



Microchemical characteristics of spherulitic pyrite from the Chiprovtsi deposit, NW Bulgaria

Микрохимична характеристика на пиритови сферолити от находище Чипровци, СЗ България

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Introduction

Pyrite is the most widespread sulfide mineral in many types of ore deposits. Spherulitic or “colloform” textures in pyrite reflect usually rapid simultaneous crystallization of multitude of <001> needle-like crystals from supersaturated solutions in open space. Such pyrites are usually enriched in As and other elements.

Materials and methods

Two types of specimens containing spherulitic pyrite from the low-temperature Fe-Hg mineralization of the Ag-Pb Chiprovtsi deposit in NW Bulgaria have been studied: 1) spherulitic pyrite with quartz, and 2) spherulitic pyrite, cinnabar, quartz, calcite, quartz, barite, fluorite, ± ankerite and kutnohorite.

Trace element concentrations in pyrite were measured 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 made using the PerkinElmer ELAN DRC-e ICP-MS equipped with a New Wave UP193-FX excimer laser ablation system. NIST SRM 610 glass was used as external standard. The laser system was operated at constant 10 Hz pulse rate; laser energy was 1.80–2.60 J/cm² on the sample for 50 μm spot size. A total of 50 analyses were made on pre-defined areas of the polished samples. The following 26 isotopes were monitored: ⁴⁹Ti, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶²Ni, ⁶⁵Cu, ⁶⁶Zn, ⁷¹Ga, ⁷³Ge, ⁷⁵As, ⁷⁷Se, ⁹⁵Mo, ¹⁰⁶Pd, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹²⁰Sn, ¹²¹Sb, ¹²⁶Te, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi. Acquisition dwell time for all masses was set to 0.01 s. Data reduction was done using SILLS ver. 1.1.0 software (Guillong et al., 2008) and Fe as internal standard. Iron contents in pyrite were measured by electron microprobe (EPMA)

at the Institute of Earth Sciences, University of Graz, Austria.

All analyzed pyrite grains were examined by reflected light microscopy and scanning electron microscopy (SEM) prior LA-ICP-MS analysis to avoid discrete sulfide inclusions.

Geological setting

The Chiprovtsi lead-silver deposit is hosted in low-grade metamorphic rocks (marbles and schists) of the Diabase-Phyllitoid Complex (Precambrian – Early Ordovician age) (Carrigan et al., 2003). The formation of the main Pb-Ag metasomatic mineralization is considered to be of Carboniferous age (Amov et al., 1981) and it is stratabound within thick siderite and calcite marble layers in the metamorphic series. The cinnabar-pyrite mineralization is observed as crosscutting veinlets, metasomatic nests and breccia fillings within the earlier formed fluorite bodies. It is considered as being the final stage of the fluorite forming process. This mineralization has a simple composition, consisting predominantly of pyrite, cinnabar, various carbonates and lesser amounts of metacinnabar, marcasite, galena, chalcopyrite, minerals of the tetrahedrite-tennantite and polybasite-pearceite series.

Results and conclusions

SEM-BSE (back scattered electrons) images and EPMA analyses of pyrite revealed a distinct microscale zoning in As distribution in the spherulite aggregate, along the axis of elongation of the needle-like crystal individuals. As it is seen in Fig. 1, the oxidized darker zones on the optical microscope image (A) correspond to lighter zones, enriched in As, observed on the BSE image (B). Tiny inclusions (≤1–3 μm) of barite filling

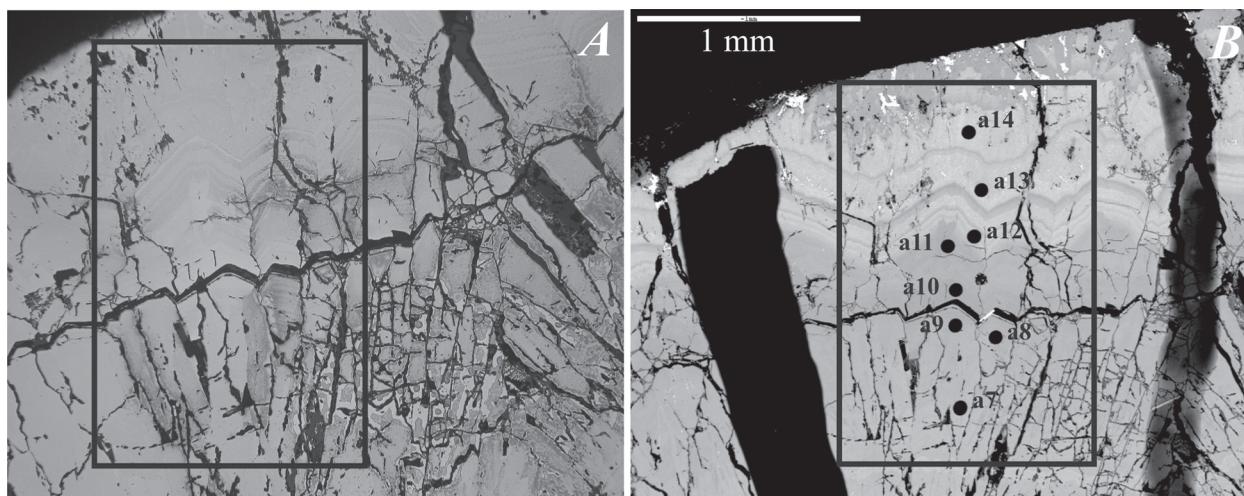


Fig. 1. (A) Optical microscope image of oxidized polished section, revealing zoning in the pyrite spherulite and (B) the same polished section in SEM-BSEI, confirming a zoning in As content in the aggregate. Black spots are craters of LA ablation. Sample LP630/3a. Spot numbers refer to LA-ICP-MS analyses.

the porous colloform aggregate are detected as well (the white inclusions in Fig. 1B). Arsenic contents vary between 0.74 and 4.78 wt.%, while Sb – <0.10 up to 2.43 wt.%.

LA-ICP-MS analysis of spots in different zones revealed fluctuations in distribution of other trace and minor elements as Sb, Tl, Cu, Co, Ni, Ag, Pb and Hg. Although, Hg could not be quantified due to its lack in the external standard, it was clearly observed with sufficient intensities in the time resolved spectra. All these data suggest fluctuations in the chemical composition of the hydrothermal solution, such as sudden supersaturation in these elements, presented in the solution most likely in the form of complex ions.

Au concentrations in the range 0.19–2.39 ppm were determined in all samples. The measured concentrations of the following minor and trace elements were (in ppm): Ti (9.94–19.14), Cr (2.45–15.76), Mn (6.91–9.98), Co (0.10–1180), Ni (1.77–3726.78), Cu (12.44–1686), Zn (4.94–1316), Ge (not detectable – 6.68), Se (3.83–19.12), Ag (146.34–6853), Sb (725–>1000), Pb (17.46–9281), Tl (12–3319) and Te (0.89–2.01). V, Cd, In, Sn, Ga, Mo and Bi were not detected.

Concentration fluctuations for some metals (Pb, Cu, Co, Zn, Ag) are significant and probably are related to inclusions of galena, chalcopyrite or tetrahedrite. However, Tl and Hg most likely occur as substitutes for Fe, showing unchangeable high intensities in the time resolved spectra.

Depletion or enrichment of some of the components in the solution, especially As and Sb, causes dis-

tinct chemical zonation of the aggregates. The rapid crystallization from the supersaturated solution facilitates the incorporation of gold as micro- to nano-sized particles (<1–2 μm) on the growth surfaces, as well as other elements substituting Fe and S in the crystal structure. The fine pores in the spherulitic pyrite aggregates are infilled with later minerals as cinnabar, tetrahedrite, barite, etc.

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