	Experiment title: **The effect of polysulfides on gold transport by hydrothermal ore-forming fluids**	**Experiment number**: EC-1092
Beamline: BM30B	**Date of experiment**: from: 13 February 2013 to: 19 February 2013	**Date of report**: 8 April 2013
Shifts: 18	**Local contact(s)**: Jean-Louis Hazemann, BM30B (FAME)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
***Maria Kokh,** ***Damien Guillaume**, ***Gleb Pokrovski** (GET, Toulouse); ***Jean-Louis Hazemann** (Institut Néel, Grenoble)

Report:

    Experimental. The solubility and molecular structure of gold in sulfur-bearing aqueous solutions were examined by X-ray absorption spectroscopy (XAS) at Au L$_3$-edge (11,919 eV) both in transmission and fluorescence mode with a Si(220) double crystal monochromator, at temperatures (T) from 200 to 450°C and pressures (P) 600 bar, using the FAME high T-P cell that enables simultaneous measurement of the total dissolved Au concentration, and its atomic environment in the fluid [1,2]. The source of sulfur in experiments was elemental S or (K,Na)$_2$S$_2$O$_3$ whose dissolution in H$_2$O(±HCl, ±NaOH) at $T > 200$°C yields sulfate (HSO$_4^-$ and SO$_4^{2-}$), sulfide (H$_2$S and HS$^-$) and trisulfur ion (S$_3^-$) as the major S aqueous forms whose concentrations may be accurately quantified using the thermodynamic properties of these species and recent in situ Raman spectroscopy measurements in similar systems [3,4,5]. Six experiments were performed with total S concentration (S$_{tot}$) of 0.5-2.0 mol/kg fluid (m) and pH 3-8. The choice of the experimental conditions was to maximize the concentration of S$_3^-$ in the system to elucidate its effect of Au solubility and speciation.

    Results from solubility measurements. At temperatures 200-250°C, at which S$_3^-$ is minor (< 0.01m), measured Au dissolved concentrations are in excellent agreement with equilibrium calculations of Au solubility using the well-constrained thermodynamic properties of the famous Au(HS)$_2^-$ ion (Fig. 1), which has been believed, over more than 40 years, to be by far the major career of Au in hydrothermal fluids [6,7]. By contrast, at T of 300-450°C, at which S$_3^-$ becomes increasingly abundant (up to ~0.3m), measured Au solubilities are at 1 to 2 orders of magnitude higher than those calculated assuming Au(HS)$_2^-$ (Fig. 1). This difference clearly demonstrates the predominance of other gold species in these solutions, very likely with S$_3^-$. If S$_3^-$ does not complex Au in such fluids, who does?

    Results from EXAFS spectra. The spectra are identical for all S-bearing solutions at all temperatures, whatever the sulfur speciation or Au solubility (Fig. 2). Modeling shows 2 sulfur atoms at 2.29±0.01 Å around Au, arranged in a linear geometry as revealed by characteristic MS features. Neither oxygen atoms (> 0.2 atom) in the Au 1st shell, nor 2nd shell neighbors (e.g., O, S) that may belong to water molecules or S$_3^-$ ligands, could be detected. This is in agreement with previous studies of Au in its S-bearing solids and solutions [2]. The linear structures of S-Au-S aqueous complexes are consistent with general gold structural chemistry [6]. This important constraint suggests that all mono-ligand complexes presumed for Au in aqueous solution (e.g., H$_2$OAuSH, AuS$_3^-$, etc.) are negligible in our systems.

    Results from XANES spectra. XANES spectra of the studied solutions confirm these findings; they clearly show Au to be in the monovalent state (Au^{1+}), in a linear geometry with two S ligands based on comparisons with reference compounds. Only very minor spectral differences could be detected between solutions where Au is in the form of Au(HS)$_2^-$ and those where Au is presumably bound to S$_3^-$ (shown by the arrows in Fig. 3). The weak spectral contrast amongst the different S-bearing aqueous species and crystalline solids of gold is a typical feature of Au(I) XANES at the L$_{III}$ edge acquired at normal resolution [2]. Because of the absence of specific model compounds of Au with HS$^-$ and S$_3^-$ ligands similar to those in aqueous solution, these small differences cannot be unambiguously assigned to a certain complex (the complexes shown in Fig. 3 are thus tentative and were suggested on the basic of thermodynamic modeling below).

    Results from thermodynamic modeling. The ensemble of Au solubility data points, coupled with additional constraints on complex structure and stoichiometry from EXAFS and XANES, allowed establishing, for the first time, the nature and stability of possible Au complexes with S$_3^-$. This was achieved using the OptimaA computer program [8] by testing how well different Au complexes of variable stoichiometry and electrical charge (see Fig. 3) describe the measured solubilities. In these calculations, the standard Gibbs free energy of each complex at given T and P (G$_{i,T,P}$) was varied to match the measured solubilities. The least variation of the G$_{i,T,P}$ value of a complex or a group of complexes (up to 3) at a given T over the experimental S$_{tot}$, S$_3^-$ and pH range means that this complex (or complexes) is the most probable candidate. In this analysis, only Au(I) complexes containing two H$_2$S/HS$^-$ and/or S$_3^-$ ligands as constrained by EXAFS and XANES data, were considered. The statistically best solubility description with the minimal variation in G$_{i,T,P}$ values was achieved with [HS-Au-S$_3$]$^-$ and/or [HS-Au-S$_3$H] in acidic (pH≤5) and with [HS-

Au-S$_3$]$^{2-}$ in neutral (5<pH<8) solutions. Work is currently in progress to refine these analyses and to provide a robust set of stability constants for these new species.

Conclusions & perspectives. This experiment yielded the first quantitative measurement of Au^I-S$_3^-$ species structure and stability in S-rich solutions typical of porphyry Cu-Au-Mo and orogenic Au deposits. Our findings shift the long-standing paradigm that hydrogen sulfide (H$_2$S/HS$^-$) is the only career of Au in hydrothermal fluids. The new species discovered in this study will require a revision of gold ore-deposit models, and also may have important implications in Au ore treatment and purification. High-resolution spectroscopy (HERFD-XANES) coupled with molecular dynamics modelling will enable a more robust determination of the exact complex stoichiometry, which is the primary requisite for using these data in modeling of Au transport and deposition across the Earth's crust conditions.

References cited

[1] Testemale D. et al. 2005, Rev. Sci. Instrum. 76, 043905-043909; [2] Pokrovski G.S. et al. 2009, Geochim. Cosmochim. Acta 73, 5406-5427; [3] Pokrovski G.S. & Dubrovinsky 2011, Science 331, 1052-1054; [4] Jacquemet N. et al. 2014. Amer. Mineralogist, in press; [5] Pokrovski G.S. & Dubessy J., 2014. Earth & Planet. Sci. Lett., submitted; [6] Pokrovski et al. 2014, Geological Society of London Special Publications 402, http://dx.doi.org/10.1144/SP402.4, in press; [7] Akinfiev N.N. & Zotov A.V. 2010, Geochemistry International 48, 714–720; [8] Shvarov Y.V. 2010, OptimA: a program for optimization of standard Gibbs free energies of aqueous complexes from experimental data, (http://www.geol.msu.ru/deps/geochems/soft/index_e.htm).
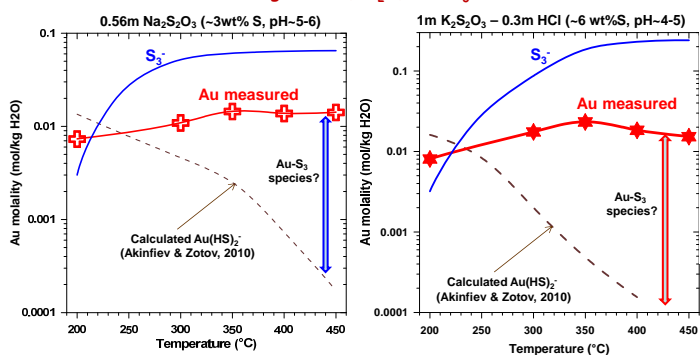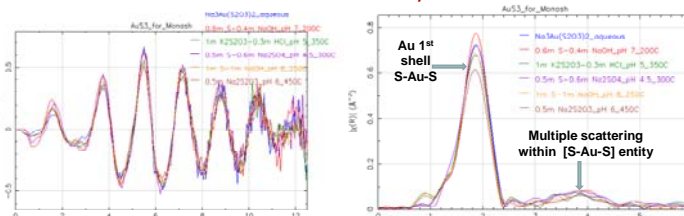
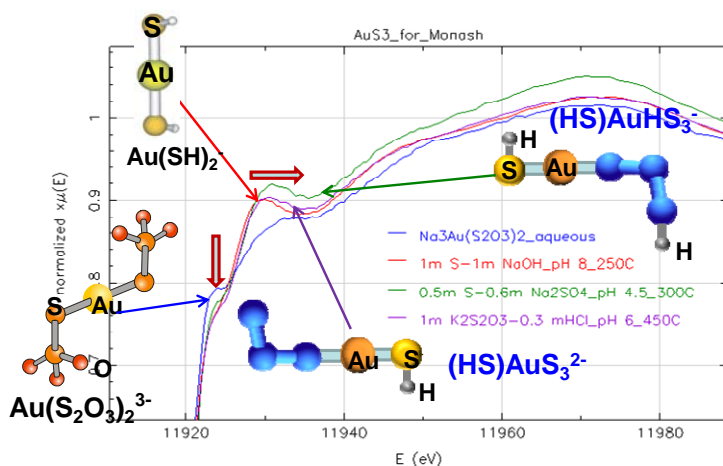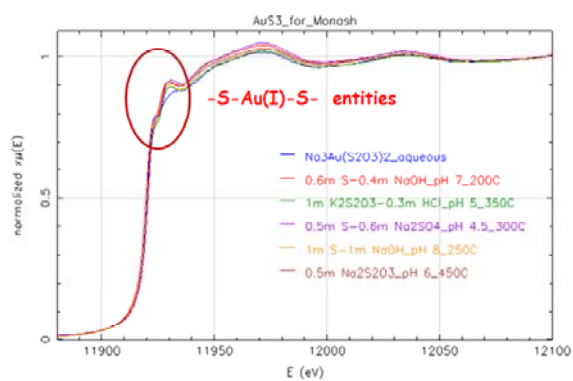**Fig. 1.** Solubility of Au in S$_3^-$ bearing solutions at indicated *T* and compositions and its comparison with predicted solubilities using the thermodynamic properties of the Au(HS)$_2^-$ complex [6,7]. Concentrations of S$_3^-$ calculated according to the stability constants of [5] are shown by the blue curves.

Fig. 2. Normalized k^2-weighted EXAFS spectra of Au in various S-bearing solutions and their corresponding Fourier Transform magnitudes, and the possible Au-S aqueous species inferred from the obtained structural parameters.

Fig. 3 Normalized XANES spectra of Au in the same solutions and a zoom on the spectral differences (the red-blue arrows), which might correspond to the tentative dominant species shown in the figure.