

XAS study of speciation and valence state of “invisible” gold in synthetic base metal sulphides

ALEXANDER TRIGUB^{1,2}, BORIS TAGIROV²,
DMITRIY CHAREEV^{2,3}, MAX NICKOLSKY²,
ANDREY SHIRYAEV^{4,2} AND KRISTINA
KVASHNINA⁵

¹NRC “Kurchatov Institute”, Russia

²Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS, Russia

³Institute of Experimental Mineralogy RAS, Russia

⁴Institute of Physical Chemistry and Electrochemistry RAS, Russia

⁵ESRF, France

e-mail: alexander.trigub@gmail.com.ru

Gold in sulfide ores often exists in the “invisible” (refractory) state disseminated in the matrix of base metal (Cu, Fe, Zn) sulfides as nanoscale particles and/or in the form of the isomorphous solid solution. The aim of this study is to investigate local atomic environment and electronic structure of the “invisible” Au in base metal sulfides and arsenides – pyrite FeS₂, löllingite FeAs₂, arsenopyrite FeAsS, and covellite CuS – synthetic analogues of natural minerals. In these Au-bearing minerals formed at high temperature, the “invisible” Au withstands quenching and can be studied at ambient temperature.

Laboratory synthesis experiments were conducted using hydrothermal (pyrite, covellite, $t = 400 - 475$ °C) and salt flux (pyrite, löllingite, arsenopyrite, covellite $495 - 700$ °C) methods. The Au L₃-edge XAFS spectra for these minerals were recorded at the ESRF (Grenoble, France) on the high-brilliance X-ray absorption/emission spectroscopy undulator beamline ID26. XANES and EXAFS spectra were collected in high energy resolution fluorescence detection (HERFD) mode using crystal X-ray emission spectrometer. Experimental spectroscopic data were combined with *ab initio* molecular dynamic simulations aimed at relaxation of crystal structure of the Au-bearing sulfides and electronic structure calculations.

Modelling of Au L₃-edge EXAFS/XANES spectra showed that Au can substitute base metal in crystalline lattice of all studied sulphides. For pyrite only finely grained powder synthesized using hydrothermal method contained chemically bound Au in the form of the solid solution, whereas Au⁰ was detected in large (n mm in diameter) crystals obtained at $t > 500$ °C in the salt flux experiments. The chemically bound Au in hydrothermal pyrite decomposed with the formation of Au⁰ during heating experiments performed in “dry” system. In pyrite, löllingite, and arsenopyrite Au atoms are octahedrally coordinated by ligands in the first coordination shell with Me-L distance enlarged by 0.13 – 0.16 Å relatively to the pure sulphide structure. In covellite Au substitutes for Cu atoms in triangular coordination with Me-S distance increased by 0.18 Å.

Financial support of this study was partly provided by the Russian Scientific Foundation (grant 14-17-00693).