New data on trace element content in pyrite and sphalerite from Sedmochislenitsi deposit

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

Victoria Vangelova¹, Dimitrina Dimitrova², Mediha Kehayova¹
Виктория Вангелова¹, Димитрина Димитрова², Медиха Кехайова¹

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

Keywords: strata-bound Sedmochislenitshi deposit, pyrite, sphalerite, trace elements, LA-ICP-MS.

Introduction

The present LA-ICP-MS study reports 62 analyses of 24 minor and trace elements in colloform pyrite and sphalerite from strata-bound base-metal Sedmochislenitsi deposit, Western Balkan. The mineralization occurs as lenses and bed-like bodies (rare veins) in dolostones and limestones from Middle Triassic Iskar Carbonate Group. The low temperature hydrothermal-metasomatic deposition was confined mostly to the cracks and cavities where typical colloform sulfide aggregates were formed (Minčeva-Stefanova, 1978, 1988). 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 (especially In, Ga, and Ge) and a potential environmental hazard due to high content of toxic elements in pyrite-bearing mine tailings. The results obtained can be used to prevent the risk of contamination in the adjacent areas.

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 4–6 Hz repetition rate and 5.6 J/cm² 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 6010 PLUS at MGU “St. I. Rilski”) by SILLs v.1.1.0 software (Guillong et al., 2008).

Results and discussion

Eight elements are established in all 26 analyses of pyrite (numbers in brackets are minimum–maximum and mean concentrations in ppm): As (374–37418; 20711), Pb (1822–15336; 6860), Tl (17–844; 250), Ag (0.4–406; 82), Mn (52–69; 58), Cr (36–55; 43), Ti (24–51; 32) and Zn (5–94; 21). Cobalt (0.4–1140; 116 with frequency of occurrence in percents W 96%), Ni (2–1519; 234; W 89%), Cu (2–733; 138; W 86%), Sb (0.6–172; 27; W 86%), Hg (0.2–0.8; 0.4; W 82%), Cd (0.8–12; 3; W 46%), Mo (0.7–5; 1.6; W 39%), and In (0.02–0.04; 0.03; W 32%) present also frequently. In single analyses are determined V (mean 0.6 ppm), Re (mean 0.08 ppm), and Bi (mean 0.05 ppm). Gallium, Se, Te, Pd, and Au are below detection limits.

Sphalerite is characterized by the presence of the following trace elements, established in all 34 analyses: Fe (967–18171; 5266), Pb (291–11452; 2672), As (136–5334; 1193), Cd (161–4487; 875), Ag (16–1742; 266), Cu (78–324; 135), Ge (30–264; 108), Ti (8–373; 79), Co (1–428; 70), Sb (2–175; 43) and Hg (17–54; 32). Manganese (3–93; 40; W 97%), Se (11–31; 20; W 94%), Ti (6–34; 10; W 74%),
Ga (1.5–25; 9; W 59%), and Ni (3–41; 13; W 25%) are also unusual components. Tin (0.4–0.9; 0.7; W 18%), In (0.03–0.1; 0.04; W 12%) and Cr (24–82; 48; W 9%) are less common. The monitored Mo, Pd, Te, Re, Pt and Au are below detection limit.

The predominantly flat depth profiles of Mn, Hg, Cr, As, Ag, Cu, Sb, Pb, Tl in pyrite (Fig. 1A, B, C) and Mn, Fe, Cd, Ag, As, Hg, Ge, Tl, Pb in sphalerite (Fig. 1D, E, F), rarely of Co and Ni (Fig. 1A, D, E) indicate their occurrence mostly as struc-
naturally bound or adsorbed cations on the growing band surfaces of the colloform aggregates, which usually form due to fast crystallization from supersaturated ore fluids. Based on the strong negative correlation between Fe and As in pyrite, As probably occurs also as heterovalent substitutions \((\text{As}^+, \text{As}^{3+})\) for \(\text{Fe}^{2+}\) together with the more typical \(\text{As}^-\) for S (Deditius et al., 2008). Irregular fluctuated signals of Co and Ni (Fig. 1B, E), as well as their positive correlation (\(R\) 0.92 in pyrite and \(R\) 0.70 in sphalerite) suggest either the presence of Co-Ni minerals or change in chemical composition of the hydrothermal solution. The rounded depth profiles of Pb, Tl, Cu, and Ag (Fig. 1C) in pyrite and respective positive correlations of Pb vs. Tl and Ag vs. Cu (\(R\) 0.66 and 0.97 respectively), as well as irregular profiles of Pb, Tl and As (Fig. 1F) in sphalerite and strong positive correlations Pb vs. Tl and Pb vs. As (\(R\) 0.95 for both) suggest the occurrence of Tl-containing galena, Ag-containing chalcopyrite, and Pb-As sulfosalts as precipitated tiny particles on the band surfaces, subsequently enclosed within the pyrite and sphalerite colloform aggregates or as veinlet cross-cuttings. Irregular signals of Ti and Zn in pyrite (Fig. 1B), as well as positive correlation Zn vs. Cd (\(R\) 0.59) imply the presence of Ti minerals and Cd-containing sphalerite.

Smooth rise of Cd intensity in the sphalerite depth profiles is a result of zonal distribution with slightly higher content of Cd in the peripheral parts. The peripheral parts in zonal pyrites are mostly enriched in Ni, Cu, As, Tl and Ag.

Compared to other genetic types of Pb-Zn deposits in Bulgaria, such as epithermal (Laky, Spathieve and Ruen ore fields), SEDEX (Gramatikovo) and metasomatic replacement Chiprovtsi, the pyrites from Sedmochislenitsi deposit stand out with the highest concentrations of Pb, as well as relatively high content of As and Tl, while sphalerites are enriched in Pb, Cd, Ag, Ge, Co and Tl.

**Acknowledgements:** This study is financially supported by the Sofia University Scientific Research Grants 80-10-2/2019 and 80-10-35/2020.

**References**


