



	Experiment title: The role of sulfide (H₂S) and sulfite (SO₂) ligands in the fate of gold in crustal fluids: Insights from in-situ XAFS spectroscopy	Experiment number: MA 324
Beamline: BM30B	Date of experiment: from: 21 Feb 2007 to: 27 Feb 2007	Date of report: 8 August 2007
Shifts: 18	Local contact(s): Jean-Louis Hazemann, BM30B (FAME), ESRF	<i>Received at ESRF:</i>
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Report:

Experimental. The dissolution and atomic structure of gold in chloride, sulfide and sulfate aqueous solutions were examined by XAFS spectroscopy at Au L₃-edge at temperatures from 250 to 500°C and pressures 600 bar, using a recently developed X-ray cell, which allows simultaneous measurement of the absolute concentration of the absorbing element in the fluid, and atomic environment around the absorber [1,2]. An improved internal cell design used in the present experiment utilizes two mobile pistons equipped with Viton joints and inserted into a glassy-carbon or polycrystalline-sapphire tube [3].

Results from the chloride system. One experiment was performed in the system Au(metal)-0.03m HAu^(III)Cl₄-0.5m NaCl-0.5m HCl at 22 and 250°C as a function of time and using a sapphire-tube cell. At ambient temperature, the XAFS spectra are fully consistent with the plane-square Au^(III)Cl₄⁻ complex with Au-Cl distances of 2.28±0.01 Å, in agreement with previous low-temperature XAFS and Raman studies [4,5]. At 250°C, there has been a rapid (within ~10 min) reduction of Au^{III} to Au^I followed by a regular decrease of Au total solution concentration without changing Au local structure during at least few hours of experiment. The EXAFS spectra are well modeled by the linear AuCl₂⁻ species (R_{Au-Cl}=2.26±0.01 Å, N_{Cl} = 1.7±0.3). To our knowledge, this is the first report of the structure of the Au^I chloride complex dominant in acidic Cl-rich natural fluids. However, our measured Au aqueous contents were 5-10 times lower than those reported from batch-reactor solubility measurements in this system [6] and thermodynamic calculations [7]. The lower and systematically decreasing AuCl₂⁻ concentrations in our XAFS experiment at 250°C might be attributed to the beam-induced reduction of AuCl₂⁻ to Au⁰ (e.g. [4]).

Results from the chloride-sulfate system. Three experiments were performed in the system Au(metal)-0.5m H₂SO₄-2m NaCl from 300 to 500°C at 600 bar using a glassy-carbon cell. The dominant Au complexing ligands in this system according to the available thermodynamics are Cl⁻ [7] and, potentially, SO₂. Gold concentrations measured in these experiments (10⁻⁵-10⁻³ m) were too low to yield exploitable EXAFS spectra. Only the XANES part could be examined and was found to be similar to that of the AuCl₂⁻ species above (Fig. 1), in agreement with thermodynamic predictions. However, our measured concentrations were 2 orders of magnitude lower than the calculated contents. This discrepancy is likely to be explained by the presence of glassy carbon generating more reducing conditions than those predicted by calculations and which are unfavorable for gold metal solubility. An odor of H₂S after these runs likely confirms this hypothesis. Thus, these experiments provide no evidence of Au^I complexes other than chlorides in acidic salt-rich oxidizing high-temperature fluids.

Results from the sulfur-sulfate system. Three experiments were performed in the system Au-0.6m S-H₂O and two in the system Au-0.6m S-0.5m Na₂SO₄ corresponding to calculated solution pH values of 2-3 and 4-5, respectively. Thermodynamic calculations indicate that the dominant S species in these systems above 300°C are H₂S (50-70% of total dissolved sulfur), SO₂ (~10-20%), and HSO₄⁻ (~10-20%), with SO₂ decreasing with increasing pH. In addition, minor amounts (<10%) of S⁰(aq), polysulfides (H_{0.2}S_n) and thiosulfates (H_{0.2}S₂O₃) have been reported in the S-H₂O system [8], but their amount and stability remain poorly quantified.

Gold solubilities derived in our experiments from the absorption edge jump increase with increasing pH. In the S-Na₂SO₄ solutions, the calculated Au contents (~2×10⁻⁴ - 10⁻³m) are 2-5 times higher than those predicted using the available thermodynamic properties of the major Au sulfide complexes, AuHS⁰ and Au(HS)₂⁻, reported in many batch-reactor solubility studies. In the S-H₂O system, measured Au concentrations are close to the detection limit of the X-ray absorption technique (10⁻⁴m) and are poorly reproducible in different runs exhibiting variations up to 2-3 times the value. Nevertheless, even within such limits, they are systematically higher, at least by an order of magnitude, than those calculated using the available stability constants of AuHS⁰ [7]. This might indicate the predominance of other species, like the neutral bi-sulfide AuHS(H₂S)⁰ reported in a single solubility study [9].

Fluorescence spectra recorded in our experiments are well modeled by complexes having linear S-Au-S units with 2±0.5 S atoms at 2.29±0.01 Å from Au; these values are very similar to those found in neutral S-NaOH solutions where Au(HS)₂⁻ is by far the dominant species [10]. In addition, EXAFS modeling of the 2nd shell spectral features in

the S-H₂O system indicates the possible presence of S atoms at ~ 3.4 Å or O atoms at 3.1 Å from Au (Fig. 2). Although the high noise and poor spectral resolution of the low concentrated (10^{-4} m Au) samples does not allow rigorous quantification of the feature, the derived Au-S and Au-O distances are in good agreement with those expected in Au polysulfide/thiosulfate (Au-S-S) or sulfite (Au-S-O₂) species. In addition, the evolution of XANES spectra with pH seems to support this conclusion (Fig. 1). Thus, it cannot be excluded that such complexes may be responsible for the elevated Au solubility in acidic S-rich fluids of our experiments. This is in agreement with the known high chemical affinity of Au^I for H₂S_n and S₂O₃ ligands at low temperatures. These new species may significantly enhance Au mobility in S-rich solutions and vapors operating in magmatic-hydrothermal systems.

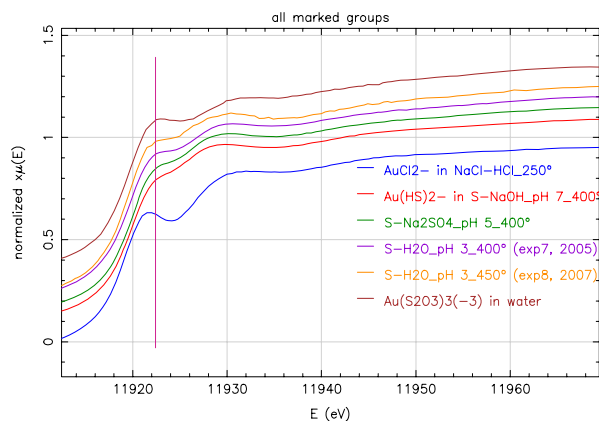


Fig. 1 Normalized Au-L_{III} XANES spectra from selected S and Cl experiments (spectra are shifted along the vertical axis for clarity). The vertical line denotes the position of the feature which might indicate the presence of Au-S-S bonds in acid S-rich solutions. Note that the AuCl₂⁻ spectrum is distinctly different from its Au(HS)₂⁻ analog.

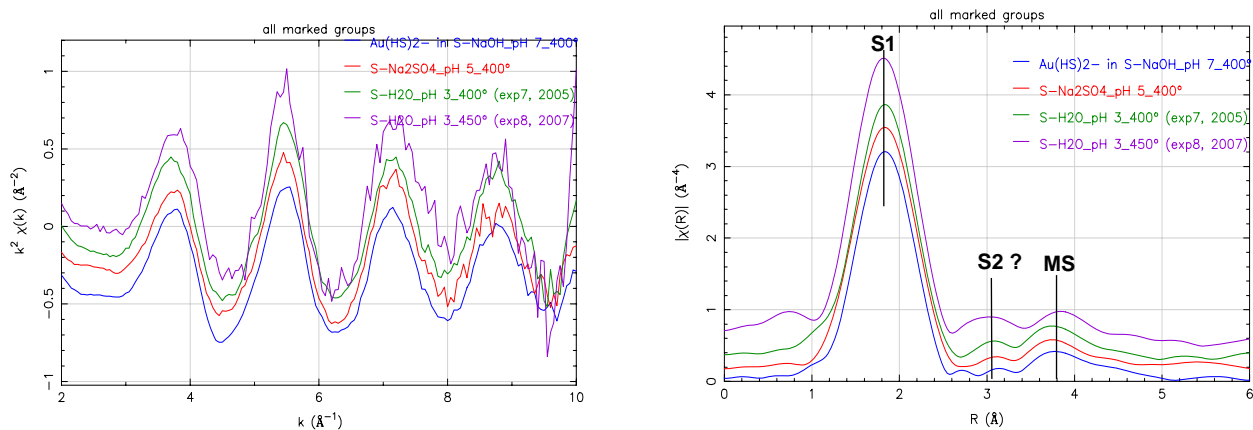


Fig. 2 Typical fluorescence EXAFS spectra and their corresponding FT for selected S-bearing fluids (spectra are shifted along the vertical axis). S1 and MS denote, respectively, single and multiple scattering within the linear S-Au-S cluster; S2 indicates a possible contribution from 2nd shell sulfur/oxygen atoms.

Conclusions & perspectives. This experiment yielded a first quantitative measurement of Au^I chloride species structure dominant in salt-rich acidic gold-forming fluids. In S-rich acidic solutions, our data provide evidence for the formation of bi-sulfide and/or polysulfide/sulfite Au complexes, and rule out the dominant presence of AuHS⁰ suggested by most solubility studies. Work is in progress to model XANES spectra of these solutions which are expected to provide additional constraints on the species stoichiometry and geometry. Quantification of these new Au-S complexes requires improved knowledge of the sulfur speciation in acidic high-temperature solutions, which will be obtained using in situ Raman or Inelastic X-ray Scattering spectroscopy.

References

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