

SULFUR ISOTOPE COMPOSITION OF SOME POLYMETALLIC DEPOSITS IN THE REPUBLIC OF MACEDONIA

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Abstract: The attempt to obtain an exact information about the origin of sulfur and other metals present in polymetallic deposits at the territory of the Republic of Macedonia have resulted in a detailed sulfur isotope composition study, which have enclosed the following deposits: Toranica, Sasa, Zletovo, Bučim and Alshar deposit. Results obtained for the formerly mentioned deposits have shown that sulfur isotope composition $\delta^{34}\text{S}$ is in the range $-7.52 \pm +2.18 \text{‰}$ in Toranica, $-1.22 \pm +6.94 \text{‰}$ in Sasa, $-3.12 \pm +3.40 \text{‰}$ in Zletovo (without ore associated barites), $+0.00 \pm +2.53 \text{‰}$ in Bučim (the narrowest range of all studied deposits) and $-6.84 \pm +0.351 \text{‰}$ in Alshar. Therefore, the most probably origin of primary sulfur in studied deposits from Earth's crust or eventually Upper Mantle. Such sources of sulfur and other mineralizing metals confirmed the theories about the endogene origin of mineralization fluids, which have formed studied deposits.

Key words: sulfur; isotopes; composition; polymetallic deposits; ore mineralization

INTRODUCTION

The study of sulfur isotopes could give us a clue about the source of this element and to point out to the source of some other components which took a part in the mineralization processes of a particular ore deposits as much as it could help us in determination of mineralization temperatures (certain mineral pairs that are in isotopic equilibrium).

Sulfur isotopic composition ($\delta^{34}\text{S}$) if grouped around the meteoritic one (Canyon Diablo Meteorite $\delta^{34}\text{S} = 0.0 \text{‰}$) with a narrow range of variance $+6$ to -4‰ , points to a sulfur origin from the upper mantle, Jensen (1959), Sakai (1968), Grinenko (1974), Јанковић (1981), Andrew (1989) and others.

The fractionation sulfur which have originated from the Upper Mantle or deep homogenized parts of the Earth's crust (different pH and Eh conditions and high temperatures) didn't caused significant changes (higher than $\pm 10 \text{‰}$) in its composition in comparison with the one in meteorites.

Preliminary data on this subject, for the polymetallic deposits in the R. Macedonia, could be obtained in Drovenik et al. (1970), Blečić (1974, 1981, 1983), Јанечка et al., (1972), Mudrinić & Petković (1976, 1982), Dimitrov (1977), Mudrinić (1978), Drovenik et al. (1983), Серафимовски (1990), Александров (1992) etc.

GENERAL GEOLOGICAL-GEOCHEMICAL FEATURES OF SOME POLYMETALLIC DEPOSITS IN THE REPUBLIC OF MACEDONIA

Sulfur isotopic studies were performed on particular polymetallic deposits enclosed in the well known Serbo-Macedonian metallogenic province at the territory of the Republic of Macedonia. The studied deposits were: Sasa-Toranica, Zletovo, Bučim and Alshar where were determined polymetallic mineralization of Pb, Zn, Cu, Au, Sb etc.

The ore mineralization in all formerly mentioned deposits spatially and genetically has been related with the Tertiary magmatism and hydrothermal ore bearing processes related with it. The study of sulfur isotopic composition of sulfides from these deposits gave us an exact review of what could happen during the genesis processes. More detailed

features of these deposits and results from sulfur isotope studies are given below.

Toranica ore deposit

The lead-zinc deposit Toranica has been localized in the Sasa-Toranica ore district in frame of the Osogovo Mountains.

The geological composition of the Toranica deposit comprise of rocks of the metamorphic complex and Tertiary igneous rocks. The most common represents are: gneiss, quartz-graphite schists, cipolines and intrusions of quartzlatites. Later ones represent the magmatic control of mineralization.

In frame of the Toranica deposit were determined layered and lens-sheeted ore bodies. The ore bodies related with quartz-graphite schists are of greatest economic importance.

Up to date complex analyses have shown the following mineralogy of the deposit: galena, sphalerite, chalcopryrite, pyrite, pyrrhotite, magnetite, martite, arsenopyrite, bornite, enargite, tetrahedrite, marcasite, barite, native gold, hematite, cubanite, native bismuth etc.

Up to date data from the research of sulphur isotopes from the Toranica Pb-Zn deposit are given in Table 1.

Table 1

Isotopic composition of sulfur in minerals from the Toranica ore field

No.	Label	Locality	Mineral	$\delta^{34}\text{S} \text{‰}$
1	12	Toranica-2	PbS	-0.60
2	2	Toranica-2	ZnS	+2.10
3	I/6	Toranica	FeS ₂	-2.94
4	I/9	Toranica	PbS	-4.19
5	I/9	Toranica	CuFeS ₂	-3.09
6	II/2	Toranica	ZnS	-4.16
7	II/10	Toranica	PbS	-5.61
8	III/3	Toranica	PbS	-7.52
9	IV/5	Toranica	ZnS	-4.08
10	IV/II	Toranica	FeS ₂	-3.59
11	IV/13	Toranica	PbS	-4.91
12	P6c	Toranica	CuFeS ₂	+1.73
13	P6p	Toranica	FeS ₂	+2.18
14	P7	Toranica	CuFeS ₂	+1.72

Note: The data numbered from 1 up to 11 are from Drovenik et al., (1970); Јанечка et al., (1972); Mudrinić & Petković (1976, 1982); Димитров (1977); Mudrinić (1978); Serafimovski (1990, 1993) while the data numbered 12, 13 and 14 are from Tasev (2003)

From the table above it can be seen that the results of the studied isotope are in the range that is very close to those of meteorites (with a certain variations), which points out that the sulfur in the Toranica ore deposit is of endogene origin, Earth's crust or even from the Upper Mantle.

Isotopic values of sulfur are mainly in the range -7.52‰ up to $+2.18\text{‰}$, with a median value of -2.34529‰ and value range of 9.7‰ units. More clearer impression of these parameters could be seen from the diagram of frequency distribution (Fig. 1).

From the obtained mean values it can be seen that in this deposit there is a general trend of decrease of heavier isotope (^{34}S) or enrichment with lighter one (^{32}S). Mainly the variations in the sulfur isotope values are direct consequence of processes of fractionation and certain increase of lighter ^{32}S (see left part of Fig. 1).

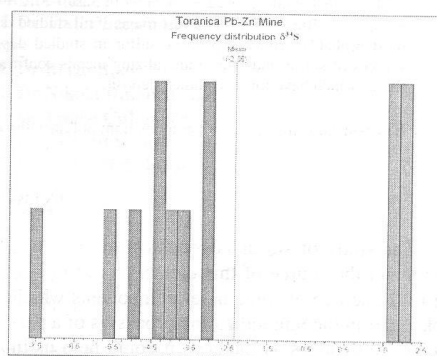


Fig. 1. Frequency distribution of sulfur isotope values of sulfides from the Toranica Pb-Zn deposit

In accordance with stable isotopic composition data were performed calculations to determine the temperatures of formation of certain minerals. Obtained temperature values coincide with temperatures obtained during the fluid-inclusions analyses. This is in accordance with statement of Shelton and Rye (1982), which said that where there is a general overprinting of the data for temperatures obtained with study of fluid-inclusions and calculated temperatures by the data of sulfur isotopic compositions, can be said for sure that the minerals of interest were formed in a isotopic equilibrium with a ore bearing fluid (on a other side the latter is a main premise for correct isotopic thermometer calculations). In the Toranica ore field calculated sulfur isotope temperatures were in the

range 277 ± 323 °C (galena-pyrite mineral pair), which corresponds with temperatures obtained during fluid-inclusions studies, range 170 ± 340 °C (Tacev, 2003).

Sasa ore deposit

The Sasa deposit has been situated in the NE part of Macedonia in frame of the Toranica-Sasa ore district near the city of Makedonska Kamenica.

In the geological composition of the Sasa ore deposit participate rocks such as: green schists, quartz-muscovite-graphite schists, marbles, phillites, gabbro, gabro-diorite, granodiorite, granite, quartzlatite, rhyodacite, latite-andesite porphyries, sanidine dacite etc.

The formation of the Sasa ore deposit has been related with the pneimatolite-hydrothermal and hydrothermal solutions that are genetically related with sanidine-dacites.

Ore bodies enclosed in frame of quartz-muscovite-graphite schists with interrelations of calc-schists and marbles, while the other part has been deposited into the green schists and Tertiary rocks. In frame of this ore field were determined two genetic types of ore formation: skarn-hydrothermal (skarns) and hydrothermal.

Intensive studies of the Sasa ore deposit determined complex mineralogical composition, which comprise mainly of: galena, sphalerite, pyrite, pyrrhotite, chalcopyrite, tetrahedrite, freibergite, tennantite, marcasite, stephanite, pirargirite, acantite, pollybasite, johansenite, rhodonite, ilvaite, rhodochrosite etc.

Sulfur isotopic composition studies of the concerning area were performed earlier but without specific research programme. Some data from the previous results could be obtained in Drovenik et al. (1970), Јанечка et al. (1972), Mudrinić & Petković (1976, 1982), Димитров (1977), Mudrinić (1978), Drovenik (1983), Серафимовски (1990), Александров (1992), etc. The latest results concerning Sasa Pb-Zn deposit are part of this paper (Table 2).

From the results in Table 2 could be concluded that the isotopic composition quite close to those of the meteorites, which undoubtedly points out that the sulfur in the Sasa deposit have originated from the deeper parts of the Earth's crust or from the Upper Mantle.

Certain isotopic variations were caused by particular sulfur fractionation as a result of slight enrichment with the heavier ^{34}S .

Table 2

Isotopic composition of sulfur in minerals from the Sasa ore field

No.	Locality	Mine level	Mineral	$\delta^{34}\text{S} \text{ ‰}$
1	Sasa	VII / 14 (1)	PbS	+3.64
2	Sasa	XII / 10 (7)	PbS	+3.00
3	Sasa	XIII (8)	PbS	+3.00
4	Sasa	XVa / 30 (9)	PbS	+2.84
5	Sasa	XIIo / 1	PbS	+2.13
6	Sasa		PbS	+2.67
7	Sasa	XVa / 30 (10)	ZnS	+3.99
8	Sasa	XVa / 30 (12)	ZnS	+5.18
9	Sasa	XVa / 43	ZnS	+4.11
10	Sasa	XIIo / 1	ZnS	-1.22
11	Sasa	1555-I	ZnS	+1.70
12	Sasa	P4	ZnS	+5.41
13	Sasa	VII / 14 (2)	Fe_{1-x}S	+3.97
14	Sasa	222	Fe_{1-x}S	+1.80
15	Sasa	XIIo / 1	Fe_{1-x}S	+1.82
16	Sasa	XII / 24 (5)	CuFeS_2	+4.41
17	Sasa	XVa / 30 (10)	CuFeS_2	+4.39
18	Sasa	P5	CuFeS_2	+2.90
19	Sasa	XII / 25 (3)	FeS_2	+4.82
20	Sasa	XII / 30 (4)	FeS_2	+4.94
21	Sasa	XII / 24 (6)	FeS_2	+5.21
22	Sasa	XVa / 43 (14)	FeS_2	+4.34
23	Sasa	IVo	FeS_2	+14.12
24	Sasa	VII / 23	FeS_2	+4.73
25	Sasa	XII / 1	FeS_2	+4.64
26	Sasa	XII / 1	FeS_2	+6.94

Note: The data numbered from 1 up to 11, 13-17 and 19-26 are from Серафимовски (1990) and Александров (1992), while 12 and 18 are from Tacev (2003)

The variations that occurred in all sulfide minerals have their own specifics and similarities, also. The galena from the Sasa ore field has been enriched with the heavier sulfur isotope. Measured range of $\delta^{34}\text{S}$ in galenas is from +2.13 up to +3.64 ‰ with a mean value of +2.88 ‰ and range of 1.13 ‰ units. Sphalerite sulfur isotopic variations are in the range from -1.22‰ up to +5.41‰ with a mean value of +3.195‰ and range of 6.63‰ units.

Pyrrhotite sulfur isotope variations are between +1.80 ‰ and +3.97 ‰ (mean +2.53 ‰) and range of 2.17 ‰ units. Chalcopyrite is characterized by variations from +2.90 up to +4.41 ‰ (mean value +3.90 ‰) and range of 1.51 ‰ units. Pyrite

variations are from +4.34 up to +14.12 ‰ (mean value +6.22 ‰) and range of 9.78 ‰ units.

If we perform an interpretation of mentioned values for the sulfide minerals in the Sasa ore deposit it could be concluded that galena has the lowest enrichment with heavier sulfur isotope while that enrichment trend is with increased intensity toward pyrrhotite, chalcopyrite and pyrite. This was caused, probably, by the temperatures of crystallization of formerly mentioned minerals in frame of this ore field.

It is important to point out that the determined variations of the sulfur isotopic compositions in the Sasa ore field is of relatively narrow intensity (range from -1.22 up to +6.94 ‰, see Fig. 2), which is in the range of variations very common for the sulfur in the endogene deposits (Гриненко, 1974 and Misra, 2000). Exception of that general trend of values is the one of +14.12 ‰ for pyrite, which is a direct consequence of influence of biogenic fractionation caused near the schists rich with organic matter. The narrow range of fractionation processes is caused by the relatively small and balanced temperature interval of mineral formation in the concerned ore field. Such a temperature interval didn't allowed some intensive fractionation of sulfur in the area. This leads us to a conclusion that the ore bearing solutions in the area were of quite homogenous character.

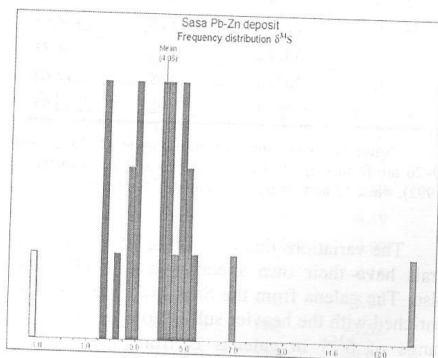


Fig. 2. Frequency distribution of sulfur isotope values for sulfides from the Sasa Pb-Zn deposit

The slight enrichment of sulfide minerals from the Sasa ore deposit with the heavier sulfur isotope can be noticed in the central part of the frequency distribution diagram shown above.

From the data concerning sulfur isotope data were calculated temperatures in the range 174 ±

490 °C (mineral pairs: sphalerite-galena, sphalerite-chalcopyrite, galena-chalcopyrite), which corresponds or is partially different with temperatures obtained during the fluid inclusions study, 129 ± 372 °C. Such a temperature range implied a conclusion that mineralization occurred as a multistage process. The rule of equilibrium fractionations of sulfide mineral pairs with hydrothermal fluid was applied here, too.

Zletovo ore deposit

Zletovo lead-zinc has been located in the eastern parts of the Kratovo-Zletovo volcanogene complex or occupies the central part of the Kratovo-Zletovo ore district.

From the geological point of view the Zletovo deposit is built of: andesite, dacite, ignimbrite with dacite composition, dacite-andesite, stratified volcanic tuff etc.

For the localization of the lead-zinc mineralization the most important geological unit is dacite-ignimbrites, which are most common volcanic represent in the area.

Dimensions of the ore bodies (ore veins) are various, long 100 – 3000 m (rarely up to 5000 m), while in depth they have been followed up to 500 m. In the same time the thickness of ore veins is between 2 cm and 5 m.

Up to date studies of the Zletovo ore deposit confirmed that the deposit was formed during the hydrothermal stage and has been built of very complex parageneses. Ore mineralogy supported by more sophisticated techniques such as Scanning Electron Microscope and Electron Microprobe confirmed existence of numerous mineral represent. The most important of them are: galena, sphalerite, pyrite, chalcopyrite, tetrahedrite, tenanite, marcasite, siderite, barite, pyrrhotite, enargite, bornite, arsenopyrite, chalcocite etc.

Preliminary results concerning sulfur isotope composition of the minerals in the Zletovo deposit were published by Drovenik et al. (1970) (Table 3). Analyses were performed on 4 sphalerite, 4 galena and 2 barite samples from the deposit. The value of $\delta^{34}\text{S}$ in sulfides varied from +2.16 ‰ up to -3.12 ‰ (mean value -0.32 ‰) and range of 5.28 ‰ units. The general conclusions in accordance with that data were that the sulfur is of endogene origin, mostly from the Upper Mantle parts.

Later analyses of sulfur in sulfides (pyrite, sphalerite, galena) and sulphate (barite), Mudrinić & Petković (1982) and Tasev (2003) on a signifi-

cant amount of samples from ore veins of the Zletovo ore field, didn't showed some important difference in comparison with the preliminary results by Drovenik et al. (1970), Table 3.

Table 3

Isotopic composition of sulfur in minerals from the Zletovo ore field

No.	Sample label	Mineral	$\delta^{34}\text{S} \text{ ‰}$
1	S 57	ZnS, light	+0.03
2	S 58	ZnS, lightbrown	+0.27
3	S 60	ZnS, lightgreen	+0.92
4	S 62	ZnS, darkbrown	+2.16
5	G 61	PbS	-3.12
6	G 59	PbS, assoc. with ZnS	+0.28
7	G 56	PbS, coarse grained	-1.09
8	G 54	PbS, assoc. with BaSO ₄	-2.00
9	Ba 53	BaSO ₄ , with PbS(G 54)	+21.43
10	Ba 55	BaSO ₄ , assoc. with FeS ₂	+18.63
11	69 z	ZnS	+0.50
12	71 z	ZnS	+1.70
13	12 z	ZnS	+0.20
14	21 z	ZnS	+1.40
15	70zA	ZnS	+3.40
16	M 39	ZnS	+0.80
17	M 71	ZnS	-2.90
18	M 22	ZnS	-2.90
19	M 24	ZnS	+1.30
20	12z	PbS	-2.70
21	70zA	PbS	+2.80
22	M 39	PbS	+0.10
23	M 60	PbS	+0.40
24	M 71	PbS	+1.10
25	M 76	PbS	-0.40
26	M 20	PbS	+1.30
27	M 29	PbS	+1.40
28	M 26	PbS	+1.40
29	M 65	FeS ₂	+0.30
30	M 6	FeS ₂	+2.10
31	M 99	BaSO ₄	+25.50
32	M 28	BaSO ₄	+22.60
33	L 1	BaSO ₄	+21.10
34	P1	PbS	-2.04
35	P9	PbS	-1.53

Note: Data numbered 1–10 are from Drovenik et al., (1970), 11–33 from Mudrinić & Petković (1982), 34–35 from Tacev (2003).

Values obtained for pyrite were mainly between +0.3 and +2.1 ‰, range of 1.8 ‰ values and mean value of +1.2 ‰. Sulfur isotope composition of sphalerites showed variations from -2.9 ‰ up to +3.4 ‰ $\delta^{34}\text{S}$ and only two samples showed negative values while all other were characterized by positive values (enrichment by the heavier isotope) from +0.2 up to +3.4 ‰. The range for all samples is 6.3 ‰ units while the mean value is +3.9 ‰.

Isotopic composition of galenas varies from -2.7 ‰ up to +2.8 ‰. The range of variations is of 5.5 ‰ units. The average arithmetic value for analyzed samples is +0.53 ‰. The S isotopic composition of analyzed barites is from +21.3 ‰ up to +25 ‰, range of 4.2 ‰ units and mean value +23.13 ‰, which is very common for hydrothermal sulfates such are these.

After the analysis of whole data set were constructed frequency distribution diagrams, once with inclusion of barite data (Fig. 3) and once without them (Fig. 4).

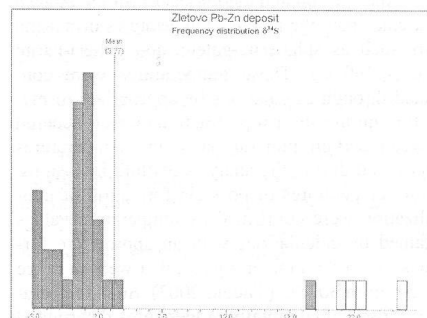


Fig. 3. Frequency distribution of sulfur isotope values for sulfides and ore associated barite from the Zletovo Pb-Zn deposit

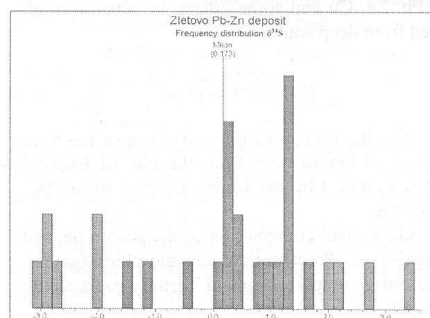


Fig. 4. Frequency distribution of sulfur isotope values for sulfides from the Zletovo Pb-Zn deposit

As it can be seen from the diagrams above (especially Fig. 4) we may conclude that sulfur isotopic composition of the minerals from the Zletovo Mine, in general, are around the meteoritic one. This leads us to a conclusion that sulfur in the deposit is mainly from endogene origin (Earth's crust or/and Upper Mantle).

The fractionation of sulfur isotopes in sulfides from the Zletovo ore deposit shows slight enrichment with heavier isotope in pyrite, sphalerite and galena. Such a fractionation trend point out to a possibility that sulfur kept homogenous character during its migration from primary source until its place of precipitation. This leads us to a conclusion that sulfur assimilation and mobilization from adjacent rocks, if even happened, was of very low intensity.

Sulfur fractionation in studied sulfides and sulfates was initiated mainly by temperature regime all together with pH and Eh features of the media during the precipitation of ore minerals.

Experimental and theoretical experiences gave us a clue about the possible temperatures of mineral pairs such as sphalerite-galena and galena-barite (150 – 360 °C). These temperatures were confirmed through calculations by appropriate formulas for equilibrium isotope fractions which occurred between certain mineral pairs and temperatures determined during the analysis of fluid inclusions. Those temperatures of possible formation of mineralization were confirmed by temperature values obtained by calculations with an appropriate formulas, for certain mineral pairs, that were in range of 134 up to 307 °C (Tacev, 2003). Such temperatures closely related with temperatures determined by fluid-inclusions analyses, too (109 – 368 °C).

In accordance with isotopic composition of sulfur in sulfides it may be concluded that ore metals Pb, Zn, Cu and some others, in general, originated from deep sources.

Bučim ore deposit

The Bučim copper porphyry deposit has been located 10 km western from the city of Radoviš and is enclosed by the Bučim-Damjan-Borov Dol ore district.

Geological composition of the Bučim deposit comprise of: Precambrian metamorphics (gneiss, micaschists, amphiboles) and Tertiary rocks (latite and andesite-latite).

According to the detailed geological explorations copper mineralization has been determined in

an area of $1.5 \div 2 \text{ km}^2$ and depth of 300 m. Mineralization has been located in four ore bodies: Central part, Bunardžik, Vršnik and Čukar. From all of them the Central part ore body is the most important one from the economic point of view. In this deposit were determined three genetical types of mineralization: primary (Central part and Bunardžik), supergene or mineralization related with oxydation-cementation zone (Čukar) and mixed type one (Vršnik). Of all of them the most important for copper production is primary sulfide mineralization.

An average copper concentration in the deposit is up to 0.3% Cu with 0.35g/t Au and 1g/t Ag. The main ore mineral is chalcopyrite associated with pyrite, magnetite, hematite, cubanite, valerite, native gold, bornite etc.

Concerning Bučim porphyry copper deposit, preliminary study was performed on 10 pyrite samples by Mudrinić & Petković (1976). While some later (Tacev, 2003) confirmed the general trend of sulfur isotope values.

Analysis of the sulfur isotopic composition of the pyrites have shown that the $\delta^{34}\text{S}$ is very narrow range of variations, with low increase of heavy sulfur isotope vs. meteoritic one (Table 4).

Table 4

Isotopic composition of sulfur in minerals from the Bučim ore field

No.	Ore body	Horizon	$\delta^{34}\text{S}\text{‰}$
1	Čukar	630	+2.53
2	Čukar	630	+0.16
3	Čukar	630	+1.02
4	Central part	605	+1.52
5	Central part	605	+0.42
6	Central part	605	+0.70
7	Vršnik	650	+0.00
8	Vršnik	650	+0.38
9	Vršnik	650	+0.80
10	Vršnik	650	+2.09
11	Central part	–	+0.99
12	Central part	–	+1.17

Note: Data numbered 1–10 from Serafimovski et al. (1996), 11–12 from Tacev (2003).

Variations of $\delta^{34}\text{S}$ for the whole Bučim ore deposit is in the range from +0.16 up to +2.53 ‰,

with an average value of 1.06 ‰ (Fig. 5). It is obvious that there is a certain variation in $\delta^{34}\text{S}$ values for particular ore bodies.

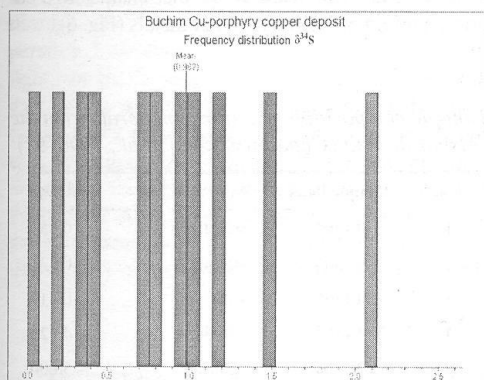


Fig. 5. Frequency distribution of sulfur isotope values for sulfides from the Bučim Cu-porphyry deposit

Very narrow $\delta^{34}\text{S}$ interval, probably is a direct consequence of the homogeneous and quite similar physical-chemical conditions during the formation of sulfide parageneses in all of the three ore bodies in the deposit. Certain difference in $\delta^{34}\text{S}$ values for different ore bodies probably was caused by the small differences in the composition of the ore fluids on its mineralization path and slight changes of physico-chemical variables (especially temperature). The range of $\delta^{34}\text{S}$ values in pyrites from all three ore bodies points out to a endogene origin of the sulfur.

In accordance with existing classifications and obtained results for $\delta^{34}\text{S}$, this deposit could be classified in the first group with an interval from 0.0 up to 0.5 ‰ $\delta^{34}\text{S}$. Ohmoto and Rye (1979) pointed out that the deposits, which values belong to this group are closely related with felsic igneous rocks. The sulfur in the deposit is of igneous origin and was obtained during the release from the silicate solutions or mobilized from sulfides in igneous rocks.

Nevertheless, the origin of the copper in the Bučim deposit has been related with primary magmatic intrusion. Since the igneous bodies – dykes and small stocks were too small for mobilization of the hydrothermal convective systems, copper amounts that we find today in the Bučim ore bodies, should be related with existence of deeper and bigger igneous bodies.

Also we should take in consideration the fact that copper could be mobilized from the serpen-

tinities, which are laying in the basement of the area where primary igneous complexes were intruded. This scenario is of especial interest if we keep on mind that the Neogene calc-alkaline igneous complexes of the Serbo-Macedonian province are poor with copper.

Temperatures of hydrothermal solutions during the formation ore minerals ranged from 200–300 °C up to 600 °C, while sometimes the lowest ones were as low as 100 °C for the youngest ore occurrences in nonproductive hydrothermal flows that have formed pyrite microfillings.

Temperatures calculations from the values of sulfur isotope composition (mineral pairs: galena-chalcopyrite) are in range from 110 up to 160 °C, which corresponds or partially doesn't correspond with temperature range obtained during the fluid-inclusions analysis (180 ÷ 200 °C) in quartz-pyrite associations (Blečić, 1974), while fluid-inclusions from some other mineral associations have shown higher temperatures. Temperature discrepancies between sulfur isotope calculations and those obtained from fluid-inclusions studies point out to a open system and disequilibrium sulfur fraction that occurred between certain mineral pairs. In this case we may speak about the existence of kinetic fractionation reactions.

Otherwise, the whole set of fluid-inclusions analyses have shown the range of temperature mineralization from 200 up to 490 °C, which is quite usual for porphyry deposits related with shallow and small subvolcanic intrusions.

Alshar ore deposit

The Alshar ore area has been located in the Vardar tectonic zone, which is a tectonic discontinuity between Pelagonian zone on the west and Serbo-Macedonian massif on the east.

Geological composition of wider area mainly consists of Precambrian albite gneiss and amphibolites, Paleozoic schist, phillite, cipoline, metasandstone, argiloschist and quartzite, Triassic marbelized limestones and dolomites, sanstones and clay-schists, Jurassic diabas-chert formation and gabbro-peridotite complex (significantly serpentized), Upper Cretaceous sediments represented by conglomerates and limestones, Late Eocene serie composed of flysch sediments, Pliocene lake sediments and pyroclasts while the Quaternary sediments are present in form of terraces and bigorovite plates. Volcano-intrusive complex is represented by calc-alkaline rocks of Pliocene age com-

posed mainly of latite, quartzlatite and andezite. K/Ar geochronology analyses of crystal tuffs at Alshar and surrounding rocks shown Pliocene age (4.5 ± 5.0 Ma).

Spatial distribution of mineralization is mainly controlled by faults, since the hydrothermal fluids used them as main pathways.

The mineral paragenesis of the Alshar deposit is relatively simple: stibnite, pyrite, arsenopyrite, marcasite, realgar, orpiment, lorandite, vrbait, limonite etc.

Mineralization in frame of the Alshar deposit has been located mainly along the contact between the altered andesites and silicified limestones and dolomites. Ore bodies are in form of ore piles, irregular nests and impregnations formed during the hydrothermal ore bearing processes.

Mineralization of Sb-As-Au-Tl-Hg in the Alshar area undoubtedly is very similar with Carlin type mineralization in western states of the USA. That similarity was induced by the geochemical association (As, Sb, Tl, Hg, Ba and traces Cu, Pb and Zn), hydrothermal alterations features (silicification, argillitization, and smaller vein alterations with quartz and calcite) and very similar mineralogy (pyrite, marcasite, realgar, stibnite etc.). Alshar mineralization is the first documented example of Carlin type gold mineralization of Late Tertiary period anywhere in the world.

The study of sulfur isotopic composition of the Alshar ore deposit has been performed on main sulfide minerals from the ore parageneses. Studies monomineral samples were of stibnite, realgar, orpiment and marcasite composition. Most of the samples were from the stibnites enclosed in different ore bodies (vein and metasomatic) of different generations. During the sampling programme special attention was given to the coarse-prismatic stibnite crystals, formed along the free fissure spaces during calm crystallization of differentiated hydrothermal solutions.

The analyses of sulfur isotopic composition of minerals from the Alshar deposit were performed at the IGEM – Moscow, Russia, while the results are given in Table 5.

From the table can be seen that the sulfur in the sulfide minerals from this deposit originated from endogene sources (deep homogenized parts of Earth's crust).

The $\delta^{34}\text{S}$ values in studied sulfide minerals is range from +0.351 up to -5.600 ‰ in stibnite, from -1.640 up to -3.77 ‰ in realgar and orpiment

and -6.840 ‰ in marcasite (Серафимовски et al., 1990–1991). All the ranges of sulfur isotopic compositions of analyzed samples, including certain variations, are within the range that characterize endogene origin of sulfur and other metals (Fig. 6).

Table 5

Isotopic composition of sulfur in minerals from the Alshar deposit (Серафимовски et al., 1990–91)

No.	Sample label	Mineral	$\delta^{34}\text{S}$ ‰
1	14564	stibnite	+ 0.351
2	14565	stibnite	- 0.337
3	14566	stibnite	- 0.419
4	14567	stibnite	- 4.728
5	14568	stibnite	- 5.600
6	14569	stibnite	- 1.750
7	14571	stibnite	- 5.220
8	14576	stibnite	- 3.560
9	14572	realgar	- 1.640
10	14573	realgar	- 3.770
11	14574	orpiment	- 3.690
12	14570	marcasite	- 6.840

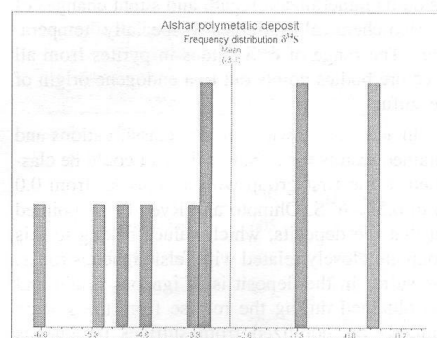


Fig. 6. Frequency distribution of sulfur isotope values for sulfides from the Alshar polymetallic deposit

Also, from the table above can be seen that sulfur in stibnite (samples No. 1, 2, 3 and 4), have shown values very close to the meteoric ones. Stibnite of later generations (sample No. 5, 7 and 8) and other sulfide minerals, especially marcasite, shown certain fractionation and noticeable enrichment with light isotope ^{32}S . This most probably was related with temperature gradient changes dur-

ing formation of certain mineral species or as a direct consequence of migration of hydrothermal solutions from distant sources and features of the area where these ore bearing solutions passed through. Such features are common for low temperature hydrothermal deposits. Enrichment with light isotope ^{32}S is emphasized in bimetallic deposits (As-Sb) such as Alshar and Lojane. If variations of $\delta^{34}\text{S}$ didn't exceeded 10%, that points out to a homogeneous character of ore bearing solutions from their place of origin until their place of deposition. Also, such values suggest that during the movement and evolution of hydrothermal solutions didn't occurred any substantial mixing, mobilization or assimilation of sulfur from the Earth's crust.

lization or assimilation of sulfur from the Earth's crust.

All these facts leads us to a conclusion that sulfur and other metals in the Alshar deposit are of endogene origin (Earth's crust or even from the Upper Mantle).

Calculated temperatures of mineralization by the sulfur isotope composition data are in the range quite similar to those formerly determined by studies of fluid-inclusions (Janković & Jelenković, 1990). Particular temperatures were in the range from 130 up to 190 °C, confirmed epithermal character of mineralization.

CONCLUSION

The complex character of data obtained during the study of sulfur isotope composition of some polymetallic deposits in the Republic of Macedonia gave us an exceptional opportunity to explore the ancient mineralization processes that have occurred during the geological history of those deposits and features of ore bearing fluids.

From the obtained mean values it can be seen that in Toranica deposit there is a general trend of enrichment with lighter one (^{32}S). Mainly the variations in the sulfur isotope values are direct consequence of processes of fractionation, which leads to a certain increase of lighter S.

It is important to point out that the determined variations of the sulfur isotopic compositions in the Sasa ore field is of relatively narrow range (-1.22 to +6.94 ‰), which is in the range of variations very common for the sulfur in the endogene deposits. Such a narrow range of fractionation processes is caused by the relatively small and balanced temperature interval of mineral formation. This leads us to a conclusion that the ore bearing solutions in the area were of quite homogenous character.

The fractionation of sulfur isotopes in sulfides from the Zletovo ore deposit shows slight enrichment with heavier isotope in pyrites, sphalerites and galenas. Such a fractionation trend point out to a possibility that sulfur kept homogenous character during its migration from primary source to the place of precipitation. This initiate a conclusion that sulfur assimilation and mobilization from adjacent rocks, if even happened, was of low intensity.

during its migration from primary source to the place of precipitation. This initiate a conclusion that sulfur assimilation and mobilization from adjacent rocks, if even happened, was of low intensity.

Very narrow $\delta^{34}\text{S}$ interval in the Bučim deposit probably is a direct consequence of the homogeneous and quite similar physico-chemical conditions during the formation of sulfide parageneses in all of the three ore bodies in the deposit. In accordance with existing classifications and obtained results for $\delta^{34}\text{S}$, this deposit could be classified in the first group with an interval from 0.0 up to 0.5‰ $\delta^{34}\text{S}$. The sulfur in the deposit is of igneous origin and was obtained during the release from the silicate solutions or mobilized from sulfides in igneous rocks.

In Alshar, enrichment with light isotope ^{32}S emphasized bimetallic features of the deposits (As-Sb). If variations of $\delta^{34}\text{S}$ didn't exceeded 10%, that points out to a homogeneous character of ore bearing solutions from their place of origin until their place of deposition. Also, such values suggest that during the movement and evolution of hydrothermal solutions didn't occurred any substantial mixing, mobilization or assimilation of sulfur from the Earth's crust.

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Резиме

ИЗОТОПЕН СОСТАВ НА СУЛФУРОТ ВО НЕКОИ ПОЛИМЕТАЛИЧНИ НАОГАЛИШТА ВО РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: сулфур; изотопи; состав; полиметаллични наоѓалишта; рудна минерализација

Обидот да се добие точна информација за потеклото на сулфурот и другите метали присутни во полиметалличните наоѓалишта на територијата на Република Македонија резултираше со детална студија за изотопен состав на сулфурот, која ги опфати следните наоѓалишта: Тораница, Саса, Злетово, Бучим и Алшар. Резултатите добиени за претходно споменатите наоѓалишта покажаа изотопен состав на сулфурот ($\delta^{34}\text{S}$) во следниот опсег: $-7,52 \pm 2,18\%$ Тораница, $-1,22 \pm 6,94\%$ Саса, $-3,12 \pm 3,40\%$ Злетово (без

баритите асоцирани со минерализацијата), $+0,00 \pm 2,53\%$ Бучим (најтесен опсег од сите проучувани наоѓалишта) и $-6,84 \pm 0,351\%$ во Алшар. Поради тоа се заклучува дека најверојатното потекло на примарниот сулфур во проучуваните наоѓалишта е од Земјината кора или евентуално од горната мантија. Таквите извори на сулфурот и другите минерализациони метали ги потврдуваат теориите за ендеогеното потекло на минерализационите флуиди, кои ги формирале овие наоѓалишта.