



	Experiment title: X-ray absorption spectroscopy study of the coupled chemistry of In and Cu in sphalerite (Zn, Fe)S	Experiment number: ES-703
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Report: Experimental data. The local atomic structure of admixture of critical metal, In, and accompanying 1st group metals – Cu and Ag in sphalerite ((Zn, Fe)S) was examined by means of XAS (XANES/EXAFS). Initially we planned to study only Cu-In-bearing sphalerites, but finally a series of Ag-In sphalerites was added to the list of samples to obtain information about the systematic changes of the local atomic structure of trace elements along the 1st group of the periodic system. The spectra were acquired at Cu *K*-edge, In *K*-edge, and Ag *K*-edge. The experiment consisted in the record of the spectra of:

- a series of synthetic Cu-In sphalerites;
- a sample of synthetic Cu-bearing (In-free) sphalerite (Cu *K*-edge spectra were recorded at ambient and high temperatures);
- a series of natural Cu-In sphalerites from Kudriavy volcano (Iturup island, Russia; Cu *K*-edge spectra of one sample was recorded at the formation temperature of 500 °C);
- a series of natural Cu-bearing sphalerites from two European deposits (only Cu *K*-edge spectra);
- two samples of Ag-In sphalerites.

Experimental results. Figure 1 shows XANES spectra for In, Cu, and Ag *K*-edges of selected samples of synthetic and natural sphalerites. The In *K*-edge spectra are identical for all the samples, including sample of Au-In sphalerite, which is shown for comparison in the left panel of Fig. 1. As indicated in Fig. 2, in all the samples studied in the course of the experiment In occupies cationic position in the structure of sphalerite. It is tetrahedrally coordinated with the nearest S atoms at a distance of 2.45 Å (Cu-In sphalerite) and 2.46 Å (Ag-In and Au-In sphalerite). In contrast, the spectra of Cu and Ag *K*-edges are dependent on the sample composition and formation conditions. The Cu *K*-edge XANES spectra of synthetic Cu-In sphalerites (samples No. 4186, 4108, top of the figure), and the spectra of natural sample No. 501 (bottom of the figure) are close to the spectra of CuInS₂. Similarly, Ag *K*-edge XANES spectra of one sphalerite sample (No. 4197) are close to the spectra of AgInS₂. Analysis of Cu and Ag *K*-edges EXAFS spectra, shown in Fig. 2, imply that in these samples the admixtures of the 1st group metals are in the solid solution state and located in the cationic position. No In has been observed in the 2nd coordination sphere of the metal, as well as no metal (Cu or Ag) are located in the second coordination sphere of In, which means that all the admixtures are statistically distributed within the sphalerite structure without Cu-In and Ag-In clustering. The distance between atoms of the 1st group metals and the nearest S atoms increases with increasing the cation size and is equal to 2.30 Å for Cu and 2.49 Å for Ag (previously we determined the Au-S distance for the solid solution Au in sphalerite as 2.6-2.7 Å which is in line with the distance for the other 1st group metals). In the absence of In, Cu in sphalerite is in the state of Cu₂S (sample No. 4065, central panel of Fig. 1), or forms Cu oxide in oxidized natural samples No. PE8 and ME77. Heating of natural sphalerite yielded no changes in the XANES spectrum, whereas heating of synthetic Cu-bearing In-free sphalerite resulted in formation of Cu oxide. Further work on the experimental data treatment will consist in investigation of details of the local atomic structure of the admixtures by the experimental spectra fitting using reverse Monte Carlo method, and simulation of the spectra for atomic geometries relaxed by means of DFT method.

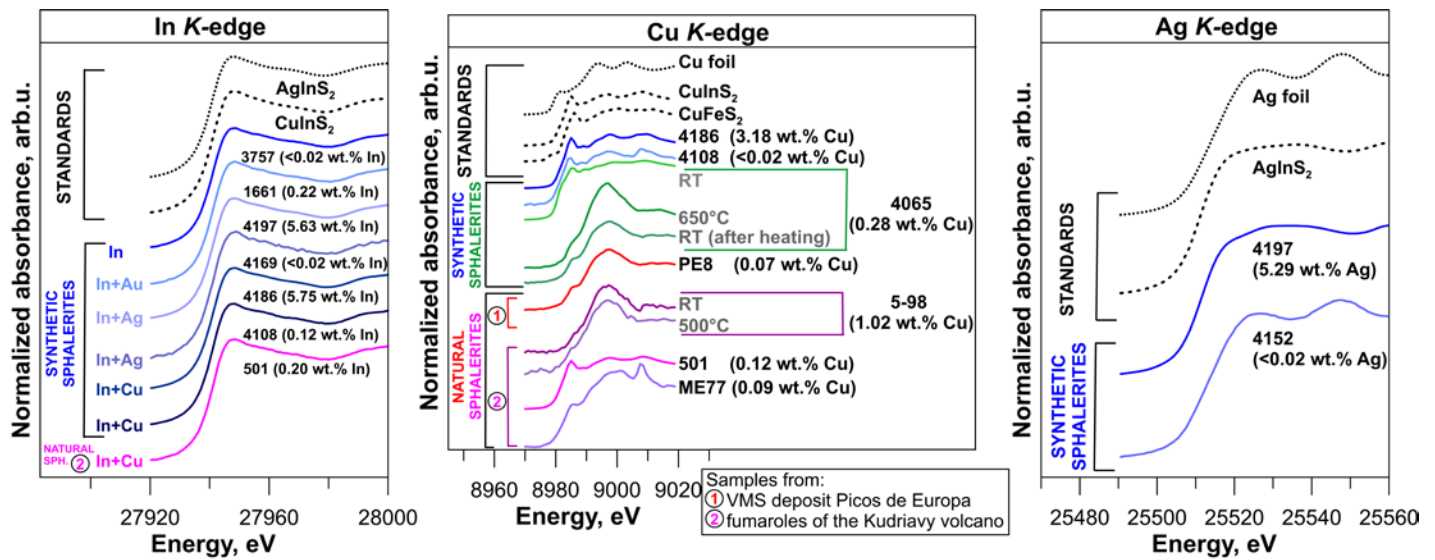


Fig. 1. XANES spectra of selected Cu-In and Ag-In-bearing sphalerites (synthetic and natural), and the spectra of standards. *Left* – In K-edge, *center* – Cu K-edge, *right* – Ag K-edge. The spectra of synthetic (No. 4065) and natural (No. 5-98) Cu-In sphalerites were recorded at ambient temperature (RT) and at high temperature (650 °C for synthetic sphalerite and 500 °C for the natural one, these temperatures correspond to conditions of the formation of these samples). All the other spectra were recorded at ambient temperature.

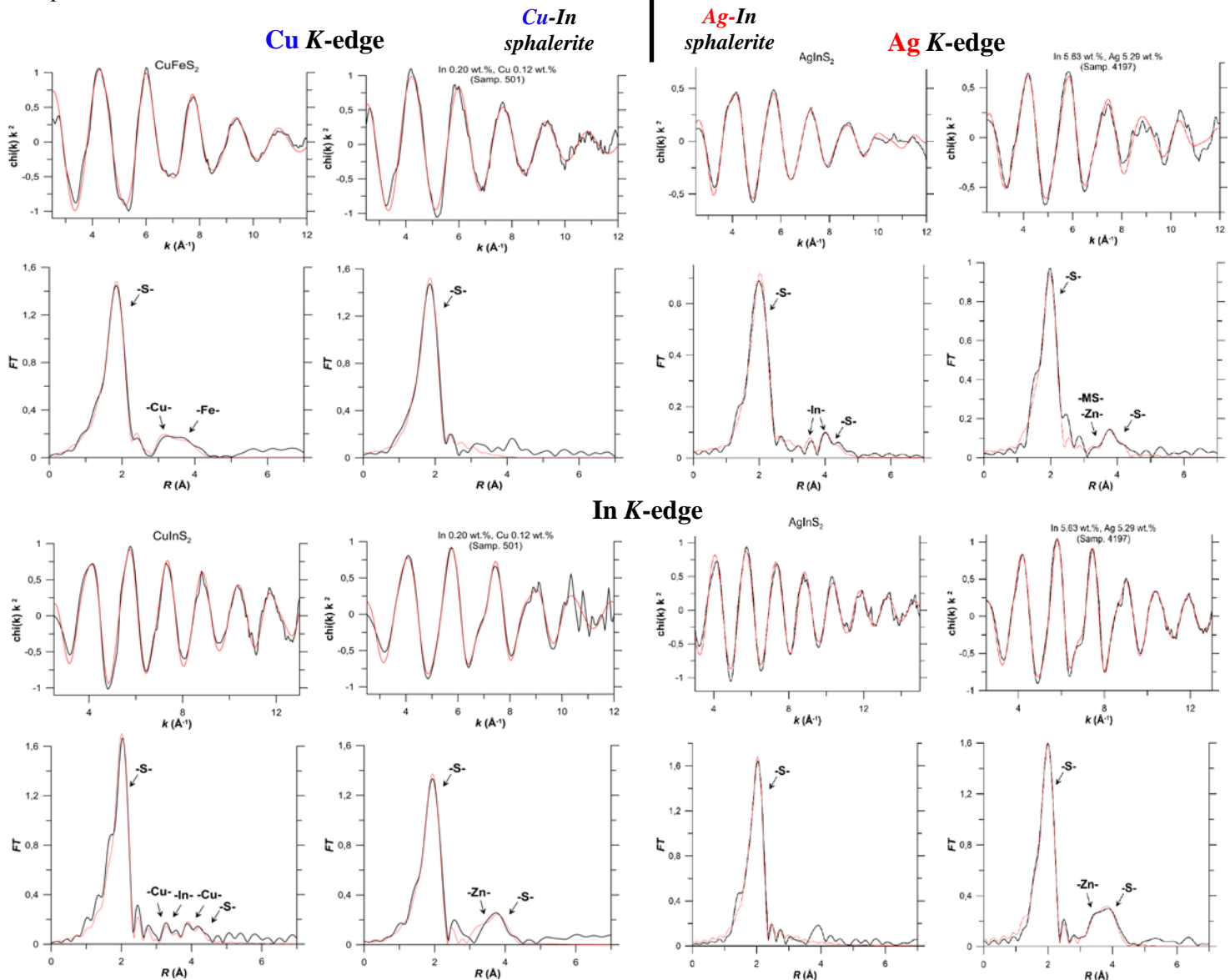


Fig. 2. Normalized k^2 weighted EXAFS spectra and their Fourier Transforms (FT) obtained from natural Cu-In (*left*) and synthetic Ag-In (*right*) sphalerites. Spectra of standards (CuFeS_2 , CuInS_2 , and AgInS_2) are shown for comparison. Black lines – experimental spectra, red lines – fit results. In both samples In and the 1st group metals are in the cationic position in the sphalerite structure, for the 1st coordination sphere $N_S = 4$, $R_{\text{In-S}} = 2.45 \pm 0.01$ Å (Cu-In sphalerite) and 2.46 ± 0.01 Å (Ag-In sphalerite); $R_{\text{Cu-S}} = 2.30 \pm 0.03$ Å, $R_{\text{Ag-S}} = 2.49 \pm 0.01$ Å. MS – multiple scattering.