



Trace elements in sulphides from the Ruen ore field

Елементи-следи в сулфиди от Руенското рудно поле

*Valentin Grozdev¹, Rossitsa D. Vassileva¹, Elitsa Stefanova¹,
Zlati Zlatev²*

*Валентин Гроздев¹, Росица Д. Василева¹, Елица Стефанова¹,
Злати Златев²*

¹ Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev str. , bl. 24, 1113 Sofia;
E-mail: val.grozdev@abv.bg

² Bulgarian Mineralogical Society, Sofia

Key words: mineral chemistry, trace elements, LA-ICP-MS, sulphides, Osogovo.

Introduction

Neozoic mineralizations in the Ruen zone are typical polygenous, polychronous and polyformational mineral products, localized in several ore fields (Munkov, 2006). Among them, the Ruen ore field was the most important source for economic Pb-Zn-Ag hydrothermal mineralization in SW Bulgaria. The subject of investigation is focused on the minor and trace element content in sulphides from quartz-galena-sphalerite ore formation (according to Munkov, 2006) from the Ruen deposits, Osogovo Mountain. Newly precise chemical data obtained by LA-ICP-MS are presented in this study, where trace element composition of representative samples from pyrite, arsenopyrite and sphalerite were studied. The questions we address, apart from the chemical composition of the ores and ranges of solid solution, are connected with the possible crystallochemical control on sulphide mineralogy.

Methodology

Trace elements analysis of ore materials is a complex process including not only the analysis itself but also sample preparation, microscope observation and data evaluation. The used LA-ICP-MS analytical system consists of a 193 nm ArF excimer laser coupled with an ELAN DRC-e ICP quadrupole mass spectrometer at Geological Institute, BAS. An energy density of 5–6 J/cm² and a laser pulse frequency of 5–2 Hz were used on the sample for controlled ablation. Analyses were performed with 50 or 75 μm beam diameters. External standardization on NIST glass standard SRM-610 and Mass 1 provides relative element contents, which were transformed into true values by internal standardization (a known element concentration determined by EPMA).

Geological background

The Ruen Pb-Zn ore field (Munkov, 1988) is localised in the Osogovo block-horst (Moskovski, 1968), which is part of the major regional Struma unit (Zagorchev et al., 2009). The Ruen magmatotectonic zone (Harkovska, 1984), in which Paleogene igneous rocks are intruded (the Kopriva volcanics/subvolcanics and granite porphyry dykes in the Osogovo block), cuts mainly the high grade metamorphic rocks (amphibolites, amphibole gneisses, biotite-amphibole gneisses and metabasites, Milovanov et al., 2007).

The investigated sulphide minerals originate from ore bodies hosted predominantly by the Kopriva type subvolcanic dykes. Both the Paleogene igneous rocks and ore veins use the tectonic fractures of the Ruen tectonomagmatic zone (mainly NW-SE and NE oriented faults). The morphogenetic types of ore bodies in the Ruen ore field are presented by ore veins and metasomatic ones (Munkov, 1988, 2006).

Results and Discussion

The *pyrite* is substantial component of most of the metallic ores is presented in all ore deposits in Ruen ore field and in the altered wall-rocks. The typical trace elements in the studied pyrite are Co, Mn and As, which average contents are 344, 317 and 350 ppm, respectively. Several extremely high As concentrations (averaging 3.26 wt%) are detected, accompanied with increased Ni (15 ppm) and Au (2.48–0.87 ppm), and depleted in Mn (82.37 ppm) content. Such incorporation suggests substitution not only for sulphur (As¹⁻), but for iron (As³⁺) as well (Deditius et al., 2008), utilising the Au enrichment in pyrite (As³⁺ + Au¹⁺ = 2Fe²⁺). Below 100 ppm are the average values for Pb 83.27, Ge 77.12, Cr 67.88 and Ti 45.23. Germanium content

is in narrow range along the studied pyrite. Although it is considered that Ge is much more typical for sphalerite, here we observe low values of Zn (generally up to 10 ppm), leading to the conclusion that Ge in pyrite could not be attributed as microinclusion of sphalerite and is rather incorporated as isomorphic substitution. The observed correlation between Pb and Ag in the studied pyrite suggests the presence of tiny inclusions of galena. In minor amounts are the mean values for Cu 9.65, Zn 8.11 and Ni 3.71 ppm. The Sb (2.44) and Ag (1.85) are in 1–3 ppm range.

Compared to pyrite, *arsenopyrite* is very poor in concentration of siderophile elements like Co, Mn, Ni etc, and the first significant trace elements are actually Ti 109 (15–565) and Sb 97.98 (62–125) ppm. The average concentrations of the other trace elements are reduced almost twice: Pb 57.48, Mn 49.59, Ge 48.16, Cr 43.88 and Zr 21.8 ppm. In minor amount are presented W 7.55, Zn 7.49, Co 4.53 and Cu 4.24 ppm. Noble metals as Ag 1.73 and Au 0.37 ppm are established as well. Chemical variation from core to the periphery is found in the arsenopyrite crystals, which is expressed by decreasing of the concentrations of the chalcophile elements such as Cu (11.73–1.97), Ag (5.50–0.73), Pb (203.26–22.46), Sb (113.16–80.12). This chemical behaviour can be explained with the detected decreasing of sulphur and increasing of As content towards the rim. Small amounts of Hg ~2 ppm are also established.

Notable concentration of iron up to 3.73 wt% is detected in the *sphalerite* from Ruen deposits. Significant abundance shows the incorporation of Cd and Mn with average values being 5661 and 4620 ppm respectively. The content of Co and Cu is in the ranges 182–325 and 105–230 ppm. The increased concentration of Cu detected in the studied sphalerite can be explained with isomorphic substitution (Cu–Zn) rather than “chalcopyrite disease”, which has not been microscopically observed in the investigated samples. Other trace elements presented as average values are Pb 38.04, Ti 18.6, Hg 7, Ge 5 and Cr 5 ppm. Within the range of 3–1 ppm fall the concentrations of Se, Ag, Tl and Ga.

Based on the microscope and BSE observation, mineral relationships, chemical composition and laser ablation profiles, the form of presence of trace elements in the studied sulphides can be assigned either as: *i*) isomorphic substitution (for instance, the geochemical isomorphic proximity between Zn, Mn and Cd in the structure of sphalerite is well outlined) or *ii*) as micro inclusions of other minerals in the analyzed crystals (the Pb–Ag correlation in pyrite evidences for galena inclusions).

Acknowledgements: The study is supported by the World Federation of Scientists Scholarship Program 2013–2014.

References

- Deditius, A. P., S. Utsunomiya, D. Renock, R. C. Ewing, Ch. V. Ramana, U. Becker, S. E. Kesler. 2008. A proposed new type of arsenian pyrite: Composition, nanostructure and geological significance. – *Geochim. Cosmochim. Acta*, 72, 2919–2933.
- Harkovska, A. 1984. Magmotectonic features of the Late Paleogene volcanism in the Ruen Zone (West Bulgaria). – In: *Materials of Working Group 3. 4. “Magmatism in the Epochs of Molasse-formation”*, Bucharest, 63–82.
- Milovanov, P., I. Klimov, V. Zhelev, D. Sinnyovski, V. Vulev, I. Petrov, E. Ilieva. 2007. *Geological Map of Bulgaria on Scale M 1:50 000. Kriva Palanka and Kyustendil Map Sheet*. Sofia, Consortium Geocomplex.
- Moskovsksi, S. 1968. Tectonic of the Pianec complex graben, S of town Kyustendil (SW Bulgaria). Structure stages. – *Bull. Geol. Inst.*, 18, 143–158.
- Munkov, S. 1988. Ruen ore field. – In: Dimitrov, R. (Ed.). *Lead-zinc Deposits in Bulgaria*. Sofia, “Tehnika”, 90–114 (in Bulgarian with an English abstract).
- Munkov, S. 2006. The ore belt “Osogovo-Besna Kobila” (ore formations, morphogenetic types of deposits and physicochemical conditions of forming). – In: *Ann. of the University of Mining and Geology “St. Ivan Rilski”*, 49, 1 – Geol. and Geophys., 119–130.
- Zagorchev, I., Ch. Dabovski, T. Nikolov (Eds.). 2009. *Geology of Bulgaria. Volume II. Part 5. Mesozoic Geology*. Sofia, Prof. Marin Drinov Academic Publishing House, 765 p. (in Bulgarian with an English abstract).