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Trace and minor elements in sphalerite: comparison between Spahievo and Laki ore fields, Rhodopes (Bulgaria)

Елементи-примеси в сфалерит: сравнение между Спахиевско и Лъкинско рудни полета в Родопите

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Introduction

The rapid increase of economic importance of Ga, In and Ge has identified them as critical raw materials (Frenzel et al., 2016). Zn-bearing ores are their basic source and sphalerite is their principal host mineral. Epithermal and some skarn deposits have higher concentrations of most trace elements in sphalerite in solid solution (Cook et al., 2009). Despite the large number of studies on epithermal deposits in Bulgaria, new data about trace elements in sphalerite as well as the possibility of their extraction from sphalerite-bearing ores is still missing. The present LA-ICP-MS study reports 124 analyses of 24 minor and trace elements in sphalerite from Oligocene Spahievo and Laki ore fields, which are representative of the two main types of epithermal low-sulfidation mineralization in Bulgaria, respectively Eastern Rhodopes gold to Au-base-metal and Central Rhodopes base-metal.

Materials and methods

The samples were selected from Chala, SKMI (Northern border of monzonitoid instrusion) deposits and Kamdzhilarski Vrah occurrence in Spahievo ore field; metasomatic and vein ore bodies of the Govedarnika, Dzhurkovo, Chetroka, Kenan Dere, Pilevo, Balkan Mahala and Belitsa deposits in the Laki ore field. All studied sphalerite grains are examined by reflected light microscopy prior LA-ICP-MS and electron microprobe analysis to avoid discrete sulfide inclusions.

Minor and trace elements in 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: 25–35 μm laser beam size with 6 Hz repetition rate and 5.0–5.6 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 by internal standardization (Zn content measured by electron microprobe SEM JEOL JSM-6010 PLUS/LA and EDS at University of Mining ang Geology "St. I. Rilski") using SILLS v.1.1.0 software (Guillong et al., 2008).

Results and discussion

The concentrations of trace elements in sphalerite from Spahievo and Laki ore fields are summarized in Table 1. In addition to the presented results in Table 1, concentrations of As (25.9 ppm), Mo (119.9 ppm), V (2 ppm), Au (0.1 ppm) and Cr (36.5 ppm) were determined in Spahievo ore field; Te (average 5.1 ppm), Ni (average 1.2 ppm), Cr (average 18.7 ppm), Au (0.2 ppm) and Tl (0.2 ppm) in Laki ore field. Bellow detected limit in the former are Ni, Te, Tl and in the later – V, Mo and As. Higher concentrations of Fe, Mn, Cu, Ag and Co are typical for Laki ore field, whereas Sn and Sb have higher content in Spahievo ore field. Cadmium, Hg, Pb, Se and Bi show almost equal values in both ore fields. The evaluation of critical metals Ga, In and Ge in sphalerites from both deposits show that Ga is enriched in Spahievo, whereas In – in Laki; Ge is rarely found, especially in Spahievo.

Strong positive correlation of Ag vs. Ga and Cu vs. Ga (Pearson coefficient R=0.88 and 0.54, respec-

Table 1. Statistic parameters of trace-element concentration in sphalerite from Spahievo and Laki ore fields

		Spahievo	Laki
Fe	N (W%) min÷max X (V%)	60 (100) 3321÷21920 12372 (32)	64 (100) 2346÷93195 34867 (60)
Mn	N (W%) min÷max X (V%)	60 (100) 65÷2762 1064 (67)	64 (100) 92÷8078 3351 (59)
Cd	N (W%) min÷max X (V%)	60 (100) 1455÷7896 2327 (64)	64 (100) 1233÷5654 2469 (55)
Cu	N (W%) min÷max X (V%)	60 (100) 91÷2340 271 (153)	64 (100) 69÷7587 657 (213)
Hg	N (W%) min÷max X (V%)	60 (100) 19÷67 37 (32)	64 (100) 9÷62 26 (40)
Ag	N (W%) min÷max X (V%)	60 (100) 0.3÷38.3 2.2 (238)	63 (98) 0.6÷82.6 6.9 (188)
Co	N (W%) min÷max X (V%)	60 (100) 0.6÷100.4 33.1 (82)	64 (92) 0,3÷4000 147.3 (358)
Pb	N (W%) min÷max X (V%)	60 (85) 0.1÷44.2 3.1 (235)	63 (89) 0.2÷35.9 3.1 (208)
Se	N (W%) min÷max X (V%)	60 (88) 11.3÷35.9 20.6 (24)	58 (40) 10.9÷29.9 19.3 (22)
In	N (W%) min÷max X (V%)	60 (65) 0.03÷31.7 1.5 (352)	64 (81) 0.05÷302.7 15.1 (308)
Ga	N (W%) min÷max X (V%)	60 (75) 1.2÷299.3 22.4 (212)	64 (53) 0.8÷8.8 2.9 (67)
Ge	N (W%) min÷max X (V%)	60 (8) 1.1÷10.6 5.2 (72)	48 (29) 0.9÷9.8 5.2 (49)
Sn	N (W%) min÷max X (V%)	60 (75) 0.7÷39.4 6.6 (118)	64 (23) 0.7÷18.5 2.7 (161)
Ti	N (W%) min÷max X (V%)	60 (70) 5.6÷15 9.5 (22)	64 (83) 5.4÷42.3 14.2 (57)
Bi	N (W%) min÷max X (V%)	60 (18) 0.19÷0.24 0.15 (32)	64 (5) 0.12÷0.19 0.15 (24)
Sb	N (W%) min÷max X (V%)	60 (8) 0.4÷88.5 18.3 (214)	64 (11) 0.4÷3.1 1.2 (79)

N, number of analyses; W%, frequency of occurrence;
min÷max, minimum and maximum values (*in ppm*);
X – average concentration (*in ppm*);
V% – coefficient of variation

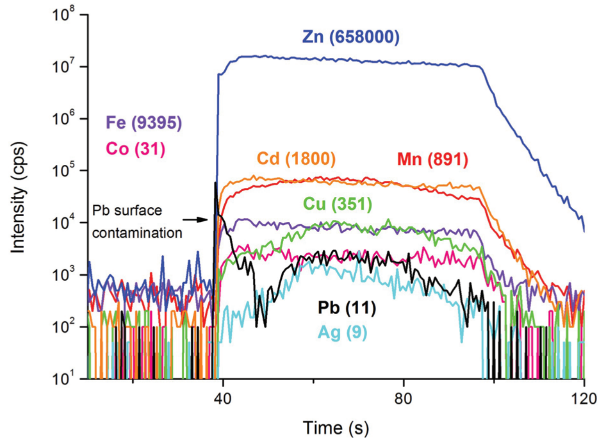

Fig. 1. Representative single-spot LA-ICP-MS spectrum for selected elements in sphalerite. Numbers in bracket are concentrations (in ppm).

tively) exist only in Spahievo ore field and support the couple substitution of type $2Zn^{2+} \leftrightarrow Ag^{+}(Cu^{+}) + Ga^{3+}$ (Cook et al., 2009). The presence of Ag-bearing galena and Ag-Cu minerals as inclusions or cross-cutting veinlets in sphalerite from both ore fields is emphasized by the rounded profiles of Pb, Cu and Ag (Fig. 1) and the strong positive correlation of Ag vs. Pb and Ag vs. Cu (R=0.95 and 0.47 in Spahievo; R=0.73 and 0.45 in Laki, respectively). In most cases, the LA-ICP-MS profiles for Fe, Mn, Cd, Co, Hg and rarely for Cu in both ore fields are flat, indicating their occurrence in solid solution (Fig. 1). Some irregular signals of Cu imply the presence of chalcopyrite inclusions.

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