



	Experiment title: The role of the trisulfur ion, S_3^-, in gold incorporation and molecular state in pyrite	Experiment number: ES-195
Beamline: BM30B	Date of experiment: from: 22 January 2015 to: 27 January 2015	Date of report: 02 September 2015
Shifts: 18	Local contact(s): Jean-Louis Hazemann, BM30B (FAME)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Maria Kokh, *Damien Guillaume, *Gleb Pokrovski (GET, Toulouse); *Jean-Louis Hazemann (Institut Néel, Grenoble)		

Report:

Experimental setup and conditions. The gold local structure in *i*) pyrite samples hydrothermally synthesized from Au-S aqueous solutions between 300 and 600°C, and *ii*) a few natural pyrite and arsenopyrite samples from gold deposits has been examined by X-ray absorption spectroscopy (XAS) at Au L_3 -edge (11,919 eV) with a Si(220) double crystal monochromator, at liquid-helium temperature in a mini-cryostat (5-15 K), and using a recently developed high-resolution set-up (1) consisting of 5 Si(660) crystal analyzers and a vortex mono-element detector (HERFD-XAS). Pellets of homogenized powder samples were fixed in a copper holder allowing for both transmission and fluorescence spectra acquisition. The measured energy resolution at the maximum of Au fluorescence line (9,712 eV) is 1.2 eV, which is at least by a factor of 5 superior to normal resolution imposed to the core-hole width. This gain allows for well-resolved XANES spectra of Au at gold concentrations as low as 10-100 ppm, even in the presence of high As content (see below). The drawback of the use of a single-element detector (imposed by the geometry of the optical and experimental HERFD set-up) is the necessity for very long acquisitions to obtain an exploitable EXAFS spectrum (10-30 hours for such Au concentrations, depending on the sample). Unfortunately, the frequent beam failure in the storage ring during the whole weekend did not allow us to examine about 30% of the samples planned.

Results from reference Au compounds. The difference between HERFD and normal resolution spectra is impressive, the former allowing unprecedented improvement in the XANES part, revealing multiple absorption resonances that are not visible in normal resolution (Fig. 1).

Results from synthetic pyrite samples. XANES spectra of these samples unambiguously reveal two Au structural states, metallic gold and chemically bound gold, as show linear combination fit analyses using the references compounds. The bound Au state is likely to be Au(I) coordinated with 2 sulfur atoms, similarly to the $Au_2S(s)$ reference, but the absence of exploitable EXAFS signals that would have required 10s hours of acquisition time, did not allow identification of the Au neighbors and interatomic distances (Fig. 2). Because only few samples could be measured (see above), we were not able to find correlations between the ratio of the chemically bound to metallic Au and the Au total concentration and speciation. This speciation is dominated by either hydrogen sulfide $Au(HS)_2^-$ or trisulfur ion $Au(HS)S_3^-$ complexes (2-4) in the fluid phase from which the pyrite was precipitated. Nevertheless, it is clear from these pioneering results that significant part of Au may be incorporated into pyrite in a chemically bound state, likely as isomorphic substitution in the mineral lattice or as $(Au_2S)_n$ clusters. The absence of adequate reference compounds Fe-S-Au with known structures is the main limitation that may be overcome using quantum-chemical modeling of our HR XANES spectra (work in progress).

Results from natural Au-bearing pyrite and arsenopyrite. Two samples of Au-rich pyrite (60 ppm Au, 4wt% As) and arsenopyrite (1340 ppm Au, 40 wt% As) concentrates from the Villeranges deposit (Massif Central, France, ref. 5) were also examined. These samples possess exclusively chemically bound gold as was shown by Mossbauer spectroscopy (5). For the first time, the As XAS signal could be filtered from the Au signal due to the HR set-up allowing high-quality of XANES (both samples) and EXAFS (Au-rich sample) spectra to be acquired (Fig. 3). This pioneering experiment allowed estimation of detection/acquisition limits for Au using the HERFD device at FAME, which are critical for future experiments. XANES spectra limits are 100 and 10 ppm of Au for $FeAsS$ and $Fe(As,S)_2$, respectively, whereas exploitable EXAFS spectra for Au concentrations of several 100s ppm would require typically ~10 hours of acquisition time (depending on As concentration). Such Au concentrations are often presented in natural sulfide samples from Carlin and orogenic Au deposits, which have a high economic value. The normalized XANES spectra of both samples are very similar, but are not matched by the available reference compounds ($AuSb_2$, $AuTe_2$, Au_2S , Fig. 4), suggesting the presence of As in the 1st shell coordination around gold. EXAFS spectra suggest the presence of both a light (likely S) and a heavy (likely As) neighbors around Au (Fig. 4). Work is currently in progress to model both XANES and EXAFS spectra and to obtain more representative Au-As-S-Fe reference compounds that would allow, for the first time, unambiguous identification of Au chemical and structure state in sulfide minerals.

Conclusions and perspectives. This preliminary experiment enabled first measurements of the chemical state of Au in pyrites and arsenopyrites, which are the major hosts of the metal in economic deposits. It is clear that high-resolution spectroscopy (HERFD-XAS), coupled with representative reference compounds and quantum-chemistry modeling of XANES spectra, is necessary to resolve one of the oldest metallogenic enigmas of the Au-As relationships in nature. More systematic measurements are needed both on synthetic samples and natural representative accurately characterized minerals, coupled with in situ studies of Au speciation in hydrothermal fluids that form ore deposits to reveal the role of arsenic and sulfur on Au fate in the Earth's crust.

References cited

- (1) Llorens I. et al. 2012, *Review of Scientific Instruments* **83**:063104; (2) Pokrovski G.S. & Dubrovinsky 2011, *Science* **331**:1052-1054; (3) Pokrovski G.S. & Dubessy J. 2015, *Earth & Planetary Science Letters*, **411**:298-309; (4) Pokrovski G.S. et al. 2015, *PNAS*, under revision; (5) Boiron et al., 1989, *Economic Geology* **84**:1340-1362.

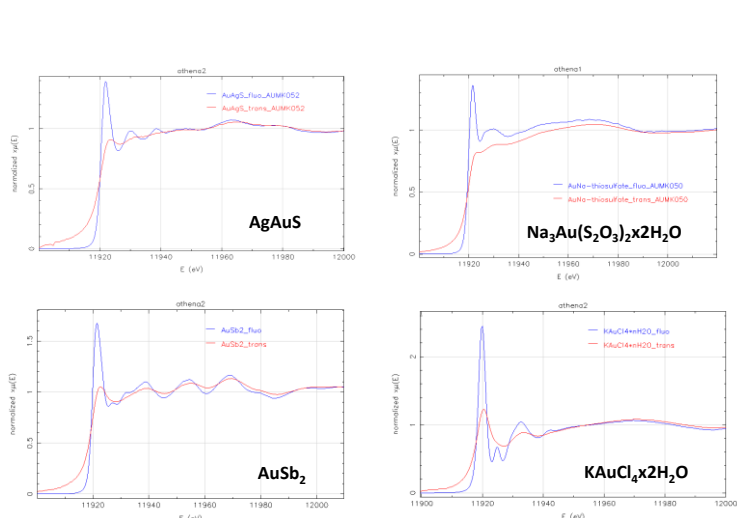


Fig. 1

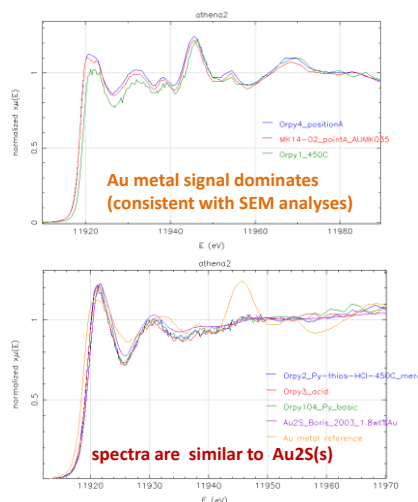


Fig. 2

Fig 1. Comparison of Au L₃-edge XANES spectra of gold reference compounds in normal (transmission, in red) and high (fluorescence, in blue) resolution mode recorded at FAME. Note significant improvement in resolution with the HERFD setup.

Fig. 2. High-resolution XANES spectra of synthetic (As-free) pyrites. Some spectra are dominated by gold metal, others by chemically bound Au, and some by a mixture of both gold states.

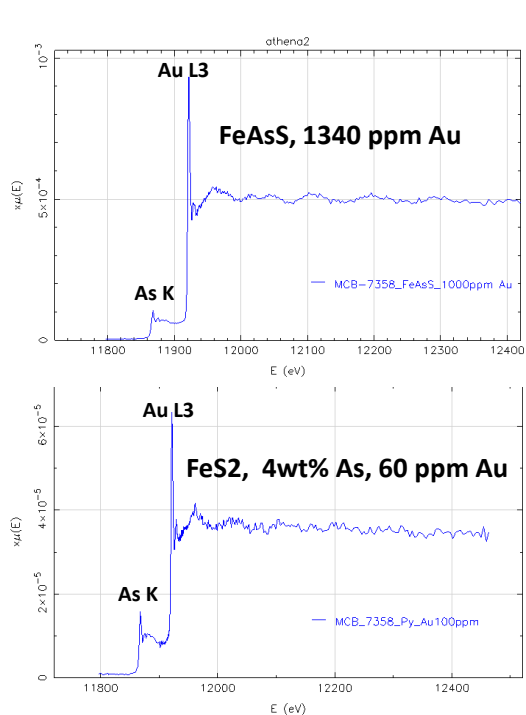


Fig. 3

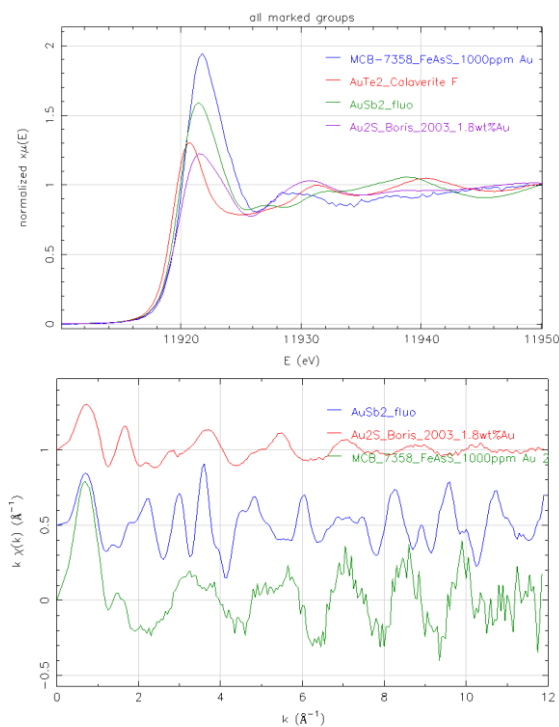


Fig. 4

Fig. 3. XANES HRFD spectra of Au-bearing pyrite and arsenopyrite. For the first time, the Au signal could be filtered from that of dominating As.

Fig. 4. Comparison of normalized HERFD XANES and EXAFS spectra of an Au-rich natural arsenopyrite with those of available reference compounds. Au in this sample is monovalent and likely to be coordinated with both S and As (work in progress).