ESRF	**Experiment title:** A XAFS spectroscopy study of local environment around gold in high T/P aqueous sulfide and chloride solutions: Implications for the mechanisms of gold deposits formation	**Experiment number**: 30 02 639
Beamline: BM30B	**Date of experiment**: from: 3 November 2003 to: 11 November 2003	**Date of report**: 5 August 2004
Shifts: 21	**Local contact(s)**: Jean-Louis Hazemann, BM30B (FAME), ESRF	*Received at ESRF:*

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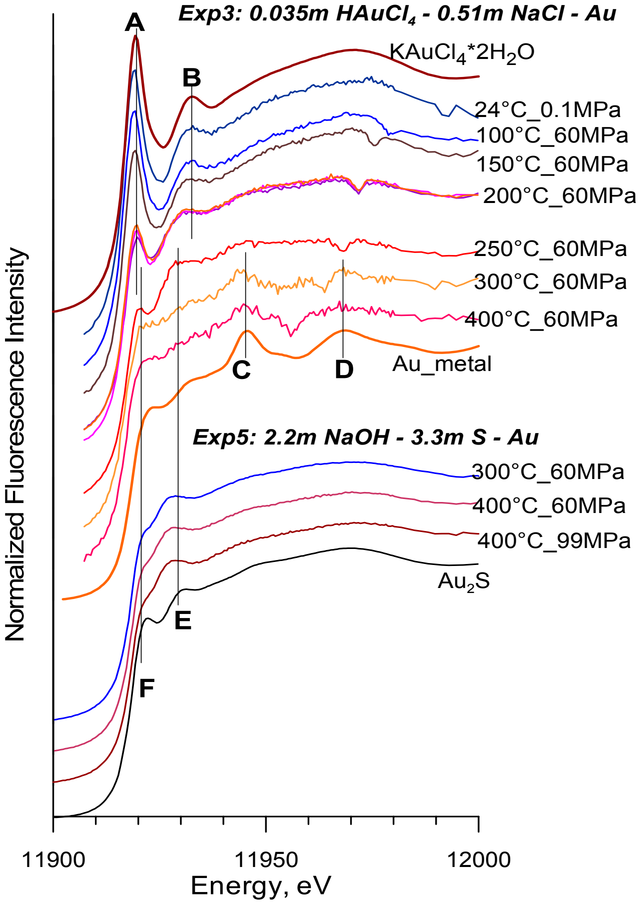
Report:

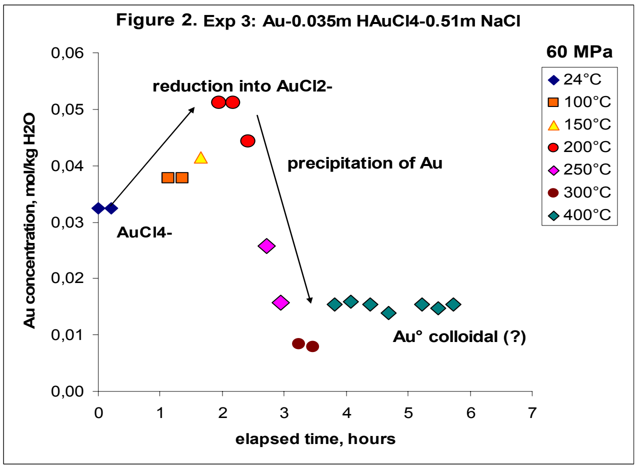
Experimental. The dissolution and atomic structure of gold in chloride and sulfide aqueous solutions were examined by XAFS spectroscopy at Au L_3-edge at temperatures to 400°C and pressures to 100 MPa, using an X-ray cell recently developed at the Laboratoire de Cristallographie (Grenoble). This cell allows simultaneous measurement of the absolute concentration of the absorbing element in the fluid (from edge-step height in transmission mode, fluid density and absorption cross-section of the element), and atomic environment around the absorber (from analysis of XANES and EXAFS spectra in fluorescence mode). Details about the cell operation and spectra analysis can be found in refs. 1 & 2. An improved cell design used for the present experiment utilizes a piston equipped with Viton joints and inserted into a thin-wall mono-crystalline sapphire tube. This construction avoids solutes precipitation in the colder parts of the cell. Unfortunately, multiple diffraction peaks arising from the mono-crystalline sapphire made impossible analysis of the EXAFS part of most spectra. Consequently, only gold total concentration and near-edge structure (XANES) could be accurately accessed.

Results on the gold-chloride system. Four experiments were performed in the system $HAu^{(III)}Cl_4$-NaCl-HCl±Au(metal) at 60 MPa as a function of temperature and time. It was found that below 200°C, the XANES spectra of Au in solution exhibit a strong before-edge feature (Fig. 1, A) corresponding to 2p-5d electronic transitions characteristic of tri-valent Au in the plane square $Au^{(III)}Cl_4^-$ complex reported in previous low-temperature XAFS and Raman studies[3,4]. At 200°C, this feature rapidly disappears indicating a reduction of this species, presumably into $Au^{(I)}Cl_2^-$ (ref. 4, 5). However, at higher temperature, the absorption-edge height shows rapid gold precipitation (Fig. 2). XANES spectra above 250°C display features characteristic of metallic gold (Fig. 1). It is not clear whether some gold still remains in solution in the form of Au° colloids or precipitated on the cell walls on the passage of the X-ray beam. The very narrow temporal and temperature interval of the Au(I) appearance in solution (Fig. 1 & 2) contradicts to the previous batch-reactor solubility studies which indicate that above 250°C, $AuCl_2^-$ should be the dominant species, and attain concentrations ~10 times higher than measured in our experiments [4,5]. This discrepancy might be attributed to a leak of oxygen through the Viton seals or reaction with these seals, thus destabilizing Au(I) chloride species in favor of metallic gold. Another possibility could be the beam-induced reduction of $AuCl_2^-$ into Au° (ref. 3).

Results on the gold-sulfide system. An experiment was performed in the system Au-NaOH-S by allowing a foil of metallic gold and sulfur crystals to react with a NaOH aqueous solution at elevated temperature. The complete dissolution of sulfur occurs above 100°C and produces sulfide (H_2S, HS^-) and sulfate (HSO_4^-, SO_4^{2-}) species. Fig. 3 shows that at 300°C and 60 MPa, gold rapidly dissolves, resulting in a spectrum similar to that of Au_2S (Fig. 1) and $Na_3Au(S_2O_3)_2$ (not shown) in which $Au^{(I)}$ is linearly coordinated by two sulfur atoms. This indicates that dissolved Au(I) is likely to be surrounded by two sulfide ligands in this solution by forming $Au(HS)_2^-$, as was suggested by solubility studies (c.f. ref. 6). Au concentrations attain a steady-state after about 4 hours of dissolution at 300°C (Fig. 3). At 400°C, however, a regular drop of Au concentration with time is observed. The before-edge absorption in transmission mode also shows a significant decrease which can be attributed to a loss of sulfur (the major contributor to the absorption below the Au L_3 edge in this solution). This could be due to a leak of the volatile and reactive H_2S through the Viton seals out of the cell. Nevertheless, such a leak does not occur at T≤300°C, and the absorption edge heights measured at steady-state at 300°C/60 MPa allow determination of Au concentration in solution in equilibrium with metallic gold: 0.091±0.020 mol/kg H_2O (pH=6.1, $m(HS^-)=0.4$, $m(H_2S)=1.5$, $m(SO_4^{2-})=0.8$). This value is in agreement with that predicted using the thermodynamic properties of $Au(HS)_2$- obtained from our recent batch-reactor solubility study (ref.7): m(Au)=0.27±0.15.

Figure 1





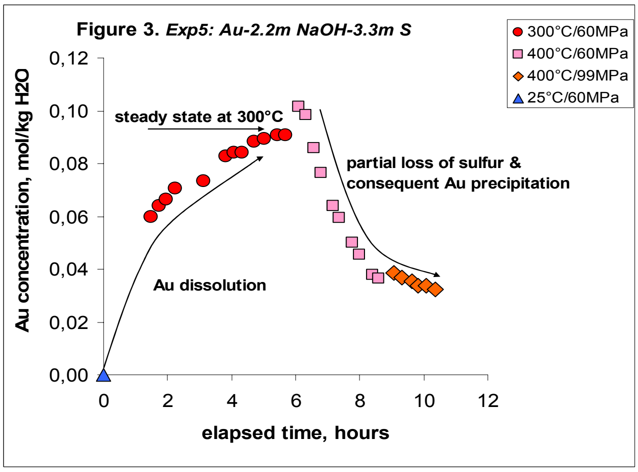


Fig. 1. Normalized near-edge fluorescence spectra of Au-bearing solids and experimental solutions at indicated conditions (concentrations are in molalities). Vertical lines show XANES features characteristic of the square $Au(III)Cl_4$ cluster (A & B), metallic gold (C & D), and linear $Au(I)S_2$ and $Au(I)Cl_2$ (E & F) configurations.

Fig. 2 & 3. Total dissolved concentration of gold as a function of time and temperature for the experiments in the systems $HAuCl_4$-NaCl-Au (Fig. 2) and Au-NaOH-S (Fig. 3) shown in Fig. 1.

Conclusions & perspectives. To our knowledge, this experiment is the first measurement of gold solubility and structure of Au(I) chloride and sulfide complexes at hydrothermal conditions using *in situ* XAFS spectroscopy. Our results demonstate the feasability of XAFS measurements of this extremely inert and weakly soluble noble metal. They bring the first undoubted spectroscopic evidence that, at least to 400°C, 1 kbar, Au(I) forms in sulfide bearing solutions linear complexes in which it is coordinated to 2 HS ligands. The ultimate goal of our future experiments will be to access, via EXAFS spectra, quantitative structural parameters of the $Au^{(I)}$ complexes dominant in natural ore-forming fluids, and to measure Au solubilities over a wide range of magmatic-hydrothermal conditions. This will be achieved using an improved cell construction (polycristalline sapphire avoiding diffraction, high-temperature joints with improved seal properties), and the high X-ray flux and sensitive detection provided by FAME or ID26 beamlines at the ESRF.

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