĆ (1956, 1988) produced the first detailed ore paragenesis from the Duboki Vagan deposit and identified the genetic position of this type of ore deposit in the MBSM. He established hypogenic and hypergenic parageneses. The hypogenic paragenesis includes barite, quartz I, siderite, pyrite, ankerite, Hg-tetrahedrite, sericite, kaolinite (?), fluorite and quartz II. The hypergenic paragenesis consists of goethite, lepidocrocite, “basic sulphates”, cinnabar, malachite, azurite, elemental gold, manganomelane, pyrolusite and chalcedony.

Examination of the waste heaps and elluvial material has revealed that barite is the main mineral, with significant quantities of quartz, lesser amounts of pyrite, significantly less Hg-tetrahedrite (exploited by Roman and medieval miners), and a considerable quantity of Au-Ag-bearing limonite.

KATZER (1907) determined the approximate relationship of the main minerals: 40.2% barite, 32.6% quartz, 2.4% tetrahedrite, 0.8% Cu and 24.8% soluble matter what is equal 100.8% in total.

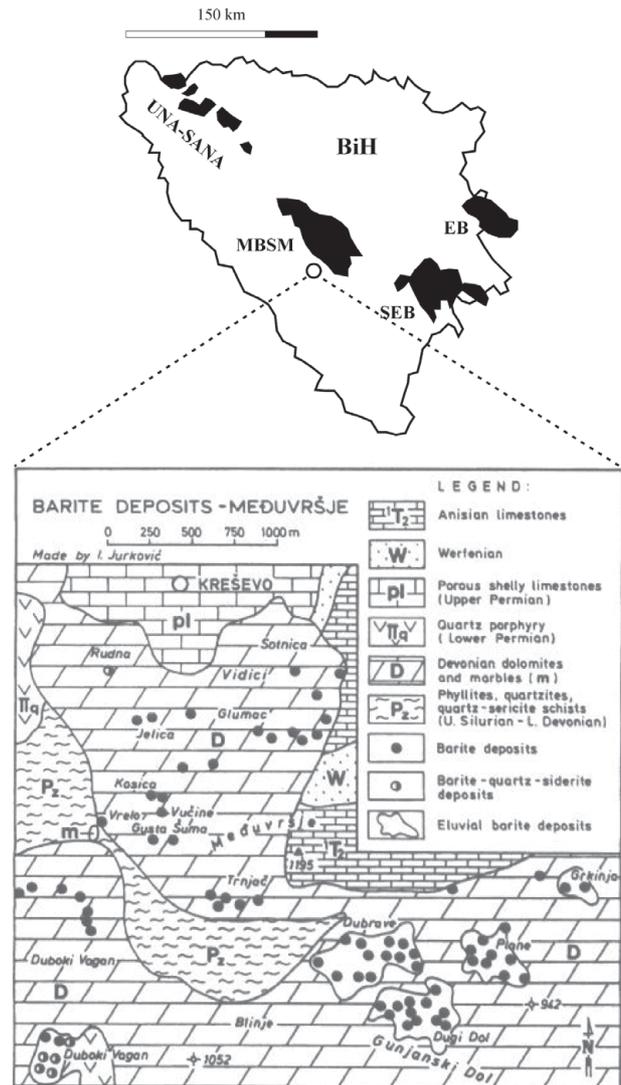


Figure 1: Geological map of the Duboki Vagan, Glumac and Dubrave-Dugi Dol barite deposits, south of Kreševo, Bosnia (modified from JURKOVIĆ, 1987).

JURKOVIĆ et al. (1997) presented the first geochemical data of barite and tetrahedrite from the Duboki Vagan barite deposit (see Tables 1 and 3).

4. ANALYTICAL METHODS

The quantitative chemical analysis of Hg-tetrahedrite (D-VAGT sample) was performed by Acme Analytical Laboratories, Vancouver Ltd., Canada (Table 1). The trace element content of Hg-tetrahedrite (D-VAGT sample) and barites (VAG and DUV samples) was analysed by inductively coupled plasma (ICP) mass spectrometry in the same laboratory (Tables 2 and 3).

The isotope composition of sulphur in the Hg-tetrahedrite (D-VAGT), oxygen in barite (VAG) and sulphur and oxygen in barite (DUV) were determined in the Stable Isotope Laboratory of the University of Laussane, Swiss, using a Finnigan Mat Facility (Table 4).

The chemical composition of Hg-tetrahedrite from the Duboki Vagan barite deposit was determined by Slobodan MIKO (in JURKOVIĆ & MIKO, 1997) by atomic absorption spectrometry (AAS) and by ICF-AES after Br-HCl digestion (Table 1).

Two clear fluorite crystals from the Dubrave-Dugi Dol barite deposits were analysed 15 years ago by INAA (Instrumental Neutron Activation Analysis) in the Institute for Petrology and Geochemistry, Karlsruhe University, Germany (PALINKAŠ & JURKOVIĆ, 1994).

5. RESULTS

5.1. Hg-tetrahedrite

The analysed Hg-tetrahedrite (sample D-VAGT) from Duboki Vagan was very fine-grained, densely dispersed in the

Table 1: Quantitative chemical analyses of fresh and weathered Hg-tetrahedrites (D-VAGT) from the Duboki Vagan barite deposit expressed in wt. %. Abbreviations: n.a. – not analysed; REE – rare earth elements; Tr. El – other trace elements; m.a. – mechanical admixtures. Column 2 – analysis of the Hg-tetrahedrite in the sample D-VAGT. Column 3 – recalculated analysis from the column 2 (elimination of the mechanical admixture).

	D-VAGT		D-VAGT	
	tetrahedrite	tetrahedrite	Mechanical admixtures in tetrahedrite	
	JURKOVIĆ et al., 1997	this work	this work	
	wt.%	wt.%	wt.%	
Cu	37.93	36.860	CaCO ₃	1.3734
Fe	1.09	0.520	BaSO ₄	1.2970
Zn	4.69	4.130	SrSO ₄	0.0470
Cd	n.a.	0.031	Pb	0.0200
Ag	0.13	>0.030		
Hg	2.45	3.795	Total	2.7374
Ni	n.a.	0.027		
Co	n.a.	0.006		
W	n.a.	<0.005		
Sn	n.a.	ppm <1.0		
Sb	24.75	15.760		
As	1.41	1.510		
Bi	0.20	0.147		
Tot/S	25.05	16.80		
Se	n.a.	ppm <0.5		
Au	ppm 0.0154	ppm 0.0039		
Tot/C	n.a.	0.61		
PO43-	n.a.	0.0399		
REE	n.a.	0.0015		
Tr. El.	n.a.	0.0010		
m.a.	n.a.	2.7374		
Total	98.3104	100.2159		

gangue consisting of barite, quartz and calcite. Tetrahedrite grains were carefully handpicked under a binocular microscope. The chemical analysis revealed that it is a mercury-bearing Cu-Sb-Zn tetrahedrite, strongly weathered, containing ~2.73 wt.% of mechanically admixed barite, (which has 3.425 wt.% SrSO₄ built into its crystal lattice), calcite and galena (Table 1). Co (63.5 ppm), Ni (266.2 ppm) and Cd (313.6 ppm) were detected in the crystal lattice of the tetrahedrite for the first time in the MBSM (Table 1). These elements, together with Bi, W, Sn and Se, are constituent elements in the tetrahedrite crystal lattice (DUDA et al., 1987). Their concentrations so far in analysed barite samples, (7 from the MBSM and 6 from the SEB), were mostly below minimal detection limits (MDL) and only rarely around MDL. This suggests that the presence of admixed barite in the analysed sample could only inconsiderably influence the abundance and distribution of trace elements in the Hg-tetrahedrite.

Very high values of Au (39 ppm) and Ag (>300 ppm) were found in this tetrahedrite (Table 1).

Standard trace element analysis including 22 elements shows the presence of only 10 elements (Rb, Ta, U, Zr, Y, Mo, Pb, Bi, Sr and Ba) in tetrahedrite, while 12 of them (Be, Sc, Cs, Ga, Hf, Nb, Sn, Th, V, W, Tl and Se) were below MDL (Table 2).

The total sum of the rare earth elements (REE) in the studied tetrahedrite is only 15.03 ppm although all 14 REE were analysed (Table 3). La shows by far the highest concentration (10.6 ppm) and the ratios of La_N/Yb_N (27.11) and ΣLREE / ΣHREE (5.530) indicate enrichment of the total LREE against the total HREE. But, excluding La, the LREE_N are depleted with regard to the HREE_N as clearly shown in the plot of REE normalized to CI chondrite values (SUN & McDONOUGH, 1989) presented in Fig. 2. The REE pattern is characterized by a pronounced positive Eu anomaly (Eu/Eu* = 2.48) and expressed as a negative Ce anomaly (Ce/Ce* = 0.220).

The δ³⁴S_{CDT} value of the investigated tetrahedrite sample is strongly negative: -11.8‰. (Table 4).

5.2. Barite

Table 2 presents the values of 30 analysed trace elements of both barite samples (VAG and DUV) taken from the Duboki Vagan barite deposit.

The group of elements between Be and Y consist of 17 elements but only Ni, Hf, Ta, W and Y were detected in both barite samples. Additionally, Ga, U and Zr were also found in the VAG sample. The values of 8 other trace elements of this group (Be, Co, Sc, Cs, Nb, Sn, Th and V) were below the MDL. The total content of the Be-Y trace element group is very low in both barite samples (<24.8 ppm in the VAG sample and <16.2 ppm in the DUV sample).

In the second group of 13 trace elements between Mo and Se only 5, (Cu, Zn, As, Sb and Hg) were detected in analyses of both barite samples. Pb and Tl were only found in the VAG sample, while Au (0.9 ppb) is present only in the

Table 2: Trace element content of Hg-tetrahedrite (D-VAGT) and barite (VAG, DUV and K-GLU) from the barite deposits, south of Kreševo. D-VAGT, VAG and DUV samples are from the Duboki Vagan deposit, while K-GLU sample is from the Glumac deposit. Data for K-GLU sample are from JURKOVIĆ et al. (2010). All values are in ppm, except those of Au, which are in ppb.

Elem.	D-VAGT	VAG	DUV	K-GLU	Elem.	D-VAGT	VAG	DUV	K-GLU
	Tetrah.	Barite	Barite	Barite		Tetrah.	Barite	Barite	Barite
	this work	this work	this work	JURKOVIĆ et al., 2010		this work	this work	this work	JURKOVIĆ et al., 2010
	ppm	ppm	ppm	ppm		ppm	ppm	ppm	ppm
Be	<1.0	<1.0	<1.0	<1.0	Mo	137.4	<0.1	<0.1	0.2
Co	63.5	<0.2	<0.2	0.3	Cu	368600.0	2.5	66.0	3.9
Ni	266.2	5.1	0.5	3.9	Pb	1464.0	0.5	<0.1	2.4
Sc	n.a.	<1.0	n.a.	n.a.	Zn	41300.0	6.0	2.0	6.0
Cs	<0.1	<0.1	<0.1	0.1	As	15100.0	87.8	13.2	<0.5
Ga	<0.5	0.5	<0.5	<0.5	Cd	313.6	<0.1	<0.1	<0.1
Hf	<0.1	1.1	0.9	0.5	Sb	157600.0	1.9	1.0	0.3
Nb	<0.1	<0.1	<0.1	<0.1	Bi	1466.0	<0.1	<0.1	<0.1
Rb	0.2	<0.1	<0.1	0.4	Ag	>300.0	<0.1	<0.1	<0.1
Sn	<1.0	<1.0	<1.0	<0.1	Au	ppb 38963	ppb<0.5	ppb 0.9	ppb <0.5
Ta	0.3	2.8	1.9	1.4	Hg	37950.0	0.6	0.4	0.2
Th	<0.2	<0.2	<0.2	<0.2	Tl	<0.1	1.7	<0.1	<0.1
U	2.3	0.3	<0.1	<0.1	Se	<0.5	<0.5	<0.5	<0.5
V	<8.0	<8.0	<8.0	13.0	Total	663194.6	101.0	82.6	13.0
W	<0.5	1.5	0.5	<0.5	Sr	224.1	11965.0	11114.0	14354.0
Zr	0.2	0.6	<0.1	1.6	Ba	7632.0	>50000	>50000	>50000
Y	7.1	1.2	1.0	1.0	Ca	5500.0	n.a.	n.a.	300.00
Total	339.8	13.1	4.8	19.2					

DUV sample. There were 5 trace elements (Mo, Cd, Bi, Ag and Se) below the MDL. The total sum of the trace elements of the Mo-Se group in the VAG sample is <102.41 ppm where As (87.8 ppm) dominates. In the DUV sample the total sum of the same elements is <84.58 ppm, but here Cu (66.0 ppm) dominates.

The analysed REE in barite are characterized by extremely low values: 7.77 ppm in total in the VAG sample and 7.98 ppm in total in the DUV sample (Table 3). The La_N/Yb_N ratio in the VAG sample corresponds to 7.18, and the $\Sigma LREE / \Sigma HREE$ ratio is 0.63, whereas in the DUV sample the same ratios are 47.03 and 1.58 respectively. The values for Nd and Sm in both samples, and also the value of Dy in the DUV sample, were below the MDL. Therefore the values of the Eu anomaly (Eu/Eu^*) could not be calculated. However, it is obvious from the plot of the REE pattern normalized to CI chondrite (SUN & McDONOUGH, 1989) that both samples have pronounced positive Eu anomalies because of the extremely low concentration of Sm (Fig. 3). The expressed negative Ce/Ce* anomaly is visible in both samples (where $Ce/Ce^* = 0.220$ in the VAG sample and 0.440 in the DUV sample).

The wt.% of $SrSO_4$ in barite varies in the VAG sample from 2.51 to 3.42 (thin fine grained and thick tabular coarse grained habits of barite crystals of the same sample) and in DUV sample equates to 2.33 (Table 4).

The $\delta^{34}S_{CDT}$ value of barite (DUV sample) is +10.4‰, while the $\delta^{18}O_{SMOW}$ values of barite in the VAG and DUV samples are +15.6 and +17.3‰ respectively (Table 4).

6. DISCUSSION

In this section, these results will be compared with those from previously published papers concerning fluid inclusion

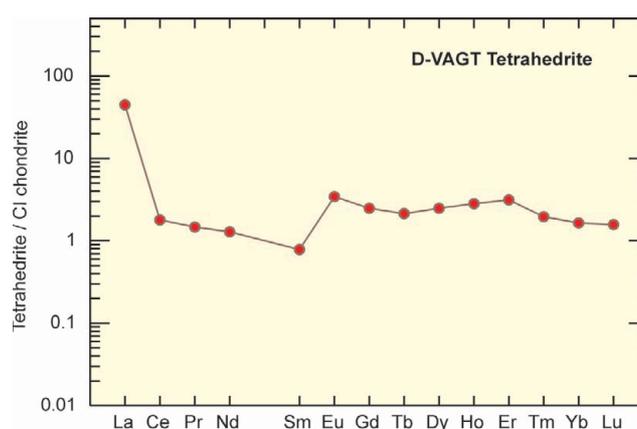


Figure 2: Plot of CI chondrite-normalized REE abundances (SUN & McDONOUGH, 1989) of Hg-tetrahedrite (D-VAGT) from the Duboki Vagan barite deposit.

Table 3: Rare earth element (REE) abundances of Hg-tetrahedrite (D-VAGT), and barites (VAG, DUV, K-GLU) in comparison to REE abundances of CI chondrites (SUN & McDONOUGH, 1989; PALINKAŠ & JURKOVIĆ, 1994). Data for sample K-GLU are from JURKOVIĆ et al. (2010). The data for fluorites (DD-FA and DD-FB) are from PALINKAŠ & JURKOVIĆ (1994). Different parameters of Hg-tetrahedrite (D-VAGT), barites (VAG, DUV and K-GLU) and fluorites (DD-FA and DD-FB) are presented in the lower part of the Table 3. Data for sample K-GLU are from JURKOVIĆ et al. (2010). Data for two fluorite samples (DD-FA and DD-FB) are from PALINKAŠ & JURKOVIĆ (1994). All values are in ppm.

REE	D-VAGT	VAG	DUV	K-GLU	CI	DD-FA	DD-FB	CI
	tetrah.	barite	barite	barite	chondrite	fluorite	fluorite	chondrite
	this work	this work	this work	JURKOVIĆ et al., 2010	SUN & McDONOUGH, 1989	PALINKAŠ & JURKOVIĆ, 1994	PALINKAŠ & JURKOVIĆ, 1994	PALINKAŠ & JURKOVIĆ, 1994
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
La	10.60	1.60	3.90	2.40	0.2370	0.0230	0.0293	0.3110
Ce	1.10	0.20	0.50	0.90	0.6120	n.d.	n.d.	0.8080
Pr	0.14	0.03	0.02	0.10	0.0950	n.d.	n.d.	0.1220
Nd	0.60	<0.30	<0.30	0.30	0.4670	n.d.	n.d.	0.6000
Sm	0.12	<0.05	<0.05	0.45	0.1530	0.1200	0.1500	0.1950
Eu	0.20	3.02	0.77	0.85	0.0580	0.0237	0.0247	0.0735
Gd	0.51	1.69	1.77	1.02	0.2055	n.d.	n.d.	0.2590
Tb	0.08	0.10	0.15	0.08	0.0374	0.0230	0.0259	0.0474
Dy	0.63	0.23	<0.05	2.78	0.2540	n.d.	n.d.	0.3220
Ho	0.16	0.23	0.29	<0.02	0.0566	0.1900	0.1100	0.0718
Er	0.52	0.43	0.43	0.03	0.1655	n.d.	n.d.	0.2100
Tm	0.05	0.03	0.04	0.02	0.0255	0.0228	0.0450	0.0324
Yb	0.28	0.16	0.06	0.07	0.1700	n.d.	n.d.	0.2090
Lu	0.04	0.05	0.05	<0.01	0.0254	0.0242	0.0210	0.0322
ΣREE	15.03	7.77	7.98	9.00	2.562	0.4267	0.4059	3.2923
ΣLREE	12.56	1.83	4.42	4.15		0.1797	0.2299	
ΣHREE	2.27	2.92	2.79	4.00		0.2370	0.1760	
ΣLREE/ΣHREE	5.53	0.63	1.58	1.04		0.8004	1.3063	
ΣREEm/ΣREEch	5.87	3.03	3.12	3.51		0.2665	0.1565	
LaN/YbN	27.11	7.18	47.03	24.71				
TmN/SmN	2.51			0.27		0.1587	1.8045	
Eu ³⁺ /Eu ²⁺	2.48			3.84				
Ce ⁴⁺ /Ce ³⁺	0.22	0.22	0.44	0.45				

studies (PALINKAŠ, 1988; PALINKAŠ & JURKOVIĆ, 1994), sulphur, carbon and oxygen isotope compositions

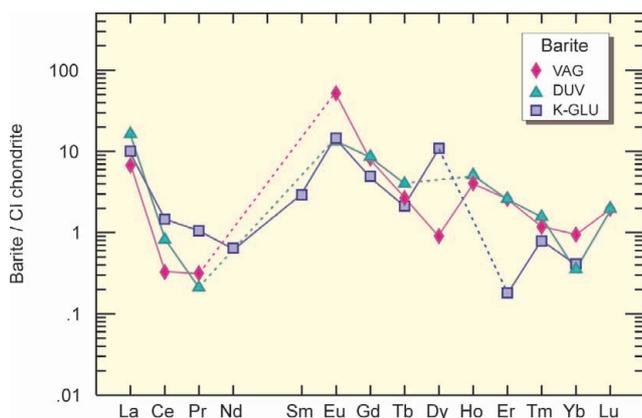


Figure 3: Plot of CI chondrite-normalized REE abundances (SUN & McDONOUGH, 1989) of barites (VAG, DUV and K-GLU) from the Duboki Vagan and Glumac barite deposits. Data for the K-GLU sample are from JURKOVIĆ et al. (2010).

(ŠIFTAR, 1988; JURKOVIĆ et al., 1997; JURKOVIĆ & PALINKAŠ, 2002; JURKOVIĆ et al., 2010) and REE analysis (PALINKAŠ & JURKOVIĆ, 1994; JURKOVIĆ et al., 2010) in barite deposits of the MBSM and SEB.

6.1. Hg-tetrahedrite

Hg-tetrahedrite from the Duboki Vagan and Dubrave-Dugi Dol barite deposits is mercury-bearing Cu-Sb-Zn tetrahedrite, characterized by strongly negative $\delta^{34}\text{S}_{\text{CDT}}$ values (Table 4). Similar $\delta^{34}\text{S}_{\text{CDT}}$ values (−12.82; −10.18; −7.91; −9.50; −10.69; −9.68; −12.77; −11.00; −12.40; −10.92; −6.96; −11.43; −5.50; −10.91; −8.20; −8.79; −15.40; −13.74 ‰) corresponding to an average of −10.49 ‰ have been found in all studied samples of Hg-tetrahedrite in the MBSM (JURKOVIĆ et al., 1997). In the SEB, only one Hg-tetrahedrite has been analyzed (Fočanska Jabuka) and its $\delta^{34}\text{S}_{\text{CDT}}$ value equates to −4.95 ‰ (HALAMIĆ et al., 1987; JURKOVIĆ et al., 2010).

Very high values for gold and silver were determined in the studied Hg-tetrahedrite, where 39 ppm Au and >300 ppm

Table 4: Sulphur, carbon and oxygen isotope compositions of Hg-tetrahedrites (D-VAGT, DV-T1, DV-T2, DD-T1 and DD-T2, K-VDT1, K-VDT2, K-VDT3), barites (VAG, DUV, BARITE-1, BARITE-2, DD-B1, DD-B2 and K-GLU, K-VDB1, K-VDB2) and calcite (DD-C, K-VDC1, K-VDC2) as also SrSO₄ content of barites from the Duboki Vagan, Dubrave-Dugi Dol and Glumac barite deposits.

		Sample	Mineral	SrSO ₄ (%)	δ ³⁴ S _{CDT} (‰)	δ ¹³ C _{CPDB} (‰)	δ ¹⁸ O _{SMOW} (‰)
Duboki Vagan	this work	D-VAGT	Tetrahedrite		-11.80		
		VAG	Barite	2.51; 3.42			15.60
		DUV	Barite	2.33	10.40		17.30
Duboki Vagan	JURKOVIĆ et al., 1997	DV-T1	Tetrahedrite		-6.96		
		DV-T2	Tetrahedrite		-11.43		
Dubrave-Dugi Dol	JURKOVIĆ et al., 1997	BARITE-1	Barite	4.40	8.20		
		BARITE-2	Barite	3.60	8.90		
		DD-T1	Tetrahedrite		-5.50		
		DD-T2	Tetrahedrite		-10.91		
		DD-B1	Barite	4.40	11.35		
Dubrave-Dugi Dol	JURKOVIĆ et al., 1997	DD-B2	Barite	6.10	11.02		23.09
		DD-C	Calcite			-2.62	
Glumac	this work	K-GLU	Barite	3.03	10.80		19.70
Glumac - Vidići	JURKOVIĆ et al., 2010	K-VDB1	Barite	6.60	9.03		
		K-VDB2	Barite	5.70	9.88		
		K-VDT1	Tetrahedrite		-8.21		
		K-VDT2	Tetrahedrite		-8.79		
		K-VDT3	Tetrahedrite		-15.40		
		K-VDC1	Calcite			-2.43	22.41
		K-VDC2	Calcite			-2.46	22.45

Ag is a typical, genetically very important characteristic of all MBSM Hg-tetrahedrites (JURKOVIĆ et al., 1997; JURKOVIĆ et al., 2010). In a tetrahedrite sample from the Duboki Vagan deposit analysed earlier (JURKOVIĆ et al., 1997), 1290 ppm Ag was obtained (Table 1). Comparing the analyses of both Duboki Vagan tetrahedrite samples, (the first analysed in 1997 and the second from the present study), it is obvious that they are very similar in Cu, Fe, Zn and As values. The analysis performed here demonstrates that Sb, Hg and S are the most rapid weathering components of Hg-tetrahedrite (Table 1).

The analysed tetrahedrite displays the pronounced positive Eu anomaly (Eu/Eu* = 2.480). According to BAU (1991), BILAL (1991) and BAU & MÖLLER (1992) such a positive Eu anomaly indicates REE mobilisation by a F⁻, OH⁻ and CO₃²⁻-fluid in a high-temperature regime. Such regimes have already been proven in the MBSM by PALINKAŠ & JURKOVIĆ (1994), JURKOVIĆ & PALINKAŠ (2002) and JURKOVIĆ et al. (2010). The Eu³⁺/Eu²⁺ ratio in aqueous solutions depends on pressure, pH and REE speciation, but the most important parameter is temperature (SVJERENSKY, 1984; WOOD, 1990, 1990a; BAU, 1991; HEND-

ERSON, 1984, 1996; GIERÉ, 1996). In natural aqueous systems the occurrences of Eu anomalies are due to the redox reaction: 2Eu³⁺ + 2OH⁻ = 2Eu²⁺ + H₂O + 0.5O₂ (BAU & MÖLLER, 1992).

In general, negative Ce anomalies are characterized by oxidizing conditions. A negative Ce anomaly appears to be a function of O₂ and pH, but is more sensitive to pH than to O₂. In natural aqueous systems, the occurrences of Ce anomalies are due to the redox reaction: 2Ce³⁺ + 0.5O₂ + 3H₂O = 2CeO₂ + 6H⁺ (BAU & MÖLLER, 1992). The generation of Ce anomalies in a high-temperature environment seems unlikely, because with increasing temperature, the Ce⁴⁺/Ce³⁺ redox equilibrium shifts toward higher fO₂. According to WOOD (1990, 1990a), with increasing temperature both the Ce⁴⁺/Ce³⁺ ratio and the Ce complex formation constants increase.

6.2. Barite

The SrSO₄ content in the barite crystal lattice ranges between 2.33 and 3.42 wt.%. The SrSO₄ contents of two barite samples obtained from the Duboki Vagan deposit by ŠIFTAR

(1988) and JURKOVIĆ et al. (1997) were 4.4 and 3.6 wt.%. Barite from the Glumac deposit (K-GLU sample) contained 3.03 wt.% (JURKOVIĆ et al., 2010), while barite from the Dubrave-Dugi Dol barite deposits has 4.4 and 6.1 wt.% SrSO_4 , and barite from the Glumac–Vidici deposit is composed of 6.60 and 5.70 wt.% SrSO_4 (JURKOVIĆ et al., 1997) (Table 4). Such SrSO_4 values in analysed barites are in accordance with the other 108 previously analysed barite samples from the MBSM, which contain on average 4.22 wt.% SrSO_4 and are of hydrothermal origin (JURKOVIĆ & PALINKAŠ, 1999).

So far, only one REE analysis was performed on the MBSM barites, which was the analysis of the K-GLU sample from the Glumac barite (JURKOVIĆ et al., 2010). The two new REE analyses performed here on the Duboki Vagan barite samples (VAG and DUV) produced almost identical results, despite the fact that there are small differences in mineral paragenesis.

It has to be stressed that the $\delta^{34}\text{S}_{\text{CDT}}$ value obtained from the analyzed barite (+10.40‰) corresponds well with earlier published data of $\delta^{34}\text{S}_{\text{CDT}}$ values in barite (+10.11‰ on average) and is typical for Permian seawater (Table 4).

The analyzed $\delta^{18}\text{O}_{\text{SMOW}}$ values ($n=3$) in the barites of Duboki Vagan (+15.6 and +17.3‰) together with the previously published $\delta^{18}\text{O}_{\text{SMOW}}$ value (19.70‰) in the barite of Glumac (JURKOVIĆ et al., 2010) illustrate that heightened $\delta^{18}\text{O}_{\text{SMOW}}$ values are typical for Hg-tetrahedrite and octahedral fluorite-bearing barite deposits located in the MBSM (JURKOVIĆ et al., 2010).

6.3. Fluorite

In order to compare the REE distribution pattern in barite and tetrahedrite analysed here with those in fluorite published by PALINKAŠ & JURKOVIĆ (1994) in the Dubrave-Dugi Dol barite deposits, the plot of REE distribution in fluorite normalized to CI chondrite is shown in Fig. 4.

The fluorite crystals (DD-FA and DD-FB) studied by PALINKAŠ & JURKOVIĆ (1994), show extremely low REE values of 0.427 and 0.406 ppm respectively. Such fluorites, with a total REE content of about only half that of chondrites, were reported by MÖLLER & MORTEANI (1983) and EPPINGER & CLOOS (1990) from limestones in the Alps, Spain, Morocco and the USA. MÖLLER & MORTEANI (1983) maintain that these fluorites have been formed under hypersaline conditions or in evaporating basins. SCHNEIDER et al. (1975), investigating fluorite in the Northern Calcareous Alps, also reported extremely low total REE values of 0.17, 0.57 and 0.72 ppm.

The La_N/Yb_N ratios of the fluorite samples from the Dubrave-Dugi Dol barite deposits (0.112 and 0.139 respectively), reflect an enrichment of the HREE over LREE (Table 4, Fig. 4). According to EKAMBARAN et al. (1986), and EPPINGER & CLOOS (1990), such a REE pattern indicates the late-stage formation of fluorites.

The formation of barite and fluorite took place under opposing environmental conditions. The Ce anomalies, although less pronounced, are also of opposite character.

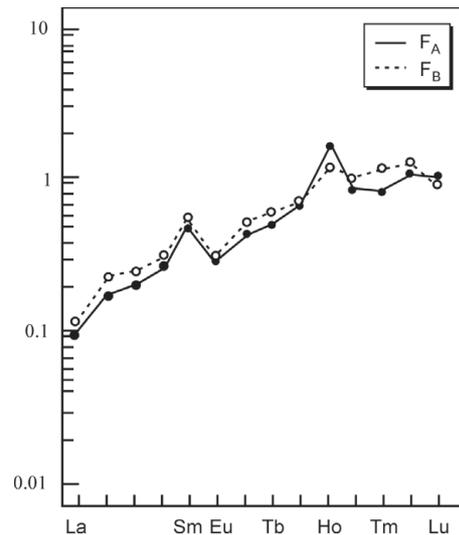


Figure 4: Plot of chondrite-normalized REE abundances of fluorites (DD-FA and DD-FB) from the Dubrave-Dugi Dol barite deposits (from PALINKAŠ & JURKOVIĆ, 1994).

The increased Sm values and decreased Tm values in the Tm_N/Sm_N ratios are, according to BOWERS & HELGESSON (1983) and WENDLANDT & HARRISON (1979), usual for fluids supersaturated with respect to CO_2 and halides.

SCHNEIDER et al. (1975, 1977), and MÖLLER et al. (1976), distinguish fluorite of hydrothermal and sedimentary origin, on the basis of the Tb/Ca atom ratio and the Tb_N/La_N ratios. Tb_N/La_N – Tb/Ca ratios for the fluorites from the Dubrave-Dugi Dol barite deposits (PALINKAŠ & JURKOVIĆ, 1994), plot into the “sedimentary field” according to SCHNEIDER et al. (1975, 1977). In contrast, barites, as evidenced by their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are of hydrothermal origin. These data support the idea that barite on the one hand, and Hg-tetrahedrite (\pm octahedral fluorite) on the other, have been formed at different times and in dissimilar environments. A Tb/La ratio >1.0 indicates late stage formation from a mineralization solution. The enrichment of the MREE and HREE relative to the LREE may have been due to the formation of their stable F^- and CO_3^{2-} complexes.

The fluid inclusion study of fluorite suggests a very high homogenization temperature ($T_h=250\text{--}330^\circ\text{C}$) with noticeable evidence of boiling and high salinity, (over 20 wt.% NaCl equivalent). Massive decrepitation started above 330°C (PALINKAŠ & JURKOVIĆ, 1994). In the fluorite-barite deposit of Žune, Ljubija, NW Bosnia, fluid inclusions in fluorites distinguish even clear boiling processes and high salinity (PALINKAŠ, 1988).

6.4. Origin of barite deposits in the MBSM and SEB

According to JURKOVIĆ et al. (2010), two paragenetic types of barite deposits have been formed in the MBSM and SEB during two mineralization phases.

The first, (older) phase, took place during the early Permian (Cisuralian), and produced veiny and metasomatic bar-

ite deposits with subordinate or scarce Fe, Cu, Zn, Pb and Sb sulphides and sulphosalts. These had positive $\delta^{34}\text{S}_{\text{CDT}}$ values (± 0 to $+5\%$), with some siderite and quartz as gangue minerals. This paragenetic type of barite deposits formed throughout the MBSM and also in the Prača-Foča region of the SEB, and in the Jajce-Jezero region (the outermost NNW part of the MBSM). The best example of this type of barite deposit is the thoroughly studied Trošnik ore deposit near Fojnica (MBSM), which formed as irregular metasomatic bodies and veins within the Lower Palaeozoic dolomite (JURKOVIĆ, 1958; JURKOVIĆ et al., 1997). Quartz, siderite and barite are the main gangue minerals. Pyrite and chalcopyrite are the main ore minerals, whereas tetrahedrite is subordinate. All sulphides are characterized by positive $\delta^{34}\text{S}_{\text{CDT}}$ values. Three tetrahedrite samples from the Trošnik ore deposit produced $+3.24\%$ and $+3.73\%$ (KUBAT et al., 1979/80) and $+4.00\%$ values (JURKOVIĆ et al., 2010). Tetrahedrite from the Trošnik deposit contains only traces of mercury ($<0.20\%$ and 0.03% according to JURKOVIĆ et al., 1997), and is formed by hydrothermal fluid from the same sulphur source, as for pyrite and chalcopyrite in the same paragenesis. This fact indicates that the Trošnik ore deposit has suffered a negligible overprint during a later phase.

The second (younger) mineralization phase took place at the end of the Permian (Permian–Triassic boundary), when Early Intracontinental Rifting started. This period was characterized by heating, dilatation and fracturing of the greater part of the MBSM, enabling the rise of mercury, fluorine and H_2S from the upper mantle. KARAMATA et al. (1995), published the highest concentration of mercury in the Dinarides which occurred in the Lower and Middle Triassic. The sulphides and sulphosalts formed during the first mineralization phase were regenerated, remobilized, partly and/or completely fluidized and reacted with ascending mercury and sulphur from the new source. These processes led to formation of the only Hg-tetrahedrite characterized by negative $\delta^{34}\text{S}_{\text{CDT}}$ values, ranging between -4.95% and -15.4% and also of high-temperature octahedral fluorite. The rifting overprint (impact metasomatism) occurred very irregularly and with very differing intensity in various parts of the MBSM, SEB and Jajce-Jezero areas. The most strongly affected areas were probably fault zones of the first and second order, and zones warmed by magmatic eruptions. The most intensive processes and overprinting took place in the Rostovo, Gornji Vakuf and Kreševo areas, whereas a very weak overprint occurred in SE Bosnia.

Barite formed during the first mineralization phase underwent strong heating and a change of pressure and $f(\text{O}_2)$ in the environment during the later second phase. These events are reflected in the shift of $\delta^{18}\text{O}_{\text{SMOW}}$ values toward higher values, and $\delta^{34}\text{S}_{\text{CDT}}$ values toward lower values in barite (JURKOVIĆ et al., 2010). Sulphide-bearing barites from SEB which are weakly overprinted, and have $\delta^{18}\text{O}_{\text{SMOW}}$ values within a narrow range ($+14.6\%$ to $+15.6\%$), whereas barite samples with Hg-tetrahedrite and fluorite from the MBSM, reveal higher $\delta^{18}\text{O}_{\text{SMOW}}$ values ranging from $+15.6$ to $+22.4\%$. The sulphur isotopes ($\delta^{34}\text{S}_{\text{CDT}}$) in the barites from the SEB span a range from $+11.6$ to $+17.7\%$ (mean $+16.4\%$).

Barites from the MBSM also display a narrow range of $\delta^{34}\text{S}_{\text{CDT}}$ values between $+10.1\%$ to $+16.8\%$, but with a significantly lower mean value of $+11.8\%$ (JURKOVIĆ et al., 2010). The most pronounced result is a very expressive positive Eu anomaly in all the overprinted barite samples, which suggests a high-temperature mineralizing fluid.

In the Fočanska Jabuka deposit (SEB), two different mineralization phases are very clearly distinguished in time. In the older (Lower Permian) phase, barite, quartz, siderite deposits formed with pyrite, chalcopyrite and galena ore minerals KUBAT et al. (1979/1980) found that the $\delta^{34}\text{S}_{\text{CDT}}$ values of sulphides are $+2.80\%$ in pyrite, $+2.49\%$ in chalcopyrite and $+3.04\%$ in galena. JURKOVIĆ et al. (2010) determined $\delta^{34}\text{S}_{\text{CDT}}$ ($+17.7\%$) and $\delta^{18}\text{O}_{\text{SMOW}}$ ($+15.1\%$) values in barite. The ore body is transected by a younger barite vein containing even younger Hg-tetrahedrite veinlets characterized by a strongly negative $\delta^{34}\text{S}_{\text{CDT}}$ value -4.95% in a later mineralization phase (HALAMIĆ et al., 1987).

7. CONCLUSION

A broad comparison of geochemical data was undertaken of barite deposits associated with subordinate or scarce Fe, Cu, Zn, As and Sb sulphides and sulphosalts, characterized by a positive $\delta^{34}\text{S}_{\text{CDT}}$ value (± 0 to $+5\%$) with barite deposits where Hg-tetrahedrite, as the only sulphide mineral, was characterized by negative $\delta^{34}\text{S}_{\text{CDT}}$ values (-4.95 to -15.4%) and which is locally associated with high-temperature octahedral fluorite.

The following facts and data were established as a result:

1) Both paragenetic barite types are contemporaneous and have an epigenetic hydrothermal origin. They also share almost the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, (the difference is only 0.0041), and very similar REE contents (on average 7.1 and 8.3 ppm respectively). The most pronounced difference between the two paragenetic types is observed in the oxygen isotopic composition of the barites. Polysulphide-bearing barites show a $\delta^{18}\text{O}_{\text{SMOW}}$ value within a narrow range ($+14.6\%$ to $+15.6\%$), whereas Hg-tetrahedrite bearing barites have $\delta^{18}\text{O}_{\text{SMOW}}$ values ranging from $+15.6$ to $+22.4\%$. Differences in the sulphur isotope composition have also been noted, but are inexplicable.

2) A new sulphur source was vital for formation of the Hg-tetrahedrite (schwazite). Most probably, it was H_2S that ascended from the upper mantle during early intercontinental rifting and/or organic sulphur being formed in the ores and rocks of completely different sedimentary environments.

3) The octahedral, high temperature fluorite occurs only in the Hg-tetrahedrite-bearing barite deposits. It is characterized by extremely low REE contents, a low $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratio indicating a very distinct enrichment of HREE and late stage formation of fluorite.

4) A very low REE (0.4 to 0.45 ppm) content indicates the formation of fluorite under hypersaline conditions or in evaporating basin. Increased values for Sm and decreased values for Tm in the $\text{Sm}_\text{N}/\text{Tm}_\text{N}$ ratios, characterize fluids supersaturated with respect to CO_2 and halides.

5) Tb_N/La_N – Tb/Ca atom ratios of fluorites from the Dubrave-Dugi Dol barite deposits plot in the sedimentary field of SCHNEIDER et al. (1975, 1977), while all barites have a hydrothermal origin. This indicates great differences in the timing and environmental circumstances of barite and fluorite formation.

6) All the described events are effects of the early intercontinental rifting which took place between the uppermost Permian and Lower Triassic. Concerning the strength and intensity of this geological event, it affected separate parts of the MBSM and SEB in very different ways. The most important event was the ascension of mercury, fluorine, boron and sulphur from the upper mantle, and very strong heating and tectonization. These circumstances enabled remobilization and partial fluidization of primary Fe, Cu, Zn, Sb and Pb sulphides and their reaction with the ascended mercury and sulphur, followed by formation of octahedral fluorite, tourmalinization and large, local masses of calcite. In a single case (Fočanska Jabuka) a new barite body was formed in this younger phase containing one even younger Hg-tetraedrite vein, characterized by a strongly negative $\delta^{34}S_{CDT}$ value -4.95% .

7) The Duboki Vagan barite deposit, together with in this work compared the Glumac and Dubrave-Dugi Dol barite deposits originated in the Late Variscan (Lower Permian). Early intercontinental rifting in the Post Variscan (Early Eoalpine phase), triggered processes that caused the shift of barite $\delta^{18}O_{SMOW}$ values, remobilization and partial fluidization of primary polysulphides and formation of Hg-tetraedrite as the only ore mineral with octahedral fluorite.

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