LA-ICP-MS study of pyrite and arsenopyrite from the Srebren deposit, West Rhodopes

LA-ICP-MS изследвания на пирит и арсенопирит от находище Сребрен, Западни Родопи

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Introduction

The Srebren gold-silver deposit is located 36 km southern from the town of Velingrad and 10 km northern of the town Sarnitsa, in the West Rhodopes. It occupies the ridge parts of the eponymous peak and covers an area of approximately 1 km^2. The deposit was explored between 2004 and 2012 years by Thrace Resources Ltd. Pyrite and arsenopyrite typically contain significant amounts of minor and trace elements including As, Pb, Zn, Sb, Au, Ag, Mn, Bi, Cu, Co, Ni, Ga, Ge, Mo, Sn, Cd, In, Y, Ta, Zr.

Materials and methods

Representative samples were collected from drill cores and exploration mining dumps from different parts of the Srebren deposit. These samples completely characterize the mineral composition of the ore zones of the deposit spatially and vertically (in depth of 200 m). All analyzed pyrite and arsenopyrite grains were examined in advance by a reflected light microscopy, prior LA-ICP-MS analysis to avoid any visible sulphide inclusions. Minor and trace element concentrations in pyrite and arsenopyrite were measured by LA-ICP-MS on polished sections at the Geological Institute (Bulgarian Academy of Sciences), Sofia, Bulgaria. The analyses were made using the PerkinElmer ELAN DRC-e ICP-MS equipped with a New Wave UP193-FX excimer laser ablation system. The laser system was operated at constant 10 Hz pulse rate and laser energy was 1.80–2.60 J/cm^2 on the sample for 50 μm spot size. NIST SRM 610 glass was used as external standard. Fe and As contents in pyrite and arsenopyrite (wt.%) were determined by electron microprobe at the Institute of Earth Sciences, University of Graz, Austria. Fe content was used as internal standard. Data reduction was done using SILLS ver. 1.1.0 software (Guillong et al., 2008).

Geological setting

The Srebren gold-silver deposit is hosted by the Rila-Rhodope granite batolith (40–35 Ma, Kamenov et al. 1999). Quartz-pegmatite veins and xenoliths of biotite gneisses, amphibolites and granitised gneiss, altered in varying degrees, are found in the area. Based on mineralogical and chemical features, the deposit was referred to the quartz-gold-silver-sulphide formation by Maneva et al. (1994) with vein and disseminated type ore body morphology. Five parallel mineralized zones were outlined along an area of 1100 m long and 100 m wide. All ore zones have identical composition and mostly parallel direction approximately striking 25°NE, slightly varying in some areas. Quartz-chloritic, quartz-sericitic and sericitic alteration types were established. Three mineralization stages were defined: quartz-scheelite, pyrite-arsenopyrite and sphalerite-galena (Vidinli et al., 2007). Gold associates mainly with pyrite and arsenopyrite from the second stage. Pyrite is formed in quartz-scheelite and pyrite-arsenopyrite stages while arsenopyrite is deposited only in the second stage.

Results and conclusions

A total of 40 LA-ICP-MS spot analyses were made on pyrite and arsenopyrite grains, as 20 of them on pyrite-I, 12 on pyrite-II and 8 on arsenopyrite. The obtained analytical data shows differences in trace and minor element concentrations of the studied minerals.

Pyrite-I is mainly euhedral, without visible cracks and inclusions. Au concentrations are low (0.30 ppm) or below the detection limit of the instrument. Concentrations of other trace elements except for Mn, Ti, Cr, Co, Ni, Zn and As are also close to the detection limits (d.l.).

Pyrite-II forms aggregates of hemihedral to euhedral crystals, intergrown with arsenopyrite. It occurs mainly as pentagonal dodecahedral and less cubic crystals and is intensively fractured, which facilitates deposition of other sulphide minerals and native gold. The LA-ICP-MS dataset shows variable concentrations of trace elements in pyrite-II. High concentrations of As (2999–44943 ppm, average 22 821 ppm), Pb (5–3930 ppm, average 634 ppm), Zn (<d.l.–3520 ppm, average 528 ppm), Sn (<d.l.–553 ppm, average 93 ppm), Cu (<d.l.–766 ppm, average 153 ppm) were detected. Other trace elements having much lower concentrations are: Mn (23–41 ppm, average 27 ppm), Sb (1–52 ppm, average 27 ppm), Cd (<d.l.–66 ppm, average 12 ppm), Ti (10–35 ppm, average 19 ppm), Cr (18–27 ppm, average 21 ppm), In (<d.l.–47 ppm, average 6 ppm), Ag (<d.l.–34 ppm, average 13 ppm) and Au (1–15 ppm, average 7 ppm). Co, Ga, Ge, Mo, W and Bi were either not detected or have concentrations close to the limit of detection.

Arsenopyrite from the Srebren deposit is hemihedral to euhedral (pseudoprismatic crystals) and intensively fractured. Fractures are infilled with later deposited sulphide minerals and native gold. LA-ICP-MS spot analyses of arsenopyrite grains show contents of Pb (63–1826 ppm, average 544 ppm), Mn (15–23 ppm, average 17 ppm), Zn (<d.l.–270 ppm, average 58 ppm), Cu (<d.l.–4908 ppm, average 153 ppm), Sb (192–1143 ppm, average 502 ppm), Bi (6–77 ppm, average 24 ppm), Ag (2–208 ppm, average 60 ppm), Ti (<d.l.–460 ppm, average 74 ppm), Cr (not detectable–21 ppm, average 8 ppm), In (<d.l.–47 ppm, average 6 ppm), Ag (<d.l.–34 ppm, average 13 ppm) and Au (2–0 ppm, average 6 ppm). Lower concentrations have Co, Zr, Y, In, Cd, Sn, Ta and W.

Main concentrators of gold in the deposit are pyrite-II and arsenopyrite. However, time resolved spectra show that gold occurs as inclusions, infilling microfractures together with other later deposited sulphides (galena, chalcopyrite, cosalite). Such positive correlation between Au and Ag, Bi, Pb, Sb observed microscopically is also proved by LA-ICP-MS analyses. There is no evidence that Au is included within the structure of these minerals and LA-ICP-MS cannot substantiate that. High As concentrations in pyrite-II and arsenopyrite probably facilitate gold deposition as it was suggested by Möller, Kersten (1994) and other researchers. Gold deposited in pyrite-II and asrenopyrite fractures have predominantly the composition of electrum as it was indicated by electron microprobe analyses. Apart from pyrite-II, pyrite-I has even lower concentrations of Au and Ag and other trace elements. However, gold deposited during the first stage within quartz and pyrite-I tend to have less impurities compared to gold associated with pyrite-II and arsenopyrite. Pyrite (I and II) and arsenopyrite have relatively low minor and trace element composition profile. Typical minor and trace elements for pyrite as Mn, Ti and Cr have very low concentrations in the range (10–40 ppm), while Co and Ni were not even detected. Sn, In and Cd are most likely related to sphalerite inclusions. Same applies for Cu, Pb, Ag, Sb and Bi, as inclusions of chalcopyrite, galena and cosalite. Low concentrations of trace elements, especially in pyrite suggest the ore-forming hydrothermal fluids were relatively deficient in these elements.

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