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New data on trace element content in sphalerite and pyrite from Ruen Deposit

Нови данни за съдържанието на елементи-следи в сфалерит и пирит от находище Руен

Victoria Vangelova[1], Dimitrina Dimitrova[2], Karolina Yordanova[1]
Виктория Вангелова[1], Димитрина Димитрова[2], Каролина Йорданова[1]

[1] Sofia University “St. Kl. Ohridski”, Department of Mineralogy, Petrology and Economic Geology;
E-mails: vpatrick@gea.uni-sofia.bg; karolina_yordanova@abv.bg;
[2] Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail:didi@geology.bas.bg

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Introduction

The present LA-ICP-MS study reports 37 analyses of 24 minor and trace elements in pyrite and sphalerite from the epithermal Pb-Zn Ruen deposit, Osogovo Mountain. The mineralization occurs as linear stockworks and stockwork-veins along large zones of faulting and cataclasis, with dominant WNW direction (Mankov, 1988, 2006). The examined sulfides from quartz-galena-sphalerite assemblage are formed within the temperature range 370–280 °C and are related to coarse-grained Oligocene porphyritic rhyodacites (Mankov, 1988, 2006). The main objective of this research is to re-evaluate the trace metal potential of abandoned sphalerite-bearing deposits with regard to critical raw materials (In, Ga and Ge in sphalerite) and invisible gold in pyrite using modern micro-analytical techniques.

Analytical procedures

Minor and trace elements in pyrite and sphalerite were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on polished sections at the Geological Institute (Bulgarian Academy of Sciences), Sofia, Bulgaria. The analyses were performed using a NW UP193-FX excimer laser ablation system combined with PE ELAN DRC-e ICP-MS at the following operating conditions: 35 μm laser beam size with 4–6Hz repetition rate and 5.6 J/cm^2 energy density on the sample. The NIST SRM 610 and MASS 1 sulfide standard were used as external standards and were measured recurrently during the course of the analyses. Data reduction was done using internal standardization (Zn and Fe content measured by electron microprobe SEM JEOL JSM-6010 PLUS at MGU “St. I. Rilski”) by SILLS v.1.1.0 software (Guillong et al., 2008).

Results and Discussion

The following elements are established in all 11 analyses of ***sphalerite*** (numbers in brackets are minimum–maximum and mean concentrations in ppm): Fe (19591–83852; 69627), Mn (289–15077; 8772), Cd (2032–2307; 2147), Cu (108–213; 144), Ag (1.6–4.8; 2.5), In (28–165; 95), Co (1.8–22.7; 12.2) and Hg (6.9–21.1; 9.9). Selenium (12.2–24.3; 16.8 with frequency of occurrence in percent W=91%), Pb (0.2–1.3; 0.5 with W=82%) and Ga (1.6–3.0; 2.4 with W=64%) are also unusual components. Chromium (11.7–15.7 ppm), Ti (8.0–9.9 ppm), Ni (2.8 ppm), Sn (0.5 ppm) and Bi (0.1 ppm) were detected in single analyses. The monitored Ge, Tl, As, Sb, Au, Pt, V, and Te are bellow detection limit.

The strong negative correlations Zn vs. (Fe, Mn, Co) and the flat LA-ICP-MS depth profiles of Fe, Mn, Cd, In, Co, Se, Ga, and Hg indicate their occurrence as structurally bound (Fig. 1a). The fluctuating intensities of Cu are result of chalcopyrite inclusions since “chalcopyrite disease” is microscopically observed in the studied sphalerites. The coupled rounded intensity profiles of Cu and Ag in the majority of samples (Fig. 1a) as well as their strong positive correlation (R=0.82) and insignificant correlation Ag vs. Pb (R=0.19) suggest that Ag is mainly bound to chalcopyrite. The strong positive

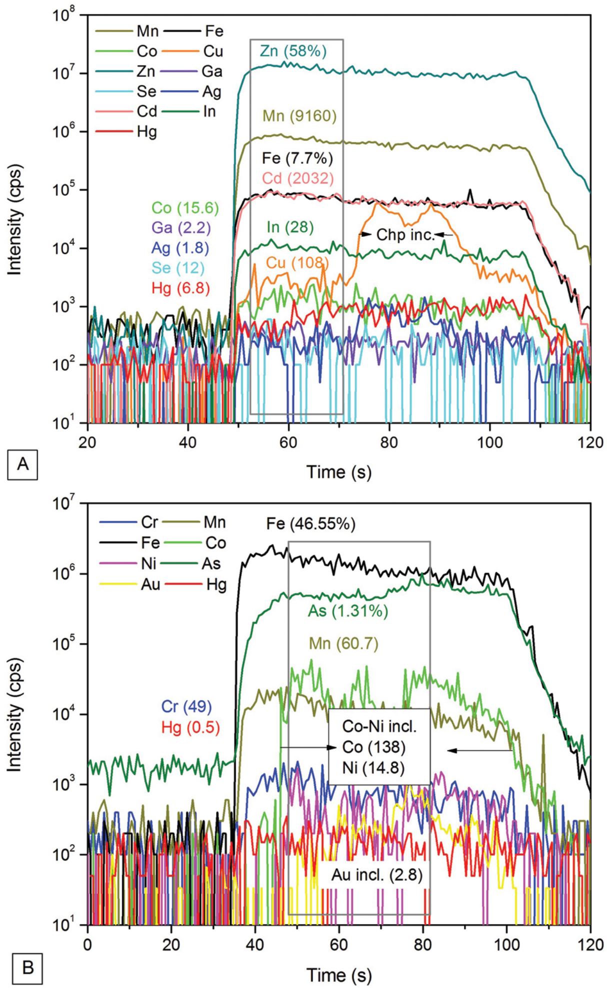

Fig. 1. Representative LA-ICP-MS depth spectra of sphalerite (*A*) and pyrite (*B*). Numbers in brackets are concentration (in ppm, except otherwise cited). Chp, chalcopyrite; incl., inclusion

correlation of Cu vs. In and Ag vs. In (respectively R=0.93 and 0.59) as well as the weaker correlation of Cu vs. Ga and Ag vs. Ga (respectively R=0.29 and 0.36) support the couple substitutions: $2Zn^{2+} \leftrightarrow Cu^{+} + In(Ga)^{3+}$ and $2Zn^{2+} \leftrightarrow Ag^{+} + In(Ga)^{3+}$ (Cook et al., 2009).

Only 4 elements are established in all 26 analyses of ***pyrite***: As (29–13104; 1631), Mn (54–104; 61), Cr (42–53; 48) and Ti (22–37; 29). Cobalt (0.3–417; 91; W=96%), Pb (0.2–219; 29; W=89%), Ni (1.2–66; 17; W=69%), Hg (0.2–0.7; 0.5; W=69%), Sb (0.3–17.4; 3.3; W=54%), Zn (2.8–318; 72; W=46%), Au (0.3–3.2; 1.3; W=42%), Cu (2–534; 72; W=35%) and Ag (0.2–12.7; 3.5; W=31%) are also infrequent components. In single analyses are determined Mo (mean 1.3 ppm), Te (mean 1 ppm), In (mean 0.1 ppm), Se (4.7–9.7 ppm), Bi (0.1–0.7 ppm), Sn (0.4 ppm), and V (0.2 ppm). Gallium, Cd, Re, Pt, and Tl are below detection limits.

The relatively flat depth profiles of As, Mn, Hg, Cr, Se and rarely of Co, Ni and Ti (Fig. 1b) indicate their occurrence mostly as structurally bound. Irregular fluctuated signals of Co and Ni (Fig. 1b), as well as their positive correlation (R=0.42) suggest the presence of Co-Ni minerals. The occurrence of Sb-containing galena and Ag-containing chalcopyrite as inclusions or crosscutting veinlets in pyrite is emphasized by the rounded profiles of Pb, Sb, Cu and Ag and the positive correlation of Sb vs. Pb and Ag vs. Cu (R=0.98 and 0.31 respectively).

Strong positive correlation Au vs. Ag (R=0.84) and their intensity profiles (Fig. 1b) suggest their presence as discrete inclusions native gold/electrum or in crosscutted tiny veinlets together with other sulfides. Their deposition within pyrite grains is facilitated probably by the semi-conductor features of As-bearing pyrite (Moller, Kersten, 1994; Simon et al., 1999).

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