

The state of Au and As in pyrite studied by X-ray absorption spectroscopy of natural minerals and synthetic phases

O.N. Filimonova¹, A.L. Trigub², M.S. Nickolsky¹, E.V. Kovalchuk¹, V.D. Abramova¹,
M. Rovezzi³, E. Belogub⁴, I.V. Vikentyev¹ and B.R. Tagirov¹

¹Institute of Geology of Ore Deposits (IGEM RAS), 35, Staromonetny per., 119017 Moscow, Russia, ²NRC “Kurchatov Institute”, Moscow, Russia, ³Université Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ⁴Institute of Mineralogy, Urals Branch of RAS, Chelyabinsk District, 456317 Miass, Russia, oliel@list.ru

Arsenian pyrite FeS₂ of hydrothermal origin can contain considerable amount of “invisible” (or refractory) Au. The Au and As contents in pyrite are often directly correlated. In the present work the oxidation states and the local atomic environments of Au and As were determined using X-ray absorption spectroscopy (XAS). The samples of natural (from Au-sulfide and Carlin type deposits) and synthetic (450 °C/ 1 kbar, 300 °C/ P_{sat}) arsenian and As-free pyrites were studied. The Au L_3 -edge and As K -edge XAS spectra were recorded at BM16 FAME-UHD beamline of ESRF (Grenoble) and STM beamline of KSRS (Moscow, Russia, only As spectra). The High Energy Resolution Fluorescence Detection mode (HERFD) was applied to record the Au spectra. The As K -edge spectra were obtained simultaneously with the Au L_3 -edge ones. The XAS data processing was performed using IFEFFIT package. The analyses of Au L_3 -edge XAS data showed that Au in pyrites is present in two forms: Au¹⁺ in the solid solution state where Au substitutes for Fe and is surrounded by 6 S atoms, and Au in Au¹⁺₂S-like clusters where Au is surrounded by 2 S atoms. Significant fraction of Au¹⁺₂S-like clusters results in decrease of the average Au-S bond length and coordination number observed by means of the EXAFS spectra fitting. The admixture of As has no effect on the Au oxidation state and local atomic environment (Fig.1), except one synthetic sample which contains a minor amount of FeAsS or FeAs₂. The presence of these phases is consistent with results of SEM/EDS and EPMA analyses. The analyses of As K -edge absorption spectra showed that As mostly presents in the solid solution state substituting S atoms in the pyrite matrix ($\text{S}^{1-} \leftrightarrow \text{As}^{1-}$). Our data demonstrate that natural pyrites of hydrothermal origin can host economic concentrations of “invisible” Au in solid solution state independently of As content.

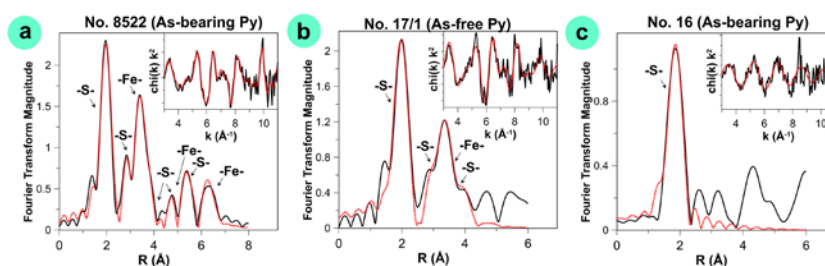


Figure 1: The k^2 -weighted background-subtracted Au L_3 -edge EXAFS spectra and their Fourier transforms (FT, not corrected for phase shift). (a) - natural; (b, c) - synthetic pyrites. The spectra of natural arsenian (a) and synthetic As-free (b) pyrites are similar; As is absent in the nearest coordination shells of Au in natural (a) and synthetic (c) arsenian pyrites.