



	Experiment title: Coupled chemistry of As and Au in minerals of the Fe-As-S system: a HERFD XAS/XES study	Experiment number: ES-602
Beamline: BM16	Date of experiment: from: 13.04.2017 to: 18.04.2017	Date of report: 4.08.2017
Shifts: 15	Local contact(s): Mauro Rovezzi, BM16, ESRF	<i>Received at ESRF:</i>
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Report:

Experimental data. The local atomic structure of As and Au in arsenian pyrites (FeS_2) was examined by means of XAFS spectroscopy at As K -edge and Au L_3 -edge. The studied samples included synthetic As-free (3 samples) and As-bearing (arsenian) pyrites (5 samples, $C_{\text{As}} = 0.5\div 1.5$ wt.%) which contained 40-130 ppm Au. The samples were synthesized in our laboratory at 300 °C, P_{sat} and 450 °C, 1kbar by means of hydrothermal technique. In addition, one sample of natural arsenian pyrite (Samolazovskoe Au-porphyry deposit, Yakutia, Russia) was studied. The sample of natural pyrite contained ca 300 ppm Au, 0.5 wt.% As, and n -wt.% of Tl and Pb. During the data collection, the samples pressed into pellets were held in the horizontal helium cryostat. The As K -edge spectra of were recorded in total fluorescence yield (TFY) detection, whereas the record of Au L_3 -edge spectra was performed in the high energy resolution fluorescence detection (HERFD) mode using an X-ray emission spectrometer. In case of the sample of natural pyrite, in addition to As and Au spectra, the TFY spectrum of Tl L_3 -edge was recorded in order to determine if this element presents in the nearest-to-Au coordination spheres.

Experimental results. Comparison of As K -edge XANES spectra of synthetic pyrites with the spectra of the reference substances (Fig. 1) shows that the chemical state (local atomic environment and valence state) of As depends on the parameters of synthesis. Low-temperature (300 °C) synthesis experiments yield samples of arsenian pyrites which contained both As^{3+} (feature with a maximum intensity at ~ 11869 eV) and As^{5+} (feature at ~ 11874 eV). For sample Py-As-5/2 the ratio $\text{As}^{3+}/\text{As}^{5+}$ changed during the experiment: the concentration of As^{3+} increased at the expense of As^{5+} (spectra Py-As-5/2-1 and -2). The high-temperature synthesis (450 °C) produced arsenian pyrites with mostly As^{3+} . The XANES spectra recorded for these samples, however, differ from those of reference substances - As-sulfides and Fe-arsenides, which suggests that As in pyrite exists in the solid solution state. We note also that the XANES spectra of the high-temperature arsenian pyrites are identical with the one of the natural sample. In contrast to As, the shapes of Au L_3 -edge HERFD XANES show no correlation with the synthesis parameters (Fig. 1). Recorded spectra of Au differ from both the spectra of Au_2S and Au-bearing arsenopyrite FeAsS . The spectra of arsenian and As-free pyrites are similar which means that the chemical state of Au in pyrite is mainly determined by the Au-S interaction. This assumption is confirmed by the wavelet transform (WT) of Au L_3 -edge EXAFS spectra (Fig. 2) which demonstrates that the most important contribution to the 1st coordination shell of Au comes from light S atoms at $k\sim 6$ Å⁻¹ with only small influence of heavier atoms at $k \geq 8$ Å⁻¹. The As K -edge and Au L_3 -edge EXAFS (Fig. 3) are consistent with the analysis of XANES spectra: differences in the chemical state of As in pyrites has little effect on the local atomic environment of Au. This unexpected result has important implications for understanding of the mechanism of formation of Au-bearing pyrite – the most important carrier of Au in the world-class gold deposits. Future work on the experimental data treatment will include determination of the local atomic and electronic structure parameters of Au and As using IFEFFIT software package, Reverse Monte-Carlo calculations, and simulations of XANES and EXAFS spectra of Au-bearing arsenian pyrite on the basis of atomic configurations produced by means of DFT calculations.

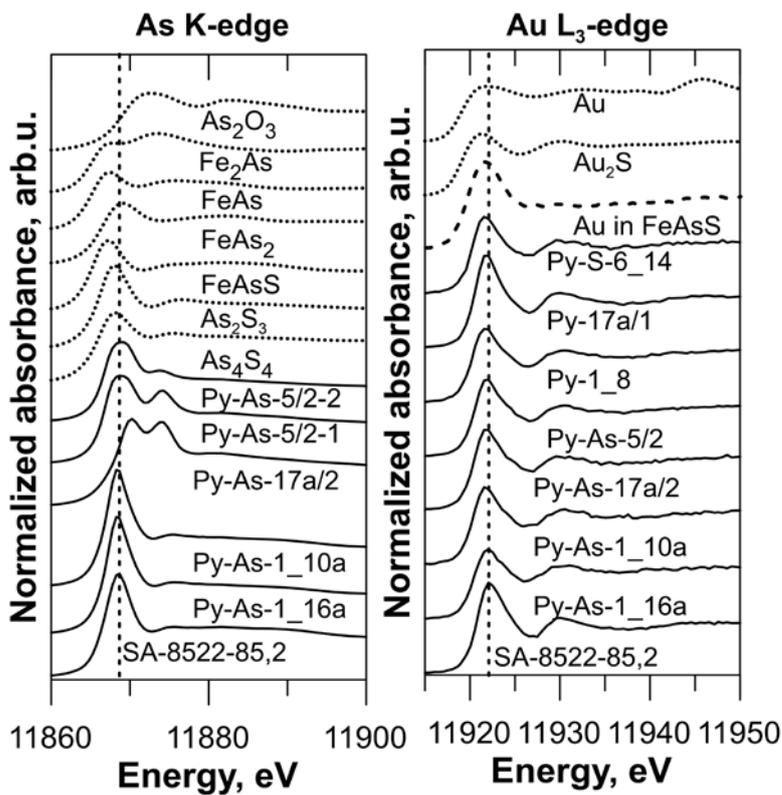


Fig. 1. Arsenic K -edge TFY XANES (*left*) and Au L_3 -edge HERFD XANES spectra (*right*) recorded from the samples of Au-bearing synthetic pyrites FeS_2 (Py-S-6_14, Py-17a/1, Py-1_8), synthetic arsenian pyrites (Py-As-5/2 (spectra 1 and 2), Py-As-17a/2, Py-As-1_10a, Py-As-1_16a), and natural arsenian pyrite SA-8522-85,2. Spectra of reference substances are shown by dotted lines. The Au L_3 -edge HERFD XANES spectra of Au-bearing arsenopyrite FeAsS from Trigub et al. (2017) is shown for comparison by dashed line.

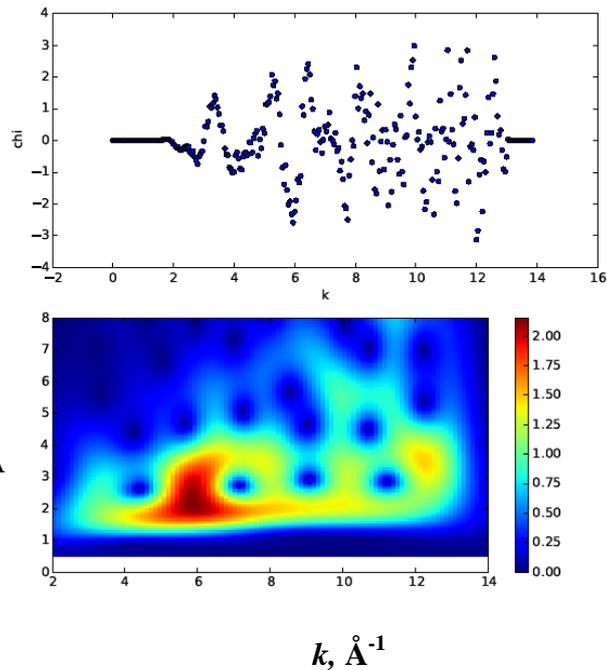


Fig. 2. Wavelet transform modulus of Au L_3 -edge EXAFS spectra of natural arsenian pyrite (SA-8522-85,2).

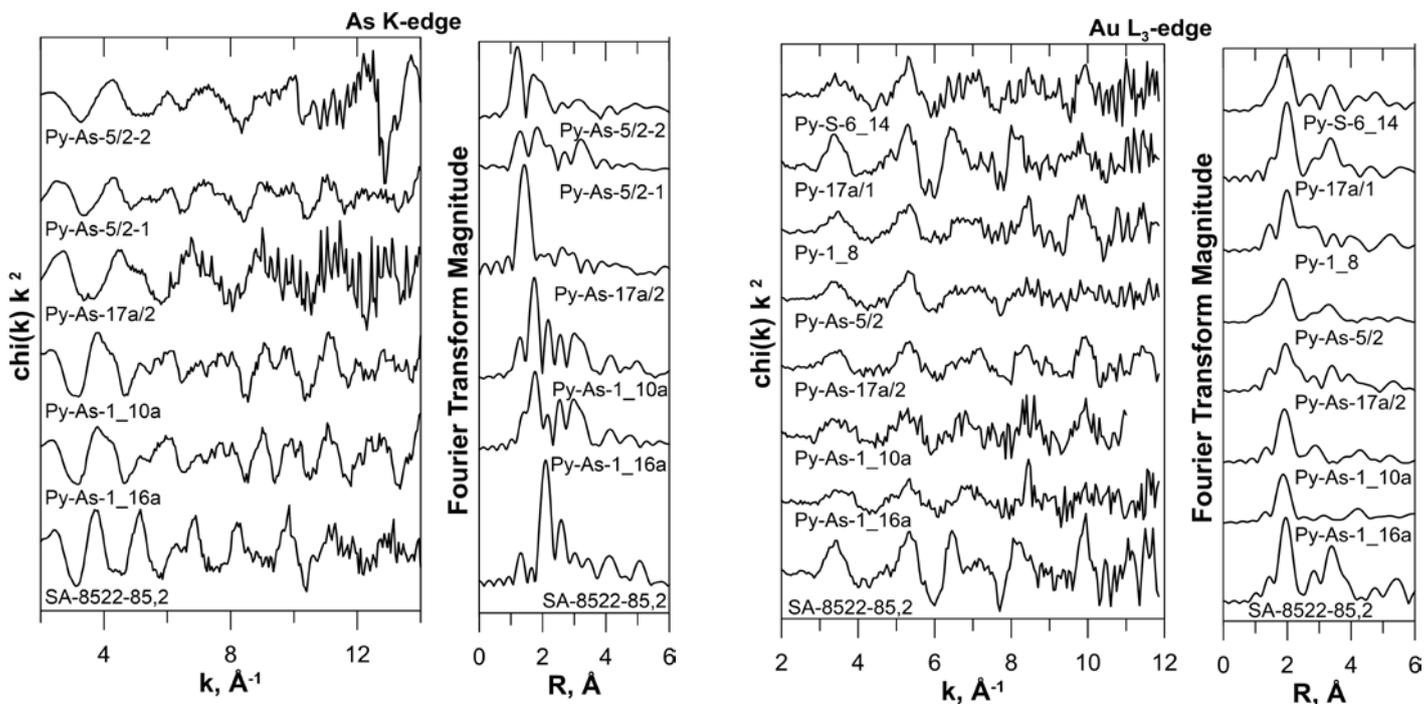


Fig. 3. Arsenic K -edge (*left*) and Au L_3 -edge (*right*) background subtracted EXAFS spectra, and Fourier transforms of the EXAFS spectra (k^2 -weighted, uncorrected for phase shift).

References

Trigub, A.L., Tagirov, B.R., Kvashnina, K.O., Chareev, D.A., Nickolsky, M.S., Shiryaev, A.A., Baranova, N.N., Kovalchuk, E.V., Mokhov, A.V., 2017. X-ray spectroscopy study of the chemical state of “invisible” Au in synthetic minerals in the Fe-As-S system. *Am. Mineral.* 102, 1057-1065.