ISOTOPIC COMPOSITION OF SULFUR IN THE BOROV DOL DEPOSIT, NORTH MACEDONIA

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A b s t r a c t: The study of the isotopic composition of sulfur is essential for the development of genetic models of porphyry copper deposits. In order to determine the origin of metals and sulfur in the Borov Dol porphyry copper deposit, a series of research and analyses of sulfur isotopes (^{32}S, ^{34}S) and their isotopic ratio ($\delta^{34}S$) were conducted. Samples were taken at the Borov Dol deposit, mainly of pyrite (from the hydrothermal temperature range of 250–350ºC), then chalcopyrite, galena, sphalerite, and chalcocite. At the Borov Dol deposit, the values show a wide range starting from –7.25‰ to +5.40‰ $\delta^{34}S$, with an average of –0.38‰ $\delta^{34}S$. Accordingly, the source of the sulfur is magmatic, associated with the deep parts of the Earth's crust or with the boundary zone between the continental crust and the upper mantle, with intrusive fractionation and partial enrichment with the light sulfur isotope, which is reflected in the negative value in the higher levels of the deposit, or in the slight enrichment of the heavy sulfur isotope, which is reflected in the positive value in the lower levels of the deposit. The sulfide parageneses in the Borov Dol porphyry system were most likely deposited from oxidized hydrothermal ore-bearing solutions, whereby there is no equilibrium in the system during the crystallization of the early-stage paragenesis. The equilibrium in the system is established during the crystallization of the paragenesis in the middle and late stages.

Key words: sulfur isotopes; ore minerals; composition; fractionation; Borov Dol deposit

1. INTRODUCTION

The Borov Dol site is located 14 km southwest of the town of Radovish. The Solway company began surface exploitation at the Borov Dol deposit in 2019 (Gjorgiev, 2020). The sulfur isotopic composition in sulfide minerals from the Borov Dol deposit has been studied so far by Serafimovski (1993), Tudžarov (1993), Serafimovski and Tasev (2005) and others. The analyses of sulfur isotopic composition have mainly been performed on pyrite, less frequently on chalcopyrite, galena, sphalerite, and chalcocite.

The question of the origin of ore metals and the mechanism of concentration of ore metals during the formation of hydrothermal deposits is of particular significance, not only for explaining the genesis process, but also in terms of determining the regularities of their spatial distribution (Čifliganec,

1987). The source of base metals in porphyry copper deposits is still a problem that poses a challenge to be solved by scientists around the world. The two most common presumed sources of copper and sulfur in porphyry copper deposits are acidic magmas or surrounding rocks unrelated to magmatism (Tasev, 2010).

In the geological community, the prevailing opinion is that the upper mantle represents one of the sources of ore metals (Silittoe, 1973; Rona, 1977) based on the very interesting results obtained from laboratory experiments and based on monitoring of modern volcanoes (Čifliganec, 1987).

The isotopic composition of sulfur ($\delta^{34}S$) normalized to the Canyon Diablo Meteorite (Canyon Diablo Meteorite – CDM, $\delta^{34}S = 0,0‰$) shows a

narrow range from +6‰ to –4‰, indicating the origin of the sulfur from the upper mantle. Fractionated sulfur originating from the upper mantle or deeply homogenized parts of the Earth's crust varies within a narrow range of ±10 ‰ compared to the CDM standard (Jensen, 1959; Sakai, 1968; Janković et al., 1980; Shelton and Rye, 1982; Andrew et al., 1989).

The stable isotopes of some elements that make up ore deposits reflect the true "history" of the natural processes and the way rocks, minerals and ores are formed, and the origin of individual elements. Among them, sulfur plays an important role (Čifliganec, 1987).

According to Janković et al. (1980), porphyry copper deposits represent a distinct genetic type in which the ore metals, including sulfur with characteristic $\delta^{34}S$ signatures, are primarily derived from parent magmatic complexes. These complexes released hydrothermal fluids that ascended through the crust, incorporating only minor amounts of copper from the surrounding rocks. The strong spatial and genetic correlation between copper mineralization and intrusive bodies further supports a predominantly magmatic origin for both metals and sulfur.

The metals in magmas could have arrived in a variety of ways, including transfer of mass from subducted parts and crustal melting. (Hedenquist and Lowenstern, 1994).

On the other hand, some researchers even believe that the source of metals and magmatic processes that took place during the final rise and differentiation of the magma are of lesser importance than the processes of metal concentration (Lowenstern et al., 1991; Lowenstern, 1993).

This paper summarizes our latest knowledge on the isotopic composition of sulfur in sulfide minerals from the Borov Dol deposit.

2. METHODOLOGY

A high-resolution inductively coupled plasma mass spectrometry system (HR-ICP-MS) was chosen to analyze the sulfur isotopic composition in 7 samples of sulfide minerals from the Borov Dol deposit, consisting of an elemental analyzer for sample combustion and SO_2 separation, connected in series with a mass spectrometer operating at constant flow. The analyses were performed in the commercial laboratory Activation Laboratories LTD, Ontario, Canada. This technique is characterized by a significant improvement over conventional extraction methods for the determination of S isotopic ratios in geological materials. It is a much faster technique that requires much smaller amounts of material for analysis. Due to its simplicity – requiring minimal mineral phase separation and allowing rapid sample introduction into HR-ICP-MS – the technique demands strict adherence to the analytical protocol to ensure quality control across multiple influencing factors (Grassineau, 2006; Tasev, 2010). The initial ("raw") results are corrected using five international and internal standards ranging from – 17.3 to +20.3‰. The measured values of S are in the range of 1–1.5% of the expected values and the reproducibility of the $\delta^{34}S$ values is 0.1‰ (1σ). The technique has so far been applied to a huge number of samples whose range of $\delta^{34}S$ measured values spans from –20 to +20‰. The oxidation of sulfides is carried out using oxygen or copper(II) oxide, while the reduction of sulfates is carried out using graphite or copper. The $\delta^{34}S$ compositions are determined from the ratio m/z = 66/64 in SO_2 with a typical precision of 0.2%, and mass spectrometry for these chemically active species dictates a long "evacuation" period, usually followed by heating of the feed in the ICP-MS to minimize memory effects and system "blank" trials. Each trial requires ~1 h, so low to medium analysis speed is possible.

The sulfide samples were carefully selected under a binocular microscope. Standards ranging from powdery to coarse-grained forms were analyzed. There is no correlation between grain size and measured sulfur amounts, as well as $\delta^{34}S$ ‰ values. The samples were weighed using microbalancing and loaded into tin capsules. A quantity of reference SO_2 gas with a purity of 99.9% was loaded before the start of each analytical session. All corrected isotope results are expressed as $\delta^{34}S$ in parts per thousand (‰) relative to the Canon Diablo Troilite (CDT) standard. The precision of the analytical technique was constantly controlled using standards: laboratory standard CP-1 (internal, –4.5807 ‰ $\delta^{34}S$), international standard NBS-123 (16.9732‰ $\delta^{34}S$), international standard NBS-127 (20.3384‰ $\delta^{34}S$), laboratory standard TB-3 (internal, 0.0895‰ $\delta^{34}S$), laboratory standard GRU 9AG (internal, –17.2829 ‰ $\delta^{34}S$) and international standard IAEA-S3 (– 31.7705‰ $\delta^{34}S$) (Tasev, 2010).

3. GEOTECTONICS AND METALLOGENETIC POSITION OF THE BOROV DOL DEPOSIT

The Borov Dol porphyry copper deposit is located in the southern part of the Bučim-Damjan-Borov Dol mining region (Serafimovski, 1990) (Figure 1), within the Vardar zone on the border with the Serbian-Macedonian massif to the east. According to its metallogenesis the Bučim-Damjan-Borov Dol ore region, is part of the Lece-Chalkidiki metallogenetic zone (Serafimovski, 1990), which is part of the Alpine-Balkan-Carpathian-Dinaride metallogenetic belt (Heinrich and Neubauer, 2002). The metallogeny of this ore region is directly related to the Tertiary intermediate calc-alkaline magmatism,

which at today's level of erosion is represented by subvolcanic-volcanic facies of andesites, latites, quartz-latites, trachytes, trachyrhyolites, and others. Endogenous mineralization of Fe, Cu, Au, and Pb-Zn is associated with this volcanogenic-intrusive formation, genetically and spatially controlled by fault structures with a direction of extension NW-SE, NNW-SSE and NE-SW, as well as at the places where they intersect. The endogenous mineralization cycle in this area is associated with the Young Alpine metallogenetic epoch.
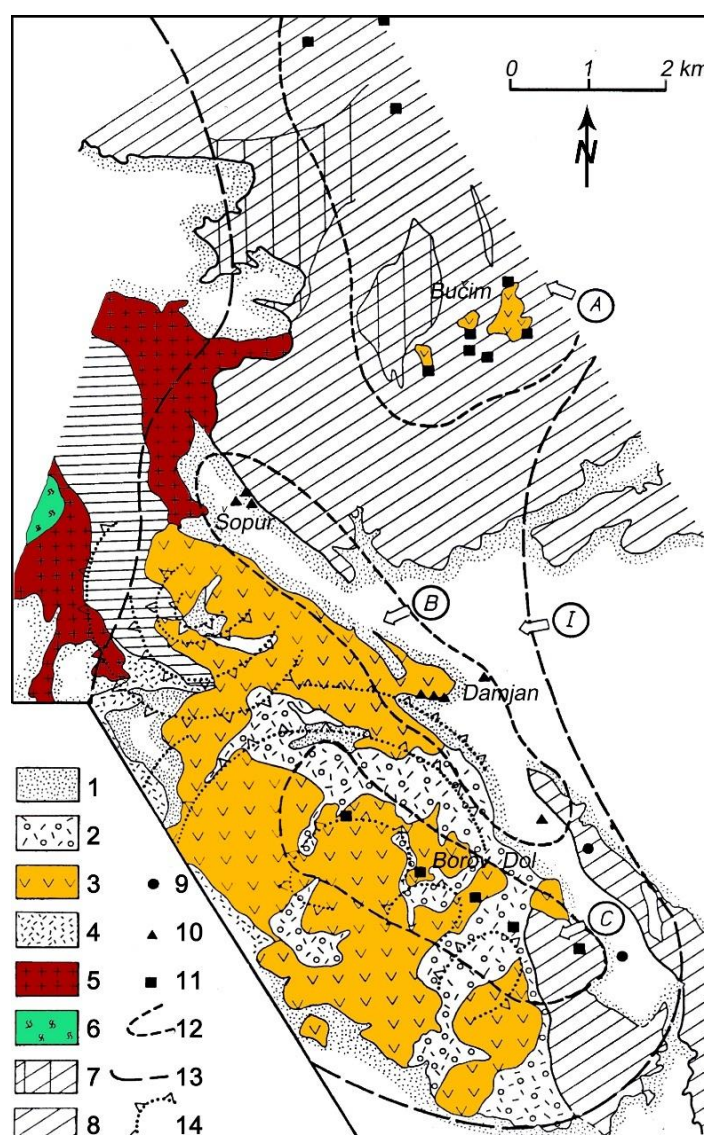

Fig. 1. Metallogenetic scheme of the ore district Bučim-Damjan-Borov Dol (Serafimovski, 1990).
1 – Paleogene and Neogene sediments, 2 – Pyroclastic sequences, 3 – Latites and andesites, 4 – Carbonatites, 5 – Granites,
6 – Serpentinites, 7 – Amphibolites, 8 – Gneiss, 9 – Pb-Zn vein type, 10 – Fe skarn type, 11 – Porphyritic type of Cu,
12 – Border of ore field, 13 – Border of ore district, 14 – Ring structure, I – Ore district Bučim-Damjan-Borov Dol,
A – Ore field Bučim, B – Ore field Damjan, C – Ore field Borov Dol

In the Bučim-Damjan-Borov Dol mining region volcanic activity began towards the end of the Oligocene, while ore mineralization was deposited during the Miocene. This ore region is dominated by significant skarn Fe deposits (Damjan and Sopur), porphyry Cu-Au deposits (Bučim and Borov Dol), and locally hydrothermal vein mineralizations of the Pb-Zn and Ba type also occur (Serafimovski, 1990) (Figure 1).

4. GEOLOGICAL STRUCTURE OF THE BOROV DOL DEPOSIT

The geological structure of the Borov Dol porphyry copper deposit mainly includes Precambrian and old Paleozoic metamorphic rocks, Jurassic ultrabasic rocks and granites, Albian-Cenozoic sediments, Upper Eocene sediments and volcanogenic-sedimentary products – tuffs and anglomerates, Tertiary andesites, Pliocene and Quaternary sediments (Tudžarov, 1993). The copper porphyry mineralization is associated with Tertiary andesites (with absolute ages between $24,04 \pm 0,77$ Ma and $24,51 \pm 0,89$ Ma; Serafimovski, 1993; Lehmann et. al., 2012), which cut the Cretaceous and Eocene sediments. Andesites are the product of two volcanic phases: early gray-white coarse-porphyry andesites and late dark gray fine-porphyry andesites. The copper mineralization is paragenetically associated with the dark gray fine-porphyry andesites and is localized in the gray-white coarse-porphyry andesites (Figure 2). It forms a ring around the dark gray fine porphyry andesites, which are in the shape of a neck.
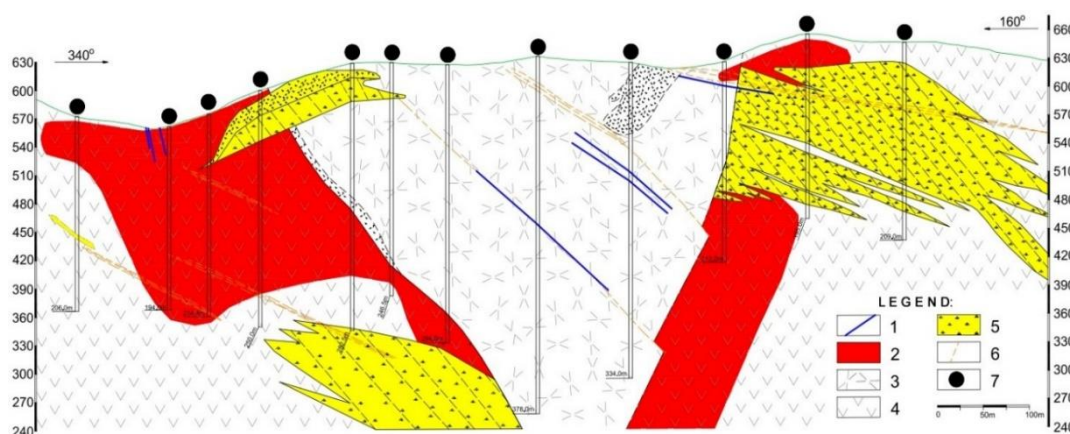

Fig. 2. Longitudinal geological profile, deposit of Borov Dol (Petrov et al., 2015). 1. Veins of Pb-Zn; 2. Ore body; 3. Dark grey fineporphyry andesites; 4. Grey white coarse-porphyry andesites; 5. Volcanic tuff; 6. Faults; 7. Investigation boreholes)

5. ORE MINERALIZATION

The ore mineralization in the Borov Dol deposit is of the stockwork-impregnation type, where the impregnation mode of occurrence prevails over the veiny one, which is not characteristic of the Bučim deposit, where we have the opposite case. Among ore minerals, pyrite, chalcopyrite, magnetite, molybdenite, hematite, native gold, etc. stand out in terms of intensity and extent. Chalcopyrite is the main carrier of copper and the most important sulfide copper mineral with economic significance (Tudžarov, 1993).

Based on previous research, mainly with deep exploratory drilling on a grid of 50×50 m, 50×100 m and 100×100 m, three ore bodies can be distinguished: Southern ore body which is in direct contact with the andesite neck and is located around Borov Dol itself, Central ore body which is still insufficiently explored, but is indicated by several holes in the deeper parts of the deposit below the andesite neck, and the Northern ore body which is indicated by multiple holes in the northern part below the andesite neck at a depth of over 100 m. These three ore bodies represent a single porphyry Cu ore deposit, where the discontinuity of mineralization is caused by the presence of low-percentage mineralized tuff sections and sterile parts of the smallest andesites (Tudžarov, 1993).

The Southern ore body (Petrov et al., 2014) is best studied and defined. The dimensions of this ore body are 430,0 m in width, 400 m in length, and up to 300 m in depth. The shape of the ore body is quite complex (Figure 3), as given by Peltekovski et al. (2023), and morphologically follows the andesite neck.
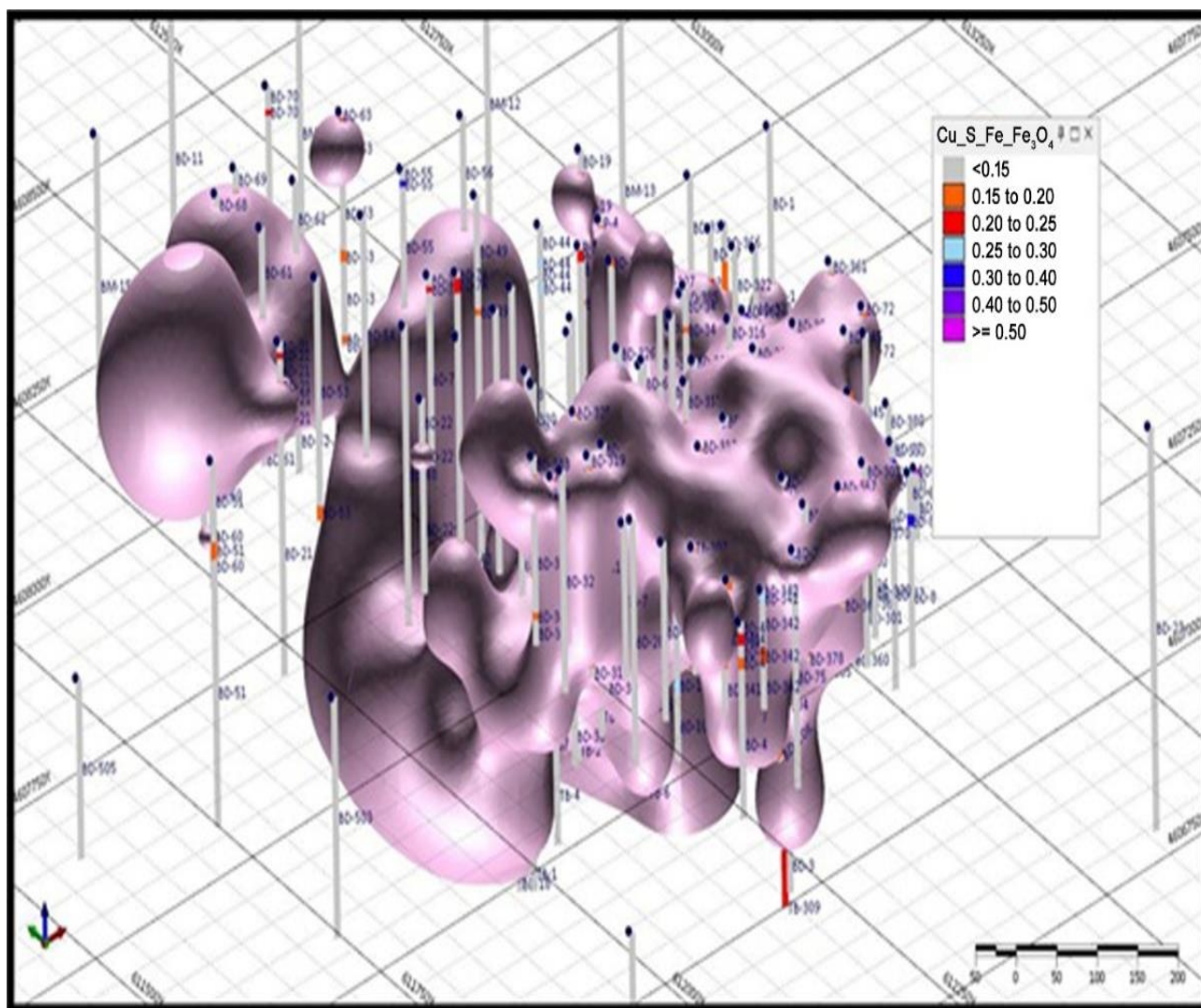

Fig. 3. Isometric shape of the ore body in the Borov Dol deposit, outlined at a cut-off grade of 0,15% Cu (Peltekovski et al., 2023).

6. RESULTS AND DISCUSSION

Within the Borov Dol deposit, the isotopic composition of sulfur $\delta^{34}S$ in individual sulfide minerals (pyrite, chalcopyrite, galena, sphalerite and chalcocite) was determined in 19 samples. The results of these tests are shown in Table 1. The variation of sulfur ($\delta^{34}S$) in the tested sulfide minerals from the Borov Dol deposit ranges from +5,40 to –7.52‰, with an average value of –0.38‰.

The $\delta^{34}S$ values in sulfide minerals from porphyry deposits are usually close to 0‰ (Figure 4), with low (negative) $\delta^{34}S$ values in sulfides that are most often deposited from sulfate-dominated hydrothermal ore-bearing solutions, i.e. oxidized hydrothermal ore-bearing solutions (Rye, 1993; Wilson et al., 2007). Higher (positive) $\delta^{34}S$ values in sulfides may result from variations in the total isotopic composition of sulfur in the magma, which may be the result of different yields in the magmatic sulfur reservoir, such as sulfur originating from the mantle, hydrothermal solutions from the subduction zone, seawater, or assimilation of surrounding rocks (Sasaki et al., 1984; Vikre, 2010).

T a b l e 1

Isotopic composition of sulfur δ³⁴S in minerals from the Borov Dol ore deposit

Ord. No.	Sample label	Microlocation	Mineral	δ³⁴S‰	³²S/³⁴S
1	BD-10/H	213.2 m	Pyrite	+0.72	22.236
2	BD-20	surface	Pyrite	–0.10	22.218
3	BD-29	94.0 m	Pyrite	–2.68	22.160
4	BD-55	28.0 m	Pyrite	+0.72	22.236
5	BD-59	280.0 m	Pyrite	–2.05	22.174
6	PS-5	45.0 m	Pyrite	–0.85	22.201
7	PS-10	34.5 m	Pyrite	–4.05	22.130
8	BM-15	35.5 m	Pyrite	–6.11	22.084
9	BD-30	surface	Pyrite	+0.05	22.221
10	BD-29	27.5 m	Chalcopyrite	–1.97	22.176
11	BD-29	94.0 m	Chalcopyrite	–3.02	22.153
12	BD-72	surface	Galena	–7.52	22.053
13	BD-335	132.0 m	Sphalerite	+3.70	22.302
14	BD-335	132.0 m	Galena	+5.40	22.340
15	BD-335	132.0 m	Chalcopyrite	+2.60	22.278
16	BD-322	121.4 m	Sphalerite	+3.60	22.300
17	BD-304	141.0 m	Galena	–0.20	22.216
18	Open pit Borov Dol	Level 615/630	Chalcozine	+1.50	22.253
19	Open pit Borov Dol	Level 615/630	Chalcozine	+3.00	22.287

Note: The analyses under ordinal numbers 1, 2, 3, 4, 5, 6, 7, 10, 11, and 12, were performed in the laboratory for isotopic analysis at IGM - AN, Moscow (1992) (Tudžarov, 1993). The analyses under ordinal numbers 8 and 9 were performed at the Jozef Stefan Institute, Ljubljana (1977). The analyses under ordinal numbers 13, 14, 15, 16, 17, 18 and 19 were performed in the commercial laboratory Activation Laboratories LTD, Ontario, Canada (2019)
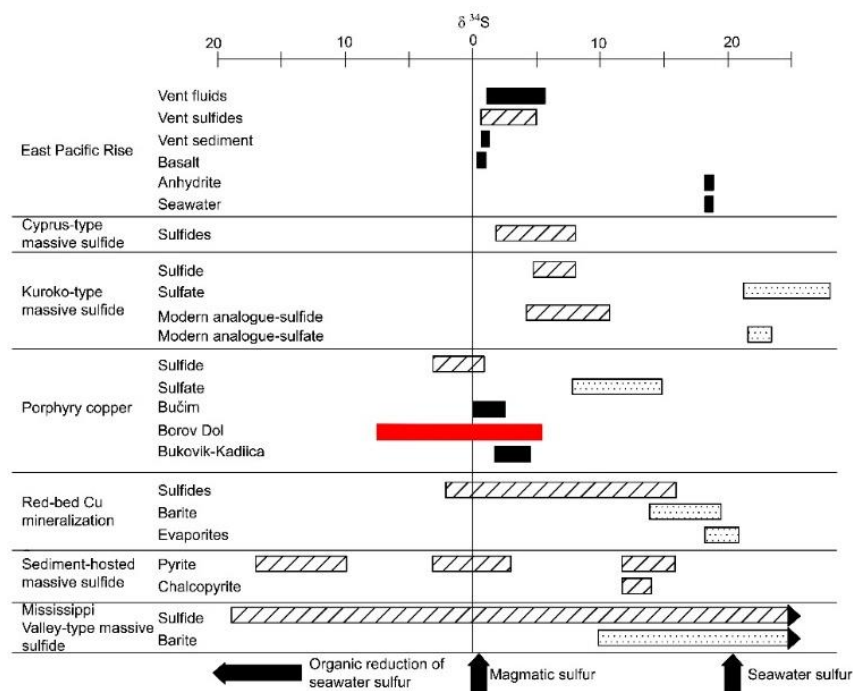

Fig. 4. δ³⁴S values for sulfur-bearing minerals in hydrothermal deposits (Data sources: Ohmoto and Rey, 1979; Čifliganec, 1987; Kerridge et al., 1988; Eldridge et al., 1988; Halbach et al., 1989; Naylor et al., 1989; Tudžarov, 1993; Tasev, 2010).

Figure 5 illustrates the sulfur isotopic composition from selected porphyry deposits and ore districts. At the Borov Dol deposit, several analyzed sulfide minerals exhibit depletion in the lighter sulfur isotope. The most pronounced enrichment in the light sulfur isotope is recorded in low-temperature galena (analysis no. 12; $\delta^{34}S$ = –7.52‰). While magmatic sulfides in porphyry systems typically display $\delta^{34}S$ values near 0‰, numerous deposits show significantly negative values. These include the Dinkidi alkaline porphyry Cu–Au deposit in the Philippines (Imai, 2001; Wolfe and Cooke, 2011), alkaline porphyry Cu–Au systems in New South Wales (Heithersay and Walshe, 1995; Wilson et al., 2007) and British Columbia (Deyell and Tosdal, 2005), as well as several calc-alkaline porphyry deposits in Chile and the southwestern USA (Ohmoto and Rye, 1979; Taylor, 1987; see Figure 5). Similar trends are also observed in high-sulfidation epithermal Au deposits (Hedenquist et al., 1994; Cooke and Simmons, 2000; Voudouris et al., 2019; Zlatkov, 2022). The negative $\delta^{34}S$ values in some Borov Dol sulfides likely reflect precipitation from sulfate-rich, i.e., oxidized hydrothermal fluids.

Sulfur isotopic studies provide important insights into sulfur reservoirs and the forms of sulfur in porphyry deposits. When magma is oxidized and begins to degas, it releases SO_2 (g), which at temperatures of around $450 – 350°C$ can be transformed by a process called disproportionation, producing three moles of SO_4^{2-} for every mole of H_2S (Rye et al., 1992; Rye, 1993). This means that, if this process is the main source of H_2S in the Borov Dol porphyry copper deposit, then sulfate should be the dominant form of sulfur in the hydrothermal ore-bearing solutions. However, numerous mineralogical investigations conducted by Tudžarov (1993), Serafimovski et al. (1993), Serafimovski and Tasev (2014) have shown that sulfides are dominant over sulfates in ores and altered rocks. Most likely, the excess SO_4^{2-} produced by the disproportionation of SO_2 (g) at the Borov Dol deposit had been tranported to the surface parts of the system. Among other things, inorganic sulfate reduction may have occurred in the Borov Dol porphyry system, which helped create additional H_2S needed for the deposition of significant quantities of pyrite, chalcopyrite, molybdenite, cubanite, valleriite, bornite – minerals characteristic of the Borov Dol porphyry deposit (Serafimovski et al., 1993; Wilson et al., 2007).

On the other hand, we assume that part of the increased positive $\delta^{34}S$ values in certain parts of the Borov Dol deposit are the result of enhanced influence from sulfur derived from meteoric waters, as is the case with the porphyry gold deposit Yao'an in Yunnan Province, southern China (Bi et al., 2004). There is a probability that in a small proportion, fluids from the magmas assimilated the sulfur from the surrounding rocks (Ohmoto and Goldhaber, 1997). The specific range of values in the sulfide minerals from the Borov Dol deposit is characteristic of ore-bearing sections in which sulfide minerals are present in rocks with granitic composition (Douglas et al., 2003) and porphyry Cu deposits (Field and Gustafson, 1976; Weihed and Fallick, 1994; Figure 5).

According to the comparative graphical analysis shown in Figure 5, the $\delta^{34}S$ values at the Borov Dol deposit are located midway between the deposits of Bisbee, USA, and El Salvador, Chile, on the one hand, and the deposits of Butte, USA, and Morococha, Peru, on the other.

The average $\delta^{34}S$ value at the Borov Dol deposit is –0.38‰, closely matching the average $\delta^{34}S$ value of –0.80 ‰ reported for the Skouries porphyry Au-Cu deposit in northern Greece (Höss et al., 2024). This similarity suggests that the ore-forming metals in both deposits – situated within the Lece-Chalkidiki metallogenic zone (Serafimovski, 2025), likely originated from sources located at comparable depths within the Earth's crust.

As shown in Figure 5, the $\delta^{34}S$ values for all three deposits within the Bučim–Damjan–Borov Dol mining region range from –7.52 to +8.68‰, confirming the endogenous origin of sulfur in the analyzed minerals, as these values fall within the typical range of –10 to +10‰ (Ohmoto and Rye, 1979; Shimazaki and Sakai, 1984) and closely align with the $\delta^{34}S$ signature of magmatic sulfur, 0‰ ± 5‰ (Field and Gustafson, 1976; Ohmoto and Rye, 1979; Shelton and Rye, 1982; Weihed and Fallick, 1994; Salas et al., 2013).The data indicate that the sulfur, and probably the ore metals within the deposits (from the Bučim-Damjan-Borov Dol mining region), are of primary origin, and the sources of sulfur are associated with the deep parts of the Earth's crust or with the boundary zone between the continental crust and the upper mantle (Serafimovski and Tasev, 2013).

Sulfur isotope fractionation between sulfide mineral pairs – isotope sulfur thermometer. Numerous theoretical and experimental determinations have been conducted on the fractionation of $\delta^{34}S$ between coexisting sulfide phases as a function of temperature (e.g., molybdenite, pyrite, sphalerite, pyrrhotite, chalcopyrite, galena, and SO_2 – Ohmoto

and Rye, 1979; anhydrite/gypsum – Ohmoto and Lasaga, 1982; bismuthinite – Bente and Nislsen, 1982; barite – Miyoshi et al., 1984). The results from these examinations refer to the sulfide thermo-meters mineral pairs: chalcopyrite-galena, sphalerite-chalcopyrite or pyrrhotite-chalcopyrite (Kajiwara and Krouse, 1971), pyrite-chalcopyrite and sphalerite-galena (Ohmoto and Rye, 1979; Clayton, 1981).
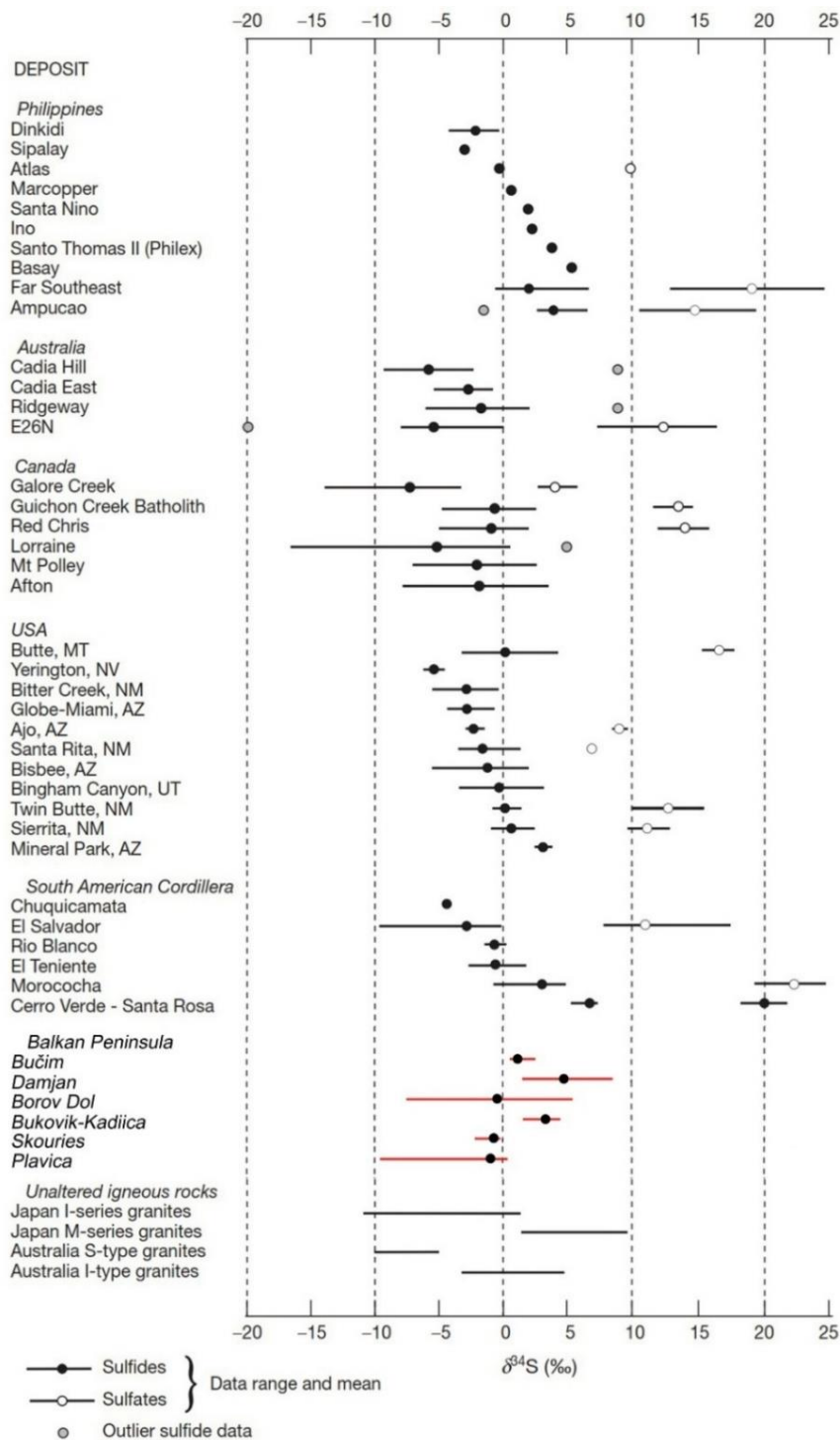

Fig. 5. Ranges of $\delta^{34}S$ sulfide values (per mil) determined for sulfide minerals from selected porphyry deposits and with granitic rocks (modified from Taylor, 1987; Wilson et al., 2007; Wolfe and Cooke, 2011). Gray circles indicate outlier sulfide data. Data sources: Ohmoto and Rye (1979), Čifliganec (1987), Taylor (1987), Tudžarov (1993), Heithersay and Walshe (1995), Baker and Thompson (1998), Akira (2000), Lickfold (2002), Deyell and Tosdal (2005), Wilson et al. (2007), Tasev (2010), Wolfe and Cooke (2011), Cooke et al. (2011), Zlatkov (2022), and Höss et al. (2024)

The analyses of the sulfur isotope composition in pyrite, chalcopyrite, galena and sphalerite, as basic ore minerals in the paragenesis in which quartz is also found, taken from the exploratory boreholes in the Borov Dol porphyry copper deposit, were partially followed by studies of fluid inclusions in the quartz (Gjorgiev, 2020). The sulfur isotope results, for the main sulfide minerals, were used to calculate geothermal temperatures and compare them with values obtained from fluid inclusions in quartz. The temperatures calculated from sulfur isotopes for sulfide-sulfide mineral pairs from Borov Dol were obtained from the guidelines given in the relevant references (Rye and Ohmoto, 1974; Ohmoto and Rye 1979; Shelton and Rye 1982; Ohmoto, 1986; Brownlow, 1996). Namely, the new sulfur isotopes data on the $\delta^{34}S$ (Table 1) in samples from the Borov Dol deposit show consistency with the values from previous researchers (Tudžarov, 1993). Regarding sulfur isotope geothermometers, it should be emphasized that a great number of experimental studies have been performed in order to determine the temperature depending on the factors of the equilibrium fractionation of sulfur isotopes between the coexisting minerals pyrite-chalcopyrite, chalcopyrite-galena, sphalerite-chalcopyrite, and sphalerite-galena (Ohmoto and Rye, 1979).

From the mineral pair pyrite-chalcopyrite that was used (in paragenesis with quartz from which the measured fluid inclusions originate), it can be seen that the obtained value for the formation temperature of 877°C is not consistent with the temperatures obtained from the fluid inclusion data, suggesting that pyrite and chalcopyrite crystallized under isotopic disequilibrium in the early phase (Yamamoto et al., 1984; Bortnikov et al., 1995; Gjorgiev, 2020; Table 2).

Sulfide mineral pairs and sulfide-sulfate mineral pairs are not always in equilibrium. This occurs when: (1) the mineral pairs are formed at low temperature ($T < 200°C$) (2) the isotopic composition of the mineralizing fluid is variable, and (3) isotopic exchange continues during the formation of the mineral phases (Ohmoto and Rye, 1979).

The existence of isotopic equilibrium is best demonstrated by determining temperature calculations between three coexisting minerals. The agreement between two calculated temperatures can be taken as evidence of equilibrium.

T a b l e 2

Analytical data for coexisting minerals pyrite-chalcopyrite and chalcopyrite-galena-sphalerite crystallized during simultaneous mineralization within the Borov Dol ore deposit, distribution, sulfur isotope fractionation and estimated mineralization temperatures

N	Sample	Mineral	$^{34}S/^{32}S$	$\delta^{34}S$	ΔA-ΔB	1000l nα	T Kelvin's	T (°C)
3	BD-29/94 m	Pyrite	22.16046	–2.68	0.34	0.340972	1150.45	877.30
11	BD-29/94 m	Chalcopyrite	22.15290	–3.02				
15	BD-335/132 m	Chalcopyrite	22.27777	+2.60	–2.80	–2.788846	481.81	208.66
14	DB-335/132 m	Galena	22.33999	+5.40				
13	BD-335/132 m	Sphalerite	22.30221	+3.70	1.10	1.096546	369.27	96.12
15	BD-335/132 m	Chalcopyrite	22.27777	+2.60				
13	BD-335/132 m	Sphalerite	22.30221	+3.70	–1.70	–1.692300	655.30	382.15
14	DB-335/132 m	Galena	22.33999	+5.40				

For the three coexisting sulfide minerals chalcopyrite-galena-sphalerite the values obtained for isotopic temperatures range from 96.12 to 382.15°C. In this case, chalcopyrite, galena, and sphalerite crystallized at isotopic equilibrium, as there is agreement between both calculated temperatures. From this it can be concluded that there is generally an equilibrium in the system at the time of deposition of the middle and late stage paragenesis.

The sulfide isotopic mineral pair sphalerite-galena yielded an isotopic temperature of 382°C, which is generally consistent with the data from primary two-phase fluid inclusions of diluted solutions (salinity 5.3 to 10.7 wt% NaCl equiv and fluid density of 0.55–0.90 g/cm³) that have a homogenization temperature in the range of 225°C to > 400°C. This indicates that the isotopic equilibrium was established between sphalerite and galena, such had been

proven for some studies using sulfur isotope fractionation in coexisting sphalerite-galena pairs have estimated formation temperatures ranging from approximately 105 to 370°C (Bortnikov et al., 1995). Thus, the sphalerite-galena geothermometer, together with the results from fluid inclusions, appears to provide accurate temperatures and also pressures for the formation of the mid-stage mineralization. This is also confirmed by the fact that the equation $1000 \ln \alpha = 0.73 \ (10^6/T^2)$ (Ohmoto and Rye, 1979)

gives a value in good agreement with homogenization temperatures.

The sulfide isotopic mineral pair chalcopyrite-galena yielded an isotopic temperature of 208°C, which also generally agrees with the data from primary two-phase fluid inclusions of diluted solutions (Gjorgiev, 2020). The chalcopyrite-galena geothermometer, together with the results of the primary fluid inclusions, likely provides accurate temperatures and pressures for the formation of late-stage mineralization.

7. CONCLUSION

The isotopic analysis of sulfur ($\delta^{34}S$) in sulfides from the Borov Dol deposit shows a wide range of values from –7.52‰ to +5.40‰. This range is within the typical values for porphyry copper deposits and indicates a dominant endogenous origin of sulfur. Negative $\delta^{34}S$ values indicate deposition from oxidized sulfate-rich hydrothermal solutions. Mineralogical data confirm that sulfides are dominant over sulfates, indicating effective sulfate reduction and generation of H_2S required for mineralization. Although it is expected that magmatic sulfur would have $\delta^{34}S$ values close to 0‰, the presence of positive and negative values indicates multiple sources of sulfur, including magmatic reservoirs, assimilation of surrounding rocks, and possible influence from meteoric waters.

A comparative analysis with other porphyry deposits positions the Borov Dol deposit within globally known ore systems, such as Bisbee, El Salvador, Butte, Morococha, and Skouries. The calculated temperatures from sulfur isotope thermometers for the mineral pairs chalcopyrite-galena and sphalerite-galena are in good agreement with the data from fluid inclusions, which confirms the isotope equilibrium during the middle and late mineralization stages. In contrast, the pyrite-chalcopyrite pair shows disequilibrium, which indicates early crystallization under variable conditions. These results confirm the applicability of isotope thermometers in reconstruction of thermodynamic conditions during the formation of ore paragenesis in the Borov Dol deposit.

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Р е з и м е

ИЗОТОПЕН СОСТАВ НА СУЛФУРОТ ВО НАОЃАЛИШТЕТО БОРОВ ДОЛ, СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: изотопи на сулфур; рудни минерали; состав; фракционација; наоѓалиште Боров Дол

Проучувањето на изотопниот состав на сулфурот е од суштинско значење за развој на генетски модели кај порфирските наоѓалишта на бакар. За утврдување на потеклото на металите и сулфурот во порфирското наоѓалиште на бакар Боров Дол се спроведени серија истражувања и анализи на изотопите на сулфурот (^{32}S, ^{34}S) и нивниот изотопски однос (δ^{34}S). Во наоѓалиштето Боров Дол беа земени примероци, главно од пирит (со хидротермалниот температурен опсег од 250–350ºC), потоа халкопирит, галенит, сфалерит и халкозин. Кај наоѓалиштето Боров Дол вредностите покажуваат широк опсег почнувајќи од –7,25‰ до +5,40‰, со просек од –0,38‰. Според тоа, изворот на сулфурот е магматски, поврзан со длабоките делови на Земјината кора или со граничната зона помеѓу континенталната кора и горната обвивка, со создавање на фракции со пулсирње и делумно збогатување со лесниот изотоп на сулфурот, што се огледа во негативната вредност во повисоките нивоа на наоѓалиштето, или со благо збогатување на тешкиот изотоп на сулфурот, што се огледува во позитивната вредност во пониските нивоа на наоѓалиштето. Сулфидните парагенези во порфирскиот систем на Боров Дол најверојатно се депонирани од оксидирани хидротермални рудоносни раствори, при што не постои рамнотежа во системот при кристализацијата на парагенезата од раната фаза. Рамнотежата во системот се воспоставува при кристализацијата на парагенезата од средната и доцната фаза.