Gold concentrations in arsenopyrite from the Govezhda and Svishti Plaz deposits, Bulgaria: a LA-ICP-MS study

Концентрации на златото в арсенопирит от находищата Говежда и Свищи плаз, България: LA-ICP-MS изследване

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Introduction

Numerous papers have considered the potential of pyrite and arsenopyrite to incorporate gold, as so called “invisible gold” (Maddox et al., 1998; Cabri et al., 2000; Morey et al., 2008, etc.). Chemical speciation and distribution patterns of gold in these minerals have been widely discussed in the cited papers as well. So far, X-ray photoelectron spectroscopy (XPS), micro X-ray absorption near edge structure (XANES) spectroscopy, field emission scanning electron microscopy (FESEM) and secondary ion mass spectrometry (SIMS) have shown that the so called “invisible gold” in arsenopyrite occurs as elemental (Au^0) and chemically bound (Au^{1+}) species. In some gold deposits, arsenopyrite accommodates a major amount of Au. This poses problems in gold extraction from the arsenopyrite-rich sulfide ores and consequent negative impact on the environment.

Materials and methods

Representative samples were collected from exploitation and exploration mining dumps of different parts of the Govezhda and Svishti plaz deposits. Minor and trace elements in arsenopyrite 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 made using the PerkinElmer ELAN DRC-e ICP-MS equipped with a New Wave UP193-FX excimer laser ablation system. The laser was run at a pulse frequency of 10 Hz and laser energy of 1.60–2.20 J/cm^2 on the sample for 50 µm spot size. Acquisition dwell time for all masses was set to 0.01 s. The NIST SRM 612 glass was used as external standard and was measured recurrently during the course of the analyses. Both Fe and As contents (wt.%) were used as internal standards in calculation of the 32 measured element concentrations using SILLS v.1.1.0 software (Guillong et al., 2008). Iron and arsenic contents in arsenopyrite were determined by electron microprobe at the Institute of Earth Sciences, University of Graz, Austria. All analyzed arsenopyrite grains were examined by reflected light microscopy prior LA-ICP-MS analysis to avoid discrete sulfide inclusions.

Geological setting

The Govezhda gold deposit is located in NW Bulgaria. It is hosted in the low grade metamorphic rocks of Diabase-Phyllitoid complex (Berkovitsa and Dalgi Del group). Mineral composition is relatively simple comprising pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, tetrahedrite and gold, and rare sulfosalts. Ore minerals are formed during 4 main ore stages. Gold occurs mainly with galena and sphalerite from the second stage, but also as so called “invisible gold” within pyrite and arsenopyrite from the first stage (Mladenova et al., 2003).

The Svishti plaz gold deposit is situated in the Central Balkan Mountains, Bulgaria. It is hosted in Paleozoic low-crystalline schists, granodioritic, dioritic and quartz-dioritic plutonic bodies and related hornfelses. Mineral composition is similar to this in the Govezhda gold deposit. Five ore stages have been distinguished (Mladenova, Kerestedjian, 2002). The ore-controlling structures in both deposits are veins, infilling fissures related to tension and shear faults. The origin of both deposits is considered to be related with the Late Carboniferous dykes crosscutting the low grade metamorphic rocks.

Results and conclusions

Similarly to SIMS, LA-ICP-MS can also give information about Au grade in arsenopyrite. However, it cannot show precise spatial distribution as SIMS mapping. Major advantage is that by single spot analysis can be obtained data about more than 30 masses simultaneously with reasonably low levels of detection limits and error (1σ). Depth penetration of laser is bigger than SIMS, can be controlled and any surface contamination of the sample can be excluded during signal data reduction. Time resolved spectra of any spot analysis can show the distribution of the measured masses in depth. Since arsenopyrite is opaque mineral there is always possibility the laser to ablate through mineral inclusions in depth. However, such inclusions of other sulfide minerals or gold are quite well discernible in the whole spectrum. Thus, with certain assurance, gold presence can be distinguished whether as being an infilling of tiny cracks (2–3 μm), major concentration of micro- to nano-sized gold particles in the analyzed volume, or eventually bound in arsenopyrite ("invisible gold"). The latter one cannot be proved with this method.

In this study, we tried using different internal standards, as As and Fe, for data reduction using SILLS software. EPMA analyses in the same spots showed that arsenopyrite from both deposits is non-stoichiometric, with S>As. Since As content (in wt.%) prevails Fe content in arsenopyrite, As also can be used as internal standard. Most of the known polyatomic interferences in ICP-MS at ^{75}As, as $^{40}Ar^{35}Cl$, $^{59}Co^{16}O$, $^{36}Ar^{38}Ar^{1}H^{+}$, etc. (May, Wiedmeyer, 1998), are less likely to be formed in plasma when ablating sulfide matrix. Comparison between data for concentrations obtained using As and Fe internal standardization showed differences. Generally, using Fe internal standard in data reduction "produces"' Au concentrations almost two times higher compared to Au concentrations obtained by As internal standard usage. Same is observed for other trace metals as well. However, it is not clear yet what is the fractionation behavior of As during ablation. Therefore, we choose to use data received by Fe internal standardization.

Analyses in 50 μm diameter spots performed in central and peripheral areas of arsenopyrite euhedral crystals from the Govezhda and Svishti Plaz deposits showed some differences. In most cases, Au shows uniform signal in the time resolved spectra in depth in the central part of the grains. The obtained Au concentrations in the central part of arsenopyrite grains from the Govezhda deposit (uniform signal) vary between 8.61 and 218.98 ppm, while in the peripheral parts – 3.15–8.66 ppm. Similarly, the Au concentrations in arsenopyrite from the Svishti Plaz deposit are between 46.88 and 118.62 ppm (central part) and 0.91–4.91 ppm (peripheral part), respectively. Some of the highest Au concentrations probably correspond to a multitude of nano-sized Au particles attached to the growth zones in the central part of arsenopyrite crystals. Isolated Au peaks in the time resolved spectra correspond to gold infillings/inclusions in tiny cracks (1–3 μm), observed in the peripheral zones. In some cases, high concentrations of Au can be related to larger Au infillings together with other sulfides (galena, tetrahedrite, sphalerite) from the second and third stage of the mineralization. Arsenopyrite in both deposits proved to be major carrier of Au similarly to As-bearing pyrite.

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