Sulfur isotope study of sulfides from some mineral deposits from the Lece-Chalkidiki metallogenic zone

Todor Serafimovski, Goran Tasev

Faculty of Mining and Geology, University "Sts. Cyril and Methodius", Skopje, 89 Goce Delchev, 2000 Stip, Republic of Macedonia; E-mail: seraft@rgf.ukim.edu.mk; gorankt asev@yahoo.com

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

Introduction

The sulfur isotope study can give a valuable information concerning the source of this element and point out the source of some other components that took a part in the mineralization processes of particular ore deposits. It could help also in determination of mineralization temperatures (certain mineral pairs that are in isotopic equilibrium). The porphyry copper, Pb—Zn and Sb-As deposits from the Lece-Chalkidiki metallogenic zone on the territory of Serbia, Macedonia and Greece were studied in the present paper.

The study of sulfur isotopic composition extended back to 1974 when the first data on the stable isotopes were obtained during the extensive research program in the Plavica region. Some data from the previous studies, concerning the polymetallic deposits in the Republic of Macedonia, can be found in Drovenik et al. (1970, 1983), Jankovic (1978, 1979), Mudrinic (1978), Serafimovski et al., (1990-91), Aleksandrov (1992), and lately in De Groot et al. (1996), Serafimovski, Tasev (2005), etc.

General data

Sulfur isotopic studies were performed on particular polymetallic deposits from the Lece-Chalkidiki metallogenic zone. Objects of study were porphyry copper (Bucim, Borov Dol, Plavica, Skouries), Pb—Zn (Sasa, Toranica, Zletovo, Olympias) and Sb-As (Krstov Dol, Lojane, Alsar) ore deposits. The ore mineralization in all of them is related to the Tertiary magmatism and hydrothermal ore-forming processes.

Geological features of the deposits

The *Buchim porphyry copper deposit* is enclosed within the Buchim-Damjan-Borov Dol ore district. The geological setting of the deposit is characterized by Precambrian metamorphics (gneiss, micaschists, amphibolites) and Tertiary rocks (latite and andesite-latite). The mineralization is located in four ore bodies: Central part, Bunardzik, Vrshnik and Chukar. Main ore mineral is chalcopyrite associated with pyrite, magnetite, hematite, cubanite, valleriite, native gold, bornite, etc.

The *Borov Dol porphyry copper deposit* is situated in the southern part of the Buchim ore district, which is a part of the Vardar zone. The mineralization in the deposit was deposited in a ring shape around the andesitic neck, which cuts across the volcanics of the older phase. The older volcanics, which are intensively hydrothermally altered, host the ore mineralization. Main ore mineral is chalcopyrite accompanied by pyrite, molybdenite, magnetite, native gold, bornite, and rarely by enargite, galena, tennantite, etc.

The *Plavica deposit* is situated in Northeastern Macedonia, near Probistip. It has a dominant position at the eastern border of the Zletovo-Kratovo volcanic area. The lithologic sequence of volcanic rocks begins with hornblende-biotite-andesites which are covered in their turn by ignimbrites of dacite and quartz latite compositions followed by tuffs and tuffobreccias with flows of dacites, quartz latites and trachytes.

The *Toranica Pb–Zn deposit* is localized in the Sasa-Toranica ore district within the frame of the Osogovo Mts. The geological setting of the deposit is characterized by rocks of the metamorphic complex as well as by Tertiary igneous rocks. The most common of them are gneisses, quartz-graphite schists, cipolines and quartz latite intrusions. The intrusions control the ore mineralization. Complex analyses showed the following mineralogy of the deposit: galena, sphalerite, chalcopyrite, pyrite, magnetite, martite, arsenopyrite, bornite, enargite, tetrahedrite, marcasite, barite, hematite, etc.

The *Sasa deposit* is situated in the northeastern part of Macedonia, near the city of Kamenica. The rocks in the region are represented by green schists, quartz-muscovite-graphite schists, marbles, phillites, gabbro, gabbro-diorite, granodiorite, granite, quartz latite, rhyodacite, porphyry latite-andesites, sanidine dacite, etc. The ore bodies are enclosed within quartz-muscovite-graphite schists with intercalations of calc-schists and marbles, while the other part deposited into the green schists and Tertiary rocks. The mineralogical composition of the deposit consists of galena, sphalerite, pyrite, chalcopyrite, tetrahedrite, tennantite, marcasite, stephanite, pirargirite, acantite, pollybasite, johansenite, rhodochrosite, etc.

The *Zletovo Pb—Zn deposit* is located within the Kratovo-Zletovo volcanogenic complex. It is built of andesite, dacite, dacite ignimbrite, dacite-andesite, stratified volcanic tuff, etc. The ore mineralization is related to dacite ignimbrites as the most common volcanic rocks in the area. The deposit was formed during the hydrothermal stage and consists of very complex parageneses. The mineral composition includes galena, sphalerite, pyrite, chalcopyrite, tetrahedrite, tennantite, marcasite, enargite, bornite, chalcocite, etc.

The *Sb—As deposits* in the Lece-Chalkidiki metallogenic zone are distributed peripherally or around the rim, with a greater or lesser telescoping of the depressed volcanics and its apparatuses. In connection with this, it is more frequent to find the localization of ore formations in the rim rocks (limestone, schists, sandstone, dacite-andesites, etc.) of varying ages from the crystalline Serbo-Macedonian Massif (Riphean—Cambrian) to the Oligocene sediments. We have paid an especial attention to the Alshar deposit in southern Macedonia. It is hosted by Pliocene volcanic-intrusive complex (altered latite, dacite, and andesite) and Triassic carbonates (dolomites and marbles). The most abundant ore minerals are realgar, stibnite, pyrite, marcasite, and other sulfides, including various Tl-bearing sulfides.

Results and discussion

Results and discussion are grouped by temperatures of formation of the porphyry copper, Pb-Zn and Sb-Au-As-Tl deposits (going from higher- to lower-temperature ones).

The study of sulfur isotope composition of sulfides from *porphyry copper deposits* was performed on 42 samples (including older and new data). The statistical analysis shows that the minimum value is at 7.52‰ δ^{34}S while the maximum one at +2.53‰ δ^{34}S, with a mean value of 0.02‰ δ^{34}S within a range of 10.05‰ (fig. 1).

The δ^{34}S variations for the Bucim ore deposit are in the 0.00 ÷ +2.53‰ range, for Borov Dol — 7.52 ÷ +0.72‰, and for Plavica — +0.41 ÷ +1.24‰. There is a certain variation of δ^{34}S values for particular deposits. Enrichment with light sulfur isotopes in Borov Dol (-7.52 ÷ -4.05‰ δ^{34}S) was determined in surface galena and near surface pyrite as a consequence of temperature of formation and certain influence of adjacent units where the thermal solutions passed through. The narrow δ^{34}S interval is a direct consequence of the homogeneous and quite similar physicochemical conditions during the formation of sulfide parageneses in all three deposits. The differences in the δ^{34}S values for particular ore bodies were caused by the small differences in the composition of the ore fluids. The δ^{34}S range in all of them points out to an endogenous origin of sulfur.

The sulfur isotope composition study of sulfides from *Pb—Zn deposits* was performed on 70 samples (both previous and new data). The statistical analysis shows a minimum δ^{34}S value at —7.52‰ while the maximum one is at +14.12‰ , with a mean value of 1.11‰ and range of 21.64‰ units (fig. 2). The δ^{34}S data for the particular deposits are as follows: Toranica — 7.52 ÷ +2.18 ‰, Sasa — 1.22 ÷ +6.94‰

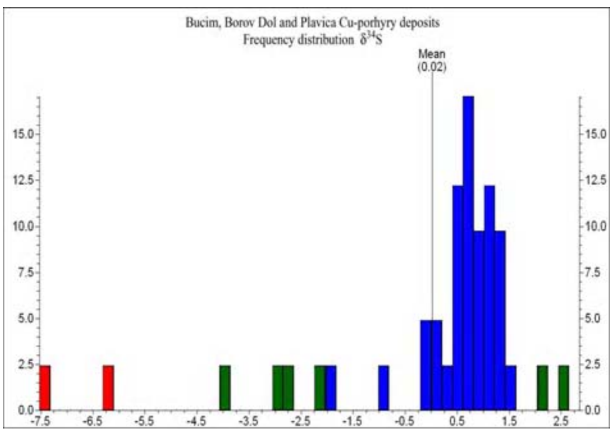

Fig. 1. Frequency distribution of sulfur isotope data for sulfides from the Bucim, Borov Dol and Plavica deposits

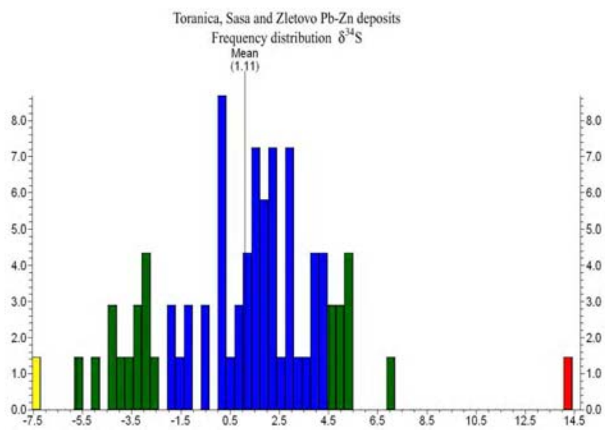

Fig. 2. Frequency distribution of sulfur isotope data for sulfides from the Toranica, Sasa, Zletovo and Olympias Pb—Zn deposits

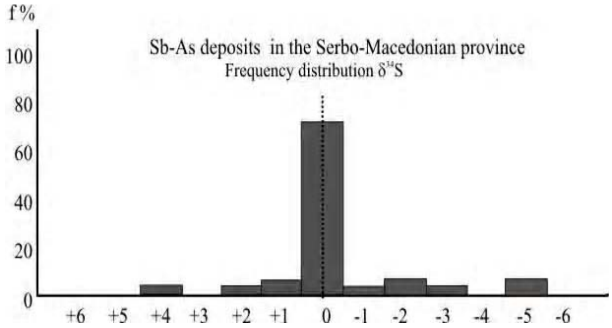

Fig. 3. Frequency distribution of sulfur isotope data in sulfides from the Sb—As deposits in SMMP

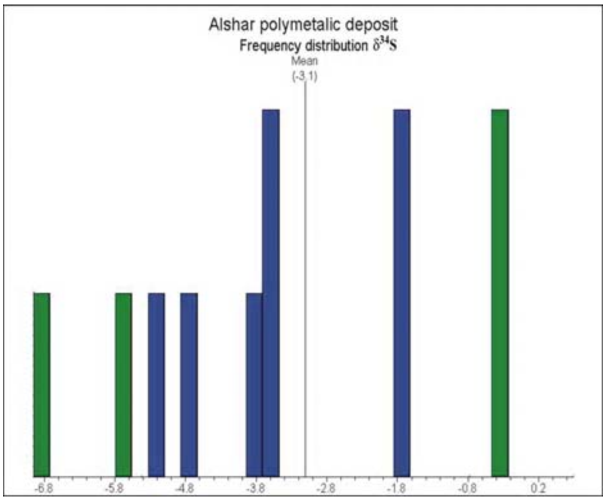

Fig. 4. Frequency distribution of sulfur isotope data for sulfides from the Alsar deposit

(+14.12‰ in one pyrite sample as a consequence of biogenic fractionation), Zletovo —3.12 ÷ +3.40 ‰, and —0.30 ÷ +2.70‰ $\delta^{34}S$ in Olympias (Northern Greece).

Based on the data on fig. 2, it can be concluded that the results are in a range very close to those of meteorites (with a certain variations), which points out that the sulfur in these deposits is of endogenous origin.

The sulfur isotope study of the *Sb–As deposits* from the Lece-Chalkidiki zone was performed mainly on stibnite and realgar minerals. The $\delta^{34}S$ isotope composition is in the range of —5.60 ÷ +3.70‰ that practically confirms their endogenous origin (fig. 3).

Slight deviations of $\delta^{34}S$ from the meteoritic composition indicate partial fractionation due to the differences in the temperature conditions of the individual deposits. It can be indirectly concluded that the ore metals trace their origin to the deeper parts of the continental crust or the upper mantle. The Sb associations are the product of endogenous processes related to the Oligocene—Miocene magmatism in Serbia and Macedonia.

The sulfur isotope study of the *Alshar ore deposit* was performed on the main sulfide minerals from the ore parageneses (stibnite, realgar, orpiment and marcasite). The $\delta^{34}S$ values for stibnite are in the range +0.35 ÷ -5.60‰, for realgar and orpiment — -1.64 ÷ -3.77, and for marcasite -6.84‰, while the whole set of studied samples varied between -6.84 and +0.35‰ at a mean value of -3.1‰. All data for sulfur isotopic compositions of the analyzed samples, incl. certain variations, are within the range characterizing endogenous origin of sulfur and other metals (fig. 4).

The sulfur isotope compositions of stibnite are also close to the meteoric ones. Later generations of stibnite as well as other sulfide minerals, especially marcasite, show certain fractionation and noticeable enrichment in the light isotope ^{32}S. That was probably caused by changes in the temperature gradient during the formation of certain mineral species or as a direct consequence of migration of hydrothermal solutions from distant sources and the features of the area where these ore-bearing solutions passed through, which is the common case for low-temperature hydrothermal deposits.

Conclusion

The obtained S isotope data for the main sulfide minerals from the studied polymetallic deposits shows that the sulfur is generally of endogenous origin. The $\delta^{34}S$ isotope values in all deposits range between -7.52 and +7.00‰. Discrepancies from the common $\delta^{34}S$ values (+14.12‰) were registered only for the Sasa deposit as a direct consequence of biogenic S fractionation in the pyrite.

References

Aleksandrov, M. 1992. *Metalogenetski karakteristiki na polimetalicnoto rudno pole Sasa-Istocna Makedonija*. Doktorska disertacija, 264 p.

De Groot, P. A., N. D. Arvanitidis, J. H. Baker. 1996. Regional Carbon, Oxygen, and Sulphur Isotopic Values in the Serbo-Macedonian and Rhodope Massifs. — *Mineral Wealth*, *98*, 17—24.

Drovenik, M., H. Leskovsek, J. Pezdic. 1970. Izotopska sestava zvepla v sulfidnih nekaterih jugoslovenskih rudisc. — *Rudarsko-metalurski zbornik*, 153—173.

Drovenik, M., J. Pezdic, S. Rakic. 1983. Izotopska sestava zvepla v piritu iz vrtine ZB-24 Plavica, Zletovsko-kratovsko vulkansko obmocje. — *Rudarsko-metalurski zbornik*, *30*, 69—76.

Jankovic, S. 1978. Izotopni sastav olova u pojedinim tercijarnim olovno-cinkovim rudistima Srpsko-makedonske metalogenetske provincije. — In: *Geol. an. Balk. pol.,* 1976, 507—525.
Jankovic, S. 1979. Antimony deposits of southeastern Europe. — *Vesn. Zav. za geol. i geofiz. istr.*, *37*, 25—48.
Mudrinic, C. 1978. *Geohemijske karakteristike Sb-As asocijacija u Srpsko-Makedonskoj metalogenetskoj provinciji*. Doktorska disertacija, Beograd, 131 p.
Mudrinic, C., T. Serafimovski. 1990—91. Geochemical and geochronological examinations by isotopes in Zletovo ore field. — *Geol. Maced.*, *5*, 1, 105—120.
Serafimovski, T. 1990. *Metalogenija na zonata Lece-Halkidiki*. Doktorska disertacija, Rudarsko-Geol. fakult., Stip, 390 p.
Serafimovski, T., B. Boev, C. Mudrinic. 1990—91. Sulphur isotopic composition of sulphides from the As-Sb deposit Alsar. — *Geol. Maced.*, *5*, 1, 165—172.
Serafimovski, T., G. Tasev. 2005. Sulfur isotope composition of some polymetallic deposits in the Republic of Macedonia. — *Geol. Maced.*, *19*, 1—11.