



Experiment title: X-ray absorption spectroscopy study of the state of Pt and As admixtures in pyrite	Experiment number: ES 1269	
Beamline: BM16	Date of experiment: from: 01.03.2023 to: 10.03.2023	Date of report: 05.04.2023 <i>Received at ESRF:</i>
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(I) The state of Pt and As in synthetic pyrites

Introduction: Multiple studies of As and Pt states in sulphides show that (i) As⁻¹ can incorporate randomly in the anionic sites of pyrite structure or can form As-As clusters in the pyrite matrix [1,2]; (ii) Pt can form a solid solution in pyrite [3]. At the same time González-Jiménez et al. [4] and Helmy et al. [5] suggested the formation of PtAs₂ nanoparticles in the matrices of the Fe-Ni-S sulphides.

Experiment: The Pt-As-doped pyrites FeS₂ were studied by means of XAS (HERFD-XANES/EXAFS) at the Pt L₃- and As K-edges in order to reveal the states of these admixtures in pyrite. The preliminary mapping was performed by EPMA in BSE mode (Fig. 1A,B). The zones containing 50–2200 ppm of As and 30–1250 ppm of Pt were detected. To find these zones we also performed X-ray fluorescence mapping using SDD detector (Fig. 1C). We chose some areas containing contrast amounts of Pt and As (Fig. 1A–C) and recorded spectra in zones N1 – N7. The experimental spectra are shown in Fig. 1D and 1E. The majority of experimental spectra of Pt in pyrite are similar to the spectrum of standard of Pt in solid solution in pyrite (Pt,Fe)S₂. The preliminary EXAFS fitting showed that the states of Pt and As in pyrite are not coupled: As and Pt are not in each other's local atomic environment. One spectrum (N1) was similar to the standard of PtS₂ indicating the presence of PtS₂-microinclusions which presence was detected on the BSE images. The state of As is similar in all the zones. The preliminary formula of the pyrites can be written as (Pt,Fe)(As,S)₂. As a general rule, the field of stability of solid solution increases with increasing temperature. Even at room temperature Pt and As enriched pyrite in the isomorphous form, that is why we preferred to study the other samples instead of performing the heating experiment.

The preliminary results of our experiment show that even though Pt and As enrich the same zones of pyrite crystals, the Pt-Pt, Pt-As, or As-As clustering is absent.

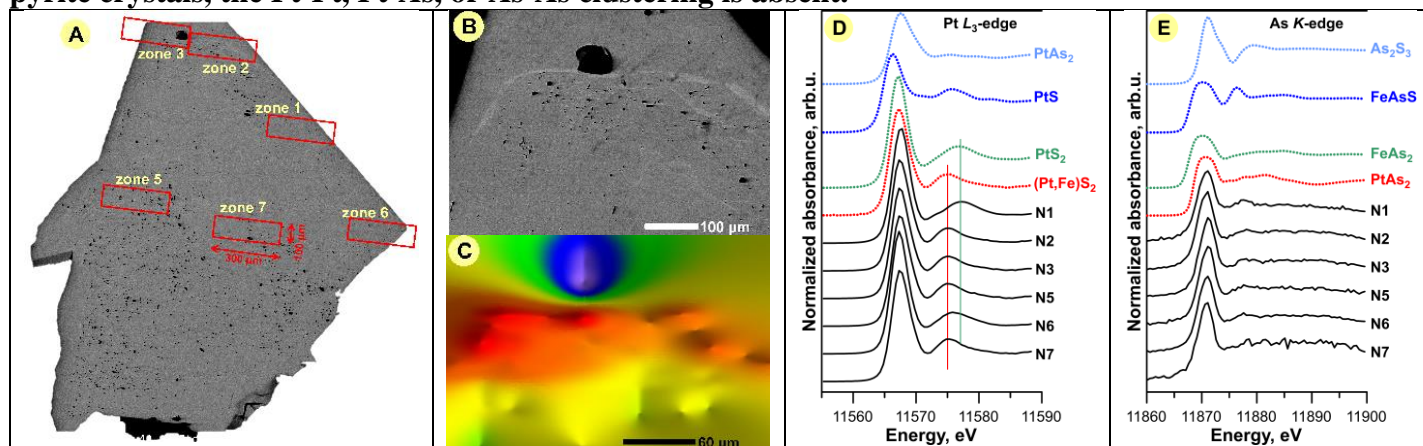


Fig. 1. (A) Back-scattered electron image (BSE) of pyrite, zones of analyses are indicated by red rectangles. (B, C) The enlarged upper portion of the grain containing growing zones (white) enriched with Pt and As and mapping of the same zone of the grain performed with SDD detector at 11567 eV incident beam energy. (D, E) HERFD-XANES spectra of Pt- and As-bearing pyrites and the spectra of standards.

[1] Filimonova et al. (2020) *Ore Geology Reviews*, 121, p.103475; [2] Manceau et al. (2020) *ACS Earth and Space Chemistry*, 4(3), pp.379-390; [3] Filimonova et al. (2019) *Economic Geology*, 114(8), pp.1649-1663; [4] González-Jiménez et al. (2019) *Contributions to Mineralogy and Petrology*, 174(5), pp.1-18; [5] Helmy et al. (2013) *Nature communications*, 4(1), pp.1-7.

(II) The state of Pt in natural pyrite *In collaboration with Prof. R. Piña García (Univ. of Madrid)*

Introduction: Even though pyrite is a relatively common phase in Ni-Cu-Platinum-Group Elements (PGE) magmatic sulphide deposits, the most of the studies do not pay attention to PGE concentrations in pyrite, ascribing all elevated PGE contents to the other sulphide minerals. Piña et al. [6] have demonstrated the presence of extremely high (in terms of natural samples) contents of Pt in pyrite of 5-30 ppm from Aguablanca Ni-Cu sulphide deposit. Note that the usual content in the enriched exploited ores is at the level of first ppms. At the same time, our previous study of synthetic samples showed that pyrite is capable of concentrating up to 4 wt% in the solid solution state in the oversaturated with Pt system [3].

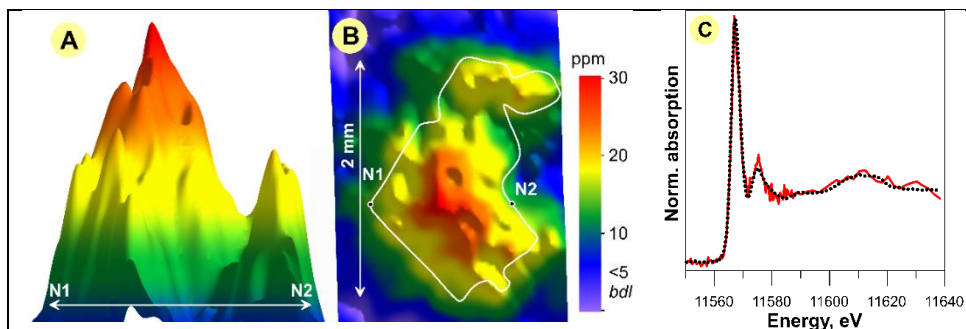


Fig. 2. Natural Pt-bearing sample from Aguablanca Ni-Cu sulphide deposit. (A, B) Mapping of the grain performed with SDD detector at 11567 eV incident beam energy. (C) HERFD-XANES spectrum of Pt in pyrite (red thick line) together with the spectrum of 0.24 wt% of Pt in solid solution in synthetic pyrite (black dotted line).

Experiment: We studied the unique natural sample of Pt-bearing pyrite (C_{Pt} up to 30 ppm) via XAS and recorded one HERFD-XANES spectrum. It appeared that the spectrum of Pt in natural sample is identical to the spectrum of Pt in synthetic pyrite in solid solution (Fig. 2).

We unambiguously proved that natural pyrite from Ni-Cu sulphide deposit can contain up to 30 ppm of Pt in the solid solution.

[6] Piña et al., *European Journal of Mineralogy*, 25(2), 241-252 (2013).

(III) The state of As in natural Au-As-bearing pyrites

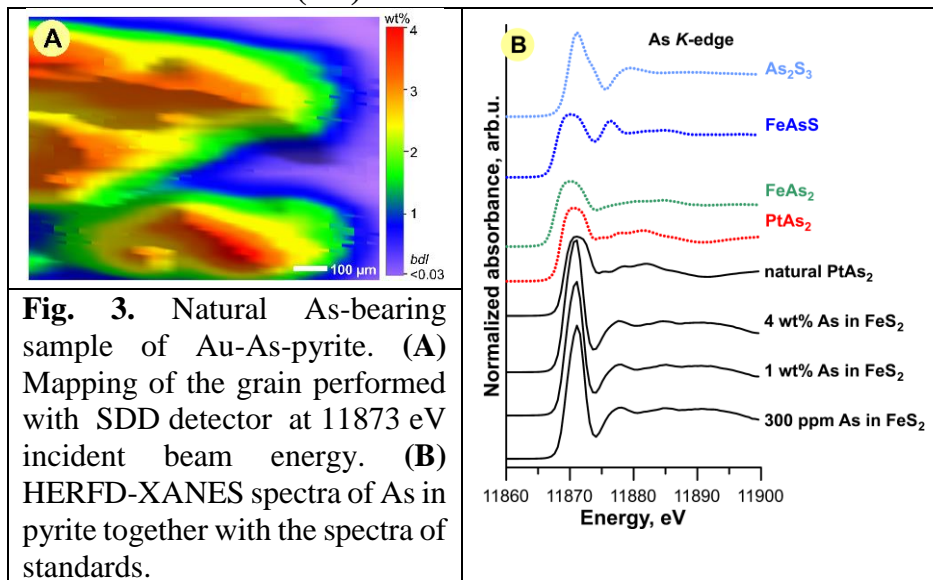


Fig. 3. Natural As-bearing sample of Au-As-pyrite. (A) Mapping of the grain performed with SDD detector at 11873 eV incident beam energy. (B) HERFD-XANES spectra of As in pyrite together with the spectra of standards.

Introduction: Arsenian pyrite is an abundant mineral occurring in many geological settings at the Earth's surface, including hydrothermal ore deposits which are the main source of Au. So-called "invisible" (or refractory) form of Au is present in pyrites in all types of these deposits, and its concentration is often directly correlated with As content [1, 7, 8]. The coupled behaviour of Au+As has been studied earlier, Pokrovski et al. [8] proposed the mechanism: $2Fe^{2+} = Au^+ + As^{3+}$. The goal of this measurement was to study the state of As in Au-rich

pyrites in order to compare it with the state of As in Pt-rich pyrites.

Experiment: The unique natural pyrites containing up to 4 wt% of As and up to 800 ppm of Au were studied. Mapping of the sample and experimental spectra together with the standards are shown in Fig. 3. The experimental spectra are similar to those of As-Pt-bearing samples (Fig. 1E and Fig. 3B). The preliminary fitting of the EXAFS data have shown that As substitutes for S in the anionic position.

[7] Reich et al., *GCA*, 69(11), 2781-2796 (2005). [8] Pokrovski et al., *GPL*, 17, 39-44 (2021).

Concluding remarks

Interpretation of the experimental data will be performed using IFEFFIT program package combined with FDMNES theoretical simulations. **This experiment was only possible due to the high brightness of the FAME-UHD BM16, which allowed us to record the HERFD-XANES spectra and high-quality EXAFS data for Pt and As in pyrite.**