



	<b>Experiment title:</b> Probing gold-arsenic relationships in sulfide ore minerals by high-resolution X-ray absorption spectroscopy	<b>Experiment number:</b> ES-378
<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 06 July 2016 to: 12 July 2016	<b>Date of report:</b> 31 January 2017
<b>Shifts: 18</b>	<b>Local contact(s):</b> Olivier Proux, BM30B (FAME)	<i>Received at ESRF:</i>
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## Report:

**Experimental setup and conditions.** Gold local structure in synthetic and natural arsenian pyrites  $\text{Fe}(\text{As},\text{S})_2$  and arsenopyrites  $\text{FeAsS}$  has been characterized by X-ray absorption spectroscopy (XAS) at Au  $L_3$ -edge (11,919 eV) using a recent high-resolution set-up at FAME consisting of 5 Si(110) crystal analyzers and a vortex mono-element detector (HERFD-XAS). A He bag was placed between the crystals and the detector to reduce X-ray absorption by air. Pellets of homogenized powder samples were fixed in a Cu holder kept in a liquid-helium cryostat (~10 K) and recorded in fluorescence mode. The energy resolution at the Au fluorescence line (9,712 eV) is 1.5 eV, which is at least by a factor of 5 superior to normal resolution imposed by the core-hole width, and allows for efficient filtering of the As signal and unprecedented improvement in the XANES part, revealing multiple absorption resonances that are not visible in “normal” spectra. Exploitable XANES spectra could be obtained for Au concentrations of 10s ppm, whereas EXAFS spectra (to at least  $10 \text{ \AA}^{-1}$ ) required much higher Au contents, typically 100s ppm, and long (>3-5h) acquisition times; this limitation is due to the use of a single-element detector as imposed by the geometry of the optical HERFD set-up at FAME. Only one sample can be fitted into the cryostat at the same time and changing the sample requires ~2h, which represented a significant beam time loss during the experiment.

**Results from synthetic pyrite.** The samples were synthesized either by reacting Au and As-bearing hydrothermal solution with  $\text{FeS}_2$  powder at 450°C/700 bar (Orpy and Aut series), or in a dry system Au-Fe-S-As at 600°C/1 bar (SF series). Fluorescence scans and XANES spectra unambiguously reveal the presence in most samples of two Au structural states, large metallic gold particles of 10-100  $\mu\text{m}$  and chemically bound gold. The gold particles could have been formed by precipitation during the synthesis at high temperature and/or exsolved from the pyrite structure on cooling. These large particles, which are easily identified as intense peaks on fluorescence scans across the pellet, could be efficiently avoided by positioning the beam at spots that show a constant fluorescent signal likely from by chemically bound Au (Fig. 1). The concentration of bound Au varies from 30 to 100 ppm independently of As content. XANES spectra are similar for As-free and As-bearing (up to 10 wt% As) samples (Fig. 2) and resemble those of  $\text{Au}_2\text{S}(s)$ . The absence of good exploitable EXAFS signals that would have required 10s hours of acquisition time, does not allow accurate quantification of Au-neighbor numbers and distances. Quantum-chemical modeling of XANES spectra (in progress) would provide further constraints as to whether Au is present as an isomorphic substitution in the mineral lattice (e.g., substituting for Fe or S) or as  $\text{Au}_2\text{S}$ -like clusters/nanoparticles.

**Results from natural pyrite.** An attempt was made to measure a few natural Au- and As-bearing pyrite samples from orogenic and Carlin gold deposits; however the signal-to-noise ratio in these low-Au samples allowed only qualitative recognition of the presence of both native and chemically bound Au states. XANES spectra of chemically bound Au look similar to those of the synthetic samples above, and thus do not demonstrate any significant effect of As on Au incorporation in pyrite.

**Results from synthetic Au-bearing arsenopyrite.**  $\text{FeAsS}$  samples were synthesized similarly to the pyrites, in three different systems all with an excess of metallic gold: NaCl or NaOH aqueous solution with  $\text{Fe}_2\text{O}_3+\text{As}+\text{S}$  at 450°C/700 bar (Aspy series); NaCl-HCl aqueous solutions with  $\text{FeS}+\text{As}+\text{S}$  at 450°C/700 bar (Aut series); and dry system  $\text{Fe}+\text{As}+\text{S}$  at 600°C/1 bar (SF series). Although all samples exhibit the presence of a few Au metal particles (that cannot be ground) as shown by fluorescence profiles and XANES spectra (Fig. 1), the bound Au also represents a significant part, with concentrations ranging from ~50 ppm (samples Aut and SF) to ~1500 ppm (samples Aspy, where Au in the fluid was highly soluble as HS- and  $\text{S}_3$ -complexes). Surprisingly, XANES and EXAFS (where available) spectra of bound Au in all samples are very similar (Fig. 2), suggesting the same structural environment despite the wide range of formation conditions. EXAFS fits for Au-richest samples (>500 ppm) indicate an As-dominant environment around Au (4-6 As atoms at 2.5  $\text{\AA}$ ) with possible presence of S (<2 atoms at 2.3  $\text{\AA}$ ) and Fe and As in next-nearest shells. These structures would be consistent with Au entering As-enriched and S-depleted Fe sites (e.g.,  $(\text{Fe},\text{Au})\text{As}_5\text{S}_1$  vs normal crystallographic site  $(\text{Fe},\text{Au})\text{As}_3\text{S}_3$ ) of arsenopyrite or  $\text{FeAs}_2$ -like nano-domains resembling a loellingite structure  $((\text{Fe},\text{Au})\text{As}_6)$ .

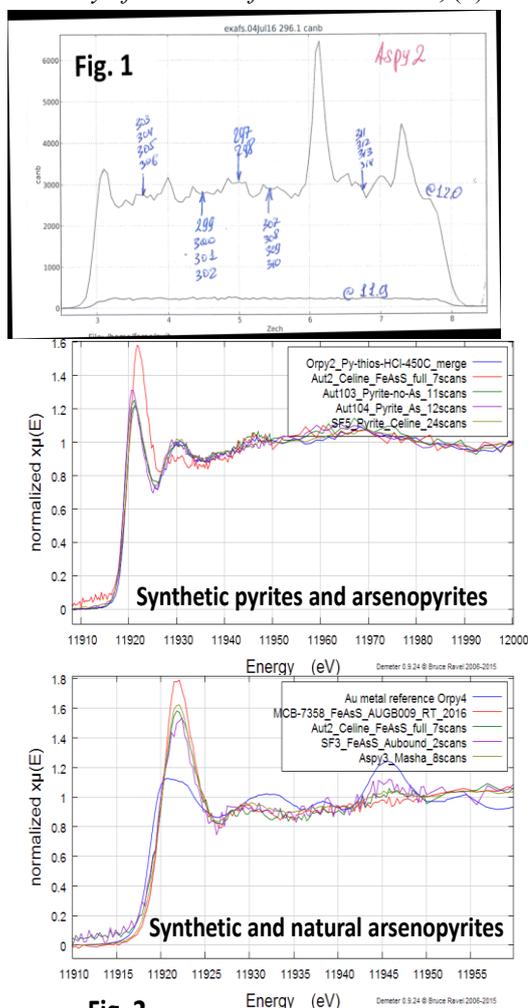
**Results from natural Au-bearing arsenopyrite.** Several samples from orogenic gold deposits were examined, but only one (MCB\_7358, with ~350 ppm Au) from the Villeranges deposit (Massif Central, France) had a sufficient signal-to-noise ratio allowing acquisition of decent XANES and EXAFS spectra (Fig. 3). These spectra are generally similar to those of synthetic arsenopyrites (with some minor differences), and are likely to be consistent with an As-rich and S-poor nearest atomic environment for Au ((Fe,Au)As<sub>6-4</sub>S<sub>0-2</sub>) in this natural sample that possesses exclusively chemically bound gold as shown by Mossbauer spectroscopy. Nevertheless, the presence of elements other than As (e.g., Te, Se, Sb, Cu, Ni) in the nearest or next-nearest Au shells cannot be fully excluded at this stage and awaits further chemical analyses (LA-ICPMS, TEM) and detailed XANES modelling using the FDMNES code (in progress). Notably, other natural arsenopyrites (MW15 and JM03) that contain far less Au, also have quite similar XANES spectra suggesting that chemically bound Au has a similar molecular environment in arsenopyrites from different geological settings (Fig. 3).

**Conclusions and perspectives.** This exploratory experiment allowed estimation of detection/acquisition limits for Au in As-rich samples using the HERFD device at FAME, which will be important for future experiments and beamline developments. Exploitable XANES spectra limits are ~100 and 10 ppm of Au for arsenopyrite (~40 wt% As) and pyrite (<10 wt% As), respectively, whereas exploitable EXAFS spectra for Au concentrations of 100 ppm would require typically ~10 hours of acquisition time (depending on As concentration). It is expected that the new HR-FAME beamline (BM16) will offer a significant improvement both in fluorescence signal intensity and spatial resolution (micro beam) that would allow far more sensitive analyses of often heterogeneous natural samples at typically lower Au concentrations (ppm-level), typical for most natural samples. The present experiment has paved a way towards such near-future studies.

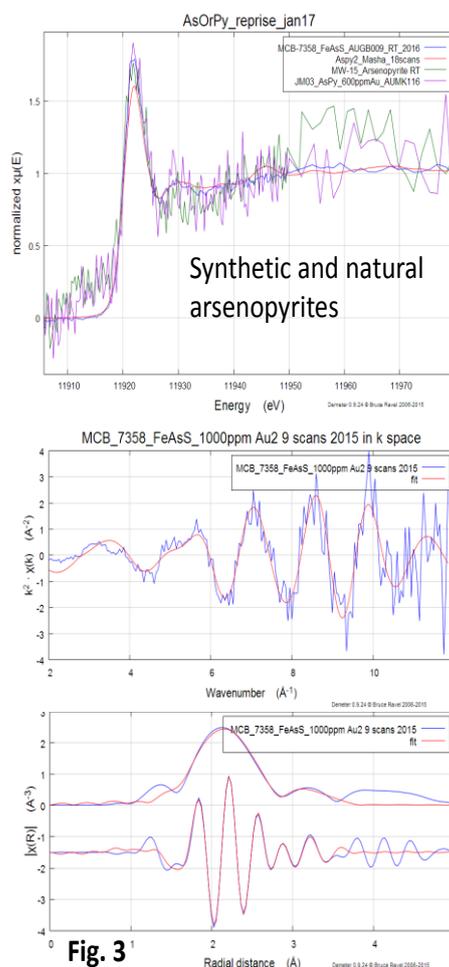
Furthermore, this study enabled first measurement of the chemical state of Au in As-pyrites and arsenopyrites, which are the major hosts of the metal in deposits. It is clear that high-resolution spectroscopy (HERFD-XAS), coupled with representative reference compounds and quantum-chemistry modeling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

### References cited

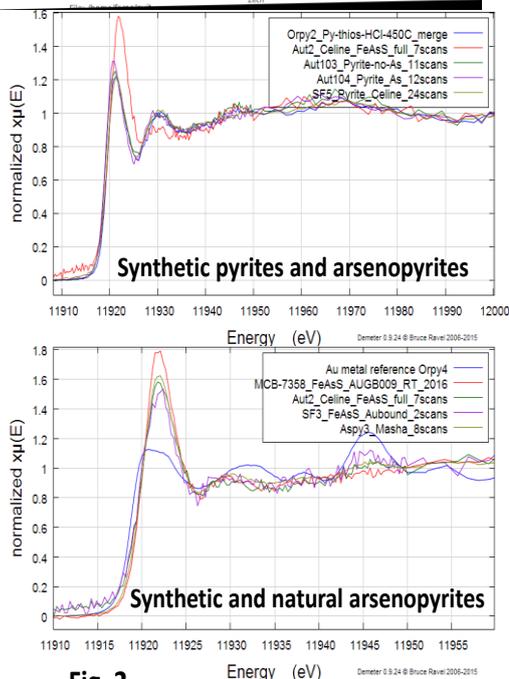
(1) Llorens I. et al. 2012, *Review of Scientific Instruments* **83**:063104; (2) Pokrovski G.S. et al. 2015, *Proceedings of the National Academy of Sciences of USA* **112**:13484; (3) Boiron et al. 1989, *Economic Geology* **84**:1340-1362.



**Fig. 1.** Fluorescence signal profile at 12.0 and 11.9 keV across an arsenopyrite pellet. Beam position for indicated scan numbers is shown by the arrows. Note several peaks from large Au particles.



**Fig 2.** HERFD Au L<sub>3</sub>-edge XANES spectra of synthetic and natural pyrites and arsenopyrites. Note the similarity of the spectra of bound Au within each mineral sample series independently of the synthesis conditions (see text), but significant differences between the two minerals.



**Fig. 3.** HERFD XANES spectra and EXAFS spectra and their fits of natural Au-bearing arsenopyrites from gold deposits. In all these samples, Au is in a chemically bound state (Au<sup>+</sup>) likely entering Fe sites of As-rich clusters or nano-domains (Au,Fe)As<sub>4-6</sub>S<sub>2-0</sub> of the arsenopyrite structure, but modeling of XANES spectra will be required (work in progress).