

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> A XAS study of chemical state of gold in the Cu-Au-S system	<b>Experiment number:</b> ES 184
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 29.10. 2014 to: 04.11. 2014	<b>Date of report:</b> 27.02.2015
<b>Shifts:</b> 18	<b>Local contact(s):</b> Sara Lafuerza	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): * <b>Kristina Kvashnina</b> & * <b>Sara Lafuerza</b> , ESRF, Grenoble * <b>Dmitry Chareev</b> Institute of Experimental Mineralogy RAS, Chernogolovka, Russia * <b>Andrei Shiryaev</b> Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia * <b>Boris Tagirov</b> Institute of Geology of Ore Deposits RAS, Moscow, Russia		

### Report:

**Experimental.** The aim of the experiment was to study the local structure of Au in synthetic Cu sulfides – analogues of natural minerals. Four experimental series were performed:

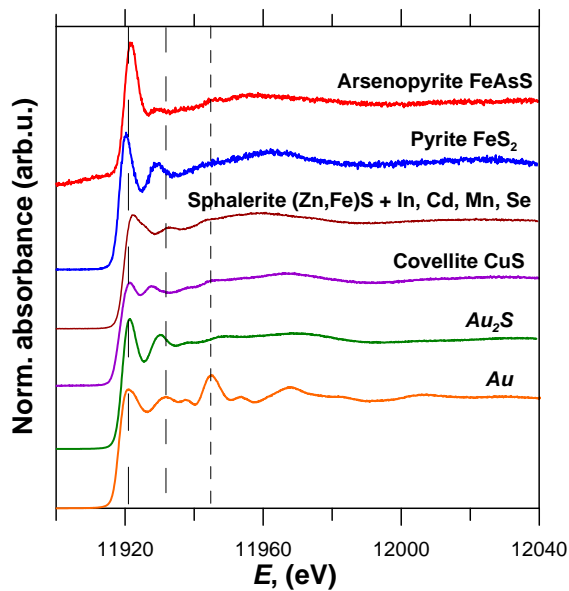
1) The Au L<sub>3</sub> and L<sub>2</sub> High energy fluorescence detection (HERFD) and Total fluorescence yield (TFY) XAFS spectra were recorded at ambient temperature for all compounds in the systems Ag-Au-S, Ag-Au-Te, Ag-Au-Se, Au-Sb, and Au-Pb. The spectra of these phases are used as standards for interpretation of the HERFD XAFS spectra of ‘invisible’ (submicroscopic) Au in sulfides, and to determine the Au 5d unoccupied density of states as a function of the composition of sulfide.

2) The Au L<sub>3</sub> HREFD XAFS spectra were recorded for samples of hydrothermal Covellite (CuS) containing from 300 to 3000 ppm (0.03 - 0.3 Wt. %) of Au in ‘invisible’ state, and for 2 types of Pyrites (FeS): high temperature well crystallized, obtained with salt-flux technique at 540 °C, and several samples of hydrothermal fine-grained aggregates of Pyrite, synthesized at different f(O<sub>2</sub>)-f(S<sub>2</sub>) conditions at 450 °C, 1 kbar (concentration of Au falls within 20-100 ppm for all the samples). In order to determine the effect of composition and crystalline structure of sulfide mineral on the chemical state of gold, the Au L<sub>3</sub> spectra were also recorded for several samples of synthetic Au-bearing Sphalerites (Zn,Fe)S and Arsenopyrites FeAsS.

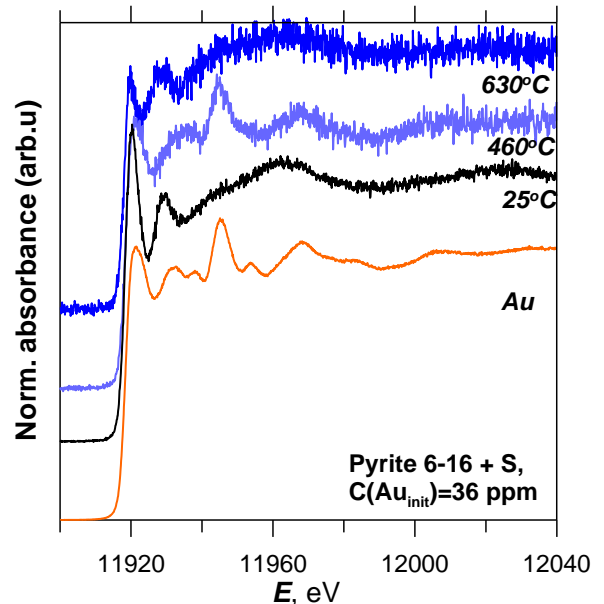
3) *Heating experiments* were performed with samples of Au-bearing Digenite (Cu<sub>1.72</sub>S+1.5 Wt.% Au), Covellite (CuS + 0.25 Wt.% Au), Intermediate solid solution (ISS, Cu<sub>1.65</sub>Fe<sub>0.69</sub>Au<sub>0.06</sub>S<sub>2.60</sub>), and pyrite (FeS<sub>2</sub>, 36 ppm of Au). Powdered samples were hermetically sealed in the silica glass capillaries (Polymicro Technologies), and heated with the aid of electrical furnace available at ESRF. This simple experimental technique was developed for Raman spectroscopic studies of solids and liquids (Chou et al., 2008), but for synchrotron experiment we used it for the first time.

4) The Cu K HREFD XAS and Kβ<sub>2,5</sub> XES spectra were recorded for samples of synthetic covellites, digenites, and standards including Cu oxides, chloride and oxalate with different oxidation degree of Cu.

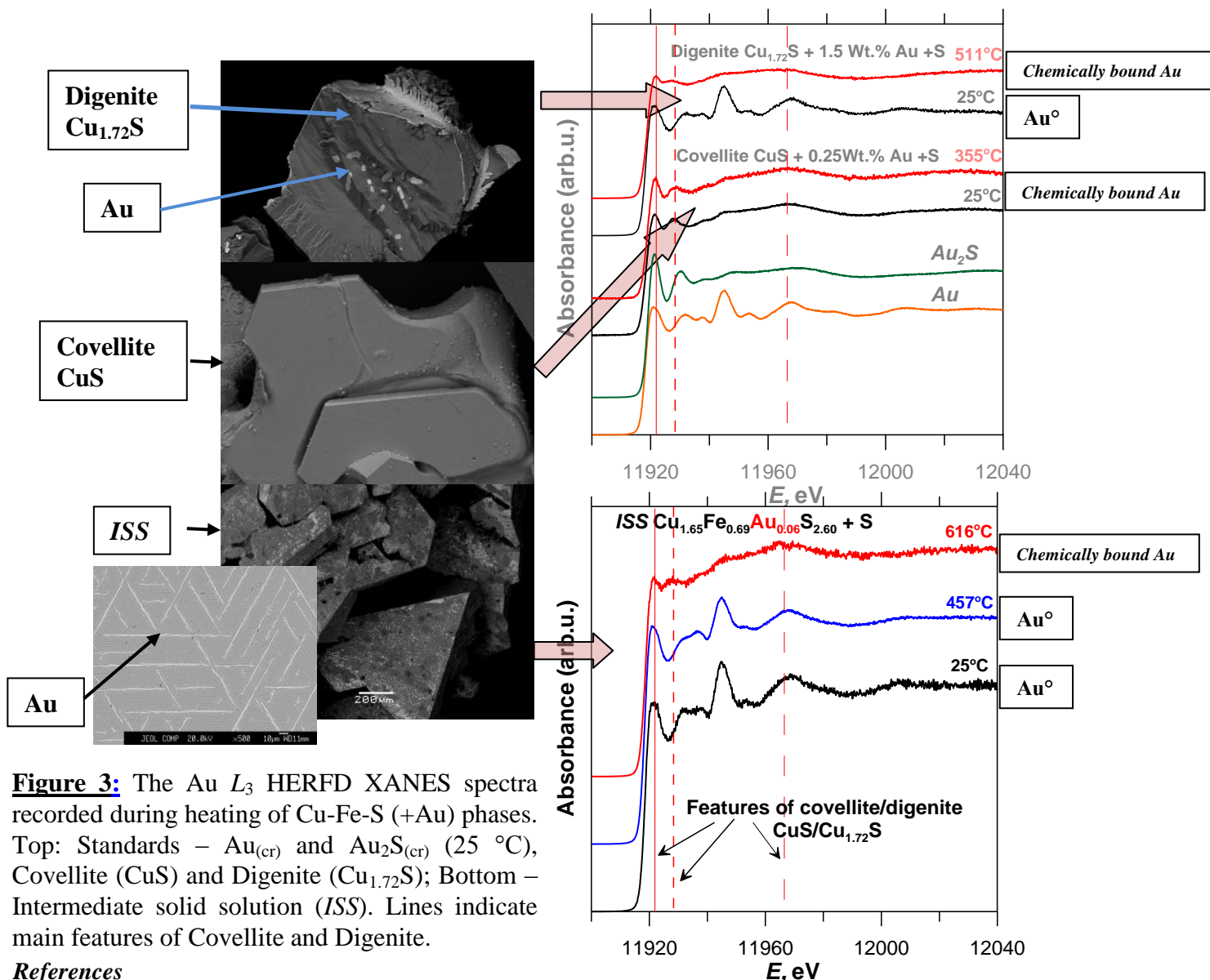
**Results.** It was shown that the Au L<sub>3</sub> spectra for the «invisible» gold in Covellite CuS, hydrothermal Pyrite FeS<sub>2</sub>, Arsenopyrite FeAsS, and Sphalerite (Zn,Fe)S differ from those of metallic Au and Au<sub>2</sub>S, as well as from the spectra of other Au and Au-Ag chalcogenides used as references (Fig. 1). Moreover, position and intensity of main features depend upon the sulfide composition. The white line (WL) intensity increases in the order CuS-(Zn,Fe)S-FeS<sub>2</sub>-FeAsS corresponding to the increase of the 5d unoccupied density of states at the Au site. The chemical state of Au in Pyrite depends on the formation conditions (or the synthesis method): fine-grained hydrothermal pyrite contains chemically bound Au due to the presence of domains of Au-bearing Tochillinite (Fe<sub>4</sub>S<sub>5</sub> with layered structure, presence of these mineral domains enriched in Au is confirmed by FEFF calculations), whereas well crystallized large grains of pyrite contain metallic Au. Heating experiments further revealed difference in the chemical state of Au (Fig. 2, 3): heating of Pyrite resulted in segregation of metallic Au even in the presence of S<sub>(l)</sub> (probably due to disappearance of Tochillinite which is not stable at high temperature), whereas for Cu and Cu-Fe sulfides increase of temperature promoted the formation of Au-bearing solid solution. The experimental data reduction is now in progress.



**Figure 1:** Au  $L_3$  HERFD XAS spectra for “invisible” Au in base metal sulfides recorded at 25 °C. Spectra of metallic Au and  $Au_2S_{(cr)}$  are given for comparison. Vertical lines show 3 main features of metallic Au.



**Figure 2:** Spectra recorded during heating of gold-bearing hydrothermal Pyrite  $FeS_2$  (Au concentration decreased with increasing temperature, at 630 °C  $C(Au) \sim 1$  ppm).



**Figure 3:** The Au  $L_3$  HERFD XANES spectra recorded during heating of Cu-Fe-S (+Au) phases. Top: Standards –  $Au_{(cr)}$  and  $Au_2S_{(cr)}$  (25 °C), Covellite ( $CuS$ ) and Digenite ( $Cu_{1.72}S$ ); Bottom – Intermediate solid solution (*ISS*). Lines indicate main features of Covellite and Digenite.

#### References

Chou I-M., Song Y. and Burruss R. C. (2008) A new method for synthesizing fluid inclusions in fused silica capillaries containing organic and inorganic material. *Geochim. Cosmochim. Acta* 72, 5217-5231.