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New data on trace elements in sphalerite from Gramatikovo ore field: a LA-ICP-MS study

Нови данни за елементи-примеси в сфалерит от Граматиковското рудно поле: LA-ICP-MS изследване

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Introduction

The worldwide demand for Ga, Ge and In has increased in recent years because they are essential for the development of high-tech industry. Sphalerite is a major source of all three elements. Therefore, the European strategy in the last years is to re-evaluate the trace metal potential of abandoned sphalerite-bearing deposits. In Bulgaria, since the first work of Dragov et al. (1976), there is no other study that has investigated trace-element concentration in sphalerite from the Gramatikovo ore field (Strandzha Unit) using modern micro-analytical techniques. The present LA-ICP-MS study reports 16 analyses of 24 minor and trace elements in sphalerite from one deposit in the ore field – Keremidoto (level 260). The stratiform Cu-base-metal-pyrite ore bodies are hosted in grey-green calc-schists (Middle Triassic Gramatikovo Formation – Čatalov, 1990). The mineralization is SEDEX type syngenetic to host rocks (hydrothermal-sedimentary according to Bogdanov, 1987 and Okeanova et al., 1988). The later dynamo-thermal metamorphism causes folding, faulting, shearing, displacement, re-crystallization and inverse vertical zoning observed in the ore bodies.

Analytical procedures

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: 20–35 μm laser beam size with 4–6 Hz repetition rate and 4.7–5.6 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 and Geology "St. Ivan Rilski") using SILLS v.1.1.0 software (Guillong et al., 2008).

Results and discussion

The following elements are established in all analyses (numbers in brackets are min÷max and mean concentrations in ppm): Fe (14 974÷71 660; 43 818), Mn (16÷840; 271), Cd (1328÷2262; 1654), Cu (145÷ 27 326; 7003), Ag (1.1÷84.9; 11.9), In (0.6÷75.1; 37.8), Bi (1.0÷219.3; 30.7), and Hg (25.7÷89.3; 52.3). Lead (1.6÷1169.1; 115.4) is also an usual component, whereas As (4.5÷31.1; 14.8), Se (26.9÷45.2; 35.1), Ga (10.4÷23.6; 15.0), Sb (0.7÷6.2; 3.4), Ti (8.8÷96.6; 38.8) and Au (0.6÷1.9; 1.3) are less common. In single analyses are determined Co (2.4 ppm), Mo (5.7 ppm) and Cr (66.9 ppm). Bellow detected limit are Ge, Tl, Sn, Ni, V, and Te.

In most cases, LA-ICP-MS profiles for Fe, Mn, Cd, In, Hg and rarely for Cu are flat, indicating their occurrence in solid solution (Fig. 1a). Some irregular signals for Fe and Cu imply the presence of pyrite and chalcopyrite inclusions (Fig. 1b). In the majority of samples the profiles of Pb, Ag and Bi are ragged (Fig. 1a, b, c), clearly showing the presence of galena, Bi-, Ag- and Bi-Pb(?)-bearing minerals. The strong positive correlation of Ag vs. Ga and Cu vs. In (with Pearson coefficient respectively R=0.96 and 0.52) sup-

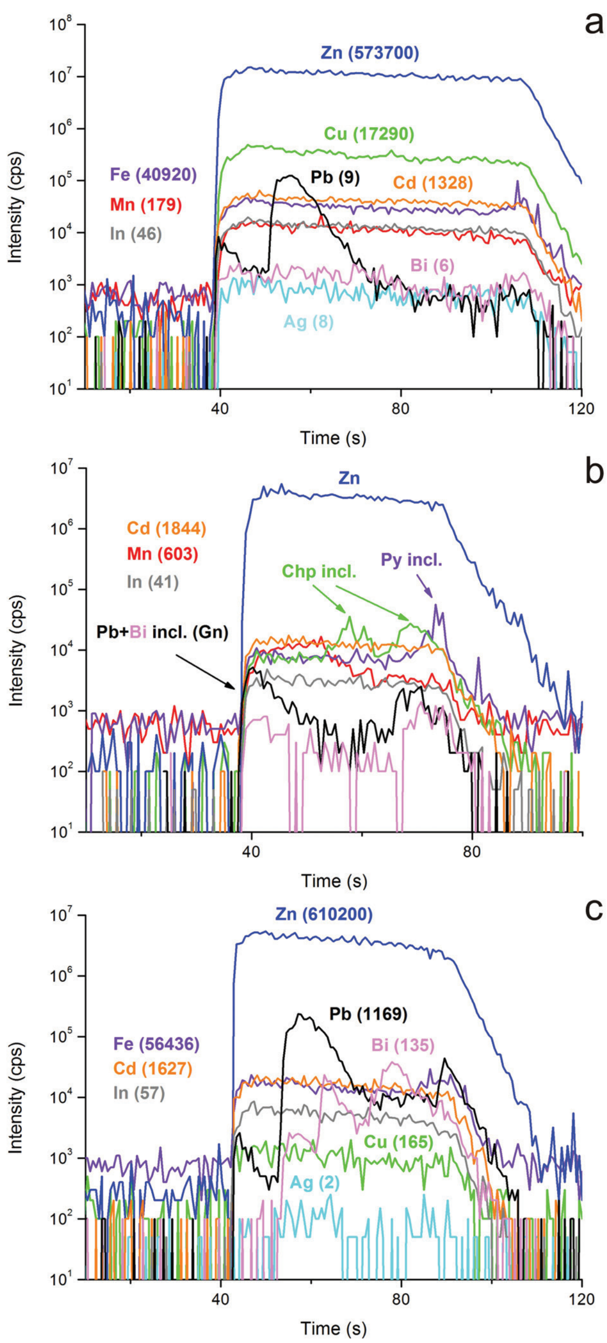

Fig. 1. Representative single-spot LA-ICP-MS spectra for selected elements in sphalerite

Numbers in bracket are concentration (in ppm); *Chp*, chalcopyrite; *Gn*, galena; *Py*, pyrite; *incl.*, inclusion

port the couple substitution of type $2Zn^{2+}\leftrightarrow Ag^{+}+Ga^{3+}$ and $2Zn^{2+}\leftrightarrow Cu^{+}+In^{3+}$ (Cook et al., 2009).

The strong positive correlation of Ag vs. Bi and Ag vs. Cu (R is 0.80 and 0.48, respectively) also suggests the presence of Ag-Bi- and Ag-Cu-bearing mineral phases or couple substitution of type $2Zn^{2+}\leftrightarrow Ag^{+}+Bi^{3+}$. The low concentrations and variability of Se and As, as well as the strong positive correlation between them indicate incorporation in solid solution.

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