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LA-ICP-MS study of pyrite from the Panicherevo deposit, Sarnena Sredna Gora mountain, Bulgaria

LA-ICP-MS изследване на пирит от находище Паничерево, Сърнена Средна гора, България

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Introduction

The Panicherevo deposit is situated in the Eastern Sarnena Sredna Gora Mountain, northwest of the town of Nova Zagora. It is hosted by the Kazan granite pluton and the rocks of the Pirdop gneiss complex (Staykov, 1963). The ore mineralization occurs as two stockwork bodies with thickness from 90 up to 140 m, orientated ENW and dipping 35–45° to SSW. They outcrop on the surface and can be traced in depth (Mankov et al., 2017[1]).

The ore veins have thickness from 1 mm to 40 cm. The main ore minerals are molybdenite and pyrite, accompanied by less common chalcopyrite, galena, sphalerite, rutile, magnetite, hematite, tennantite-tetrahedrite. The main gangue minerals are quartz and calcite. The host rocks have undergone K-feldspar, propylitic and sericitic alteration.

Pyrite occurs in quartz veins as fractured aggregates with thickness up to 5 cm, rarely as euhedral-subhedral crystals (Fig. 1a), colloform aggregates and disseminated in the host rocks.

Methods

Pyrite-bearing mineral assemblages were studied in polished sections using optical microscopy in reflected light. Minor and trace element composition of pyrite was determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). NIST SRM 610 glass and MASS1 sulfide standards were used for external standardization. A total of 113 spot LA-ICP-MS analyses were done on 18 polished sections from the prospecting areas Demir Boklu and Kohuk Dere.

Results and conclusions

The LA–ICP-MS analyses show that trace elements detected in pyrite from Panicherevo deposit are related to: 1) isomorphic substitutions of Co, Ni, Mn for Fe and As, Sb, Se for S; 2) discrete mineral inclusions bearing Pb, Bi, Ag, Cu, Mn, Zn, Sb, Sn, Ge, Hg, Tl, Mn, etc. Copper, Mn, Cu, Tl, Hg and Pb can also occur in colloform pyrite as structurally bound cations.

Cobalt contents vary between 0.1 and 6549.7 ppm and Ni contents between 0.5 and 193.2 ppm. The flat intensities in down-hole ablation profiles suggest their incorporation in pyrite structure (Fig. 1b). The highest Co contents are detected in pyrite from the Demir Boklu area.

The content of Mn varies from 53 to 1336 ppm. Zhang et al. (2014) reports that Mn may either enter in pyrite as oxide inclusion or as incorporated

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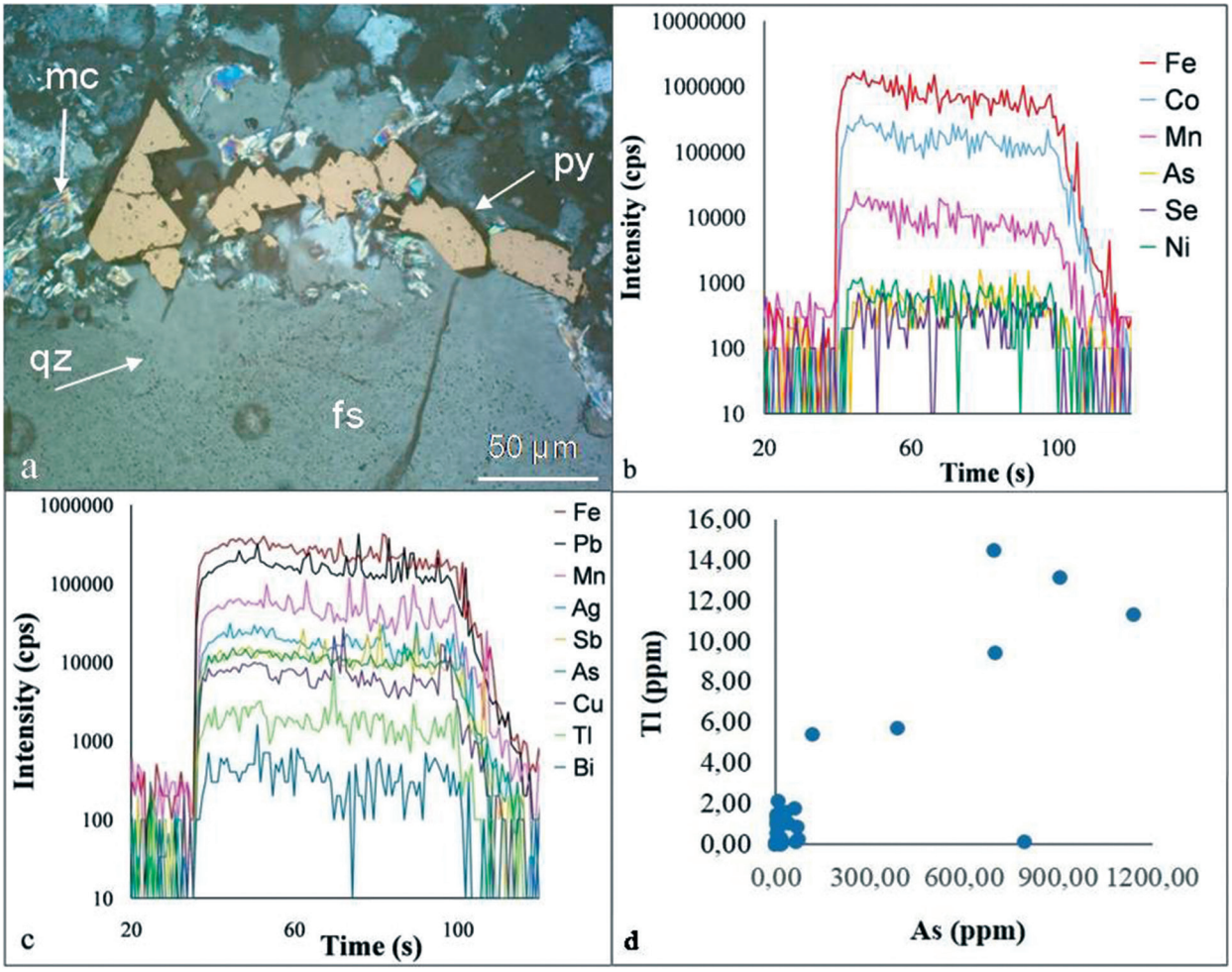

Fig. 1. *a*, euhedral pyrite in quartz vein from the Panicherevo deposit, polarized reflected light; *b-c*, LA-ICP-MS time-resolved spectra of: *b*, pyrite from Demir Boklu, enriched in Co, Ni, Mn, As and Se (drill-core № 22, depth 26.80 m); *c*, colloform pyrite (drill-core № 17, depth 269.20 m); *d*, positive correlation between Tl and As

in its lattice. Copper ranges from 0.6 to 2502 ppm. High Cu contents in pyrite as well as fluctuations of Cu intensity in the ablation depth profiles (Fig. 1c) indicate either a multitude of discrete Cu-bearing mineral inclusions (chalcopyrite, tennantite-tetrahedrite) or a Cu-enriched zone in the colloform pyrite. Silver contents range from undetectable (below detection limits) to 1748.0 ppm. It has positive correlations with As, Cu and Pb. This could suggest its presence as inclusions of galena and chalcopyrite/tennantite. Bismuth contents are also related to galena based on their positive correlations. Molybdenum contents are connected with inclusions of molybdenite, which occurs in the mineralization.

Arsenic contents vary between 0.4 and 1692 ppm (Fig. 1b–c). High As concentrations are determined mainly in samples from depths of 250–270 m and are typical for colloform pyrite. At shallow depths, As is not present. A positive correlation exists between As and most trace elements detected in pyrite. This suggests a change of the hydrothermal fluid composition and conditions of deposition among pyrites from different assemblages, as well as possible substitutions for Fe, especially in colloform pyrite (Abraitis et al., 2004). Based on flat downhole ablation profiles and the positive correlation between As and Tl (Fig. 1c–d), a coupled substitution, such as $As^{3+}+Tl^{+}$ for $2Fe^{2+}$ could be suggested (George et al., 2019).

Selenium has a positive correlation with As and an almost homogeneous distribution in pyrite, while Te is rarely detected. Both Se and Te are able to substitute S in the pyrite lattice, resulting in the formation of dianions with S.

Gold is determined only in 3 analyses with concentrations from 0.6 to 1.2 ppm (one is in colloform pyrite, 269 m). Its presence is either as discrete inclusions in pyrite or as crack infillings.

The pyrite from the two prospecting areas in the Panicherevo deposit has similar trends of trace element distribution. However, pyrite from the Demir Boklu area is characterized with higher content of Co, Ni and Mn, whereas pyrite from the Kohuk Dere area, is characterized with higher contents of Cu, Pb and Ag related to mineral inclusions. The contents of Mn, Cu, Pb, Ag generally increase with increasing of the As content, especially in colloform pyrite in samples from greater depth.

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