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Report:

Experimental. Using small volume silica glass capillaries (615 μm OD, 300 μm ID, internal volume ~ 10 - 30 μL) we have performed Au solubility experiments with *in situ* acquisition of Au L_3-edge HERFD XAFS spectra in the temperature interval from 350 to 650°C. An experimental system contained Au metal together with aqueous solution (H_2O, buffer of O_2 fugacity, and complexing ligands) or eutectic chloride salt mixture + O_2 source. The experimental system components were hermetically sealed inside the silica glass capillary. The capillaries were prepared and tested at IGEM RAS (Moscow). At ESRF they were heated using Microtomographic furnace with *in situ* record of HERFD XAFS (XANES and EXAFS) spectra. To our mind this is the first use of the capillary technique for high temperature study of fluid systems at a Synchrotron radiation source. The experimental systems included:

(1) Au in oxidized sulfide system, pH neutral. The system contained $Na_2S_2O_3$ solutions (to 3*m*) which decomposed upon heating with the formation of H_2S and H_2SO_4. One experiment was performed with mixed chloride (NaCl)-sulfide system;

(2) Au in reduced sulfide system, pH neutral. The system contained H_2S (to 5*m*)/NaOH. To avoid oxidation of S^{2-} we used Al_2S_3 as a source of H_2S. A small amount of Al_2S_3 crystals (synthesized in our laboratory) of known mass (to 20 μg) was loaded into the capillary together with Au_{cr} and NaOH solution, and the capillary was immediately sealed. The Al sulfide reacts with water with the formation of H_2S, whereas the concentration of oxidized S species is negligible;

(3) Au in oxidized sulfur system, pH acidic: capillaries were loaded with H_2SO_4/SO_2 solution (to 1.5*m* each).

(4) Au in chloride solutions: H_2SO_4/SO_2 served as an oxygen buffer, and HCl or NaCl were added as the source of Cl ligand;

(5) Au in eutectic chloride mixture: RbCl/LiCl or CsCl/KCl/NaCl.

In order to check the effect of the second coordination shell on Au L_3-edge spectra, two additional heating experiments (to 650 °C) were performed with Au-bearing $Cu_{2-x}S$ and Cu_5FeS_4 phases.

Results: In all the experiments the stationary equilibrium Au concentration was attained within several minutes after stabilization of the temperature. The Au L_3-edge HERFD XAFS spectra for several experimental systems are shown in Fig. 1. The HERFD XANES spectra (Fig. 1a) for chloride solutions are different from the spectra of sulfide systems. The edge jump position for chloride solutions is shifted to lower energies and the spectral features are more strongly-pronounced. An interesting peculiarity is exhibited by weak diffuse feature at E > 11950 eV. In pure sulfide system it is absent, but rises in intensity with increase of NaCl concentration. However, this feature is absent in “dry” chloride melt. The nature of this behavior will be revealed with the aid of the electronic structure calculations. Two spectra of sulfide Au solutions (top of Fig. 1a), recorded for oxidized and reduced systems, are identical. This can indicate that the same Au complex predominates in both the systems, but this conclusion needs to be confirmed by EXAFS and XANES spectra modeling.

Figures 1b and 1c show preliminary results of Au L_3-edge EXAFS spectra modeling for “dry” chloride melt (Fig. 1b) and oxidized sulfide system (Fig. 1c). In these systems Au is coordinated with 2 ligands with close Au-L distance. This experiment demonstrates that Au can be effectively accumulated and transported by high-temperature chloride melt. To our mind this result is of fundamental importance for geochemistry as it can explain why Au is strongly fractionated towards fluid phase relative to the magmatic source even at low activities of H_2O (for “dry” chloride salt system the dissolution reaction can be written as $Au^0 + O^- + 2\ NaCl = AuCl_2^- + Na_2O$).

The experimental data showed that the count rate for oxidized hydrothermal solutions/fluids, salt melts, and solid sulfides can reach the $2\cdot10^4$ - $1\cdot10^5$ cps range (ketek detector). This makes possible acquisition of Au $L_{\beta5}$ XES and valence band RIXS spectra (11.919 keV), which were not recorded during this experiment because of time constraints. Our first experience of the use of capillary technique to study high temperature fluid systems showed that the quality of the spectra can be substantially improved by minor modification of the furnace in order to reduce the temperature gradient along the capillary.

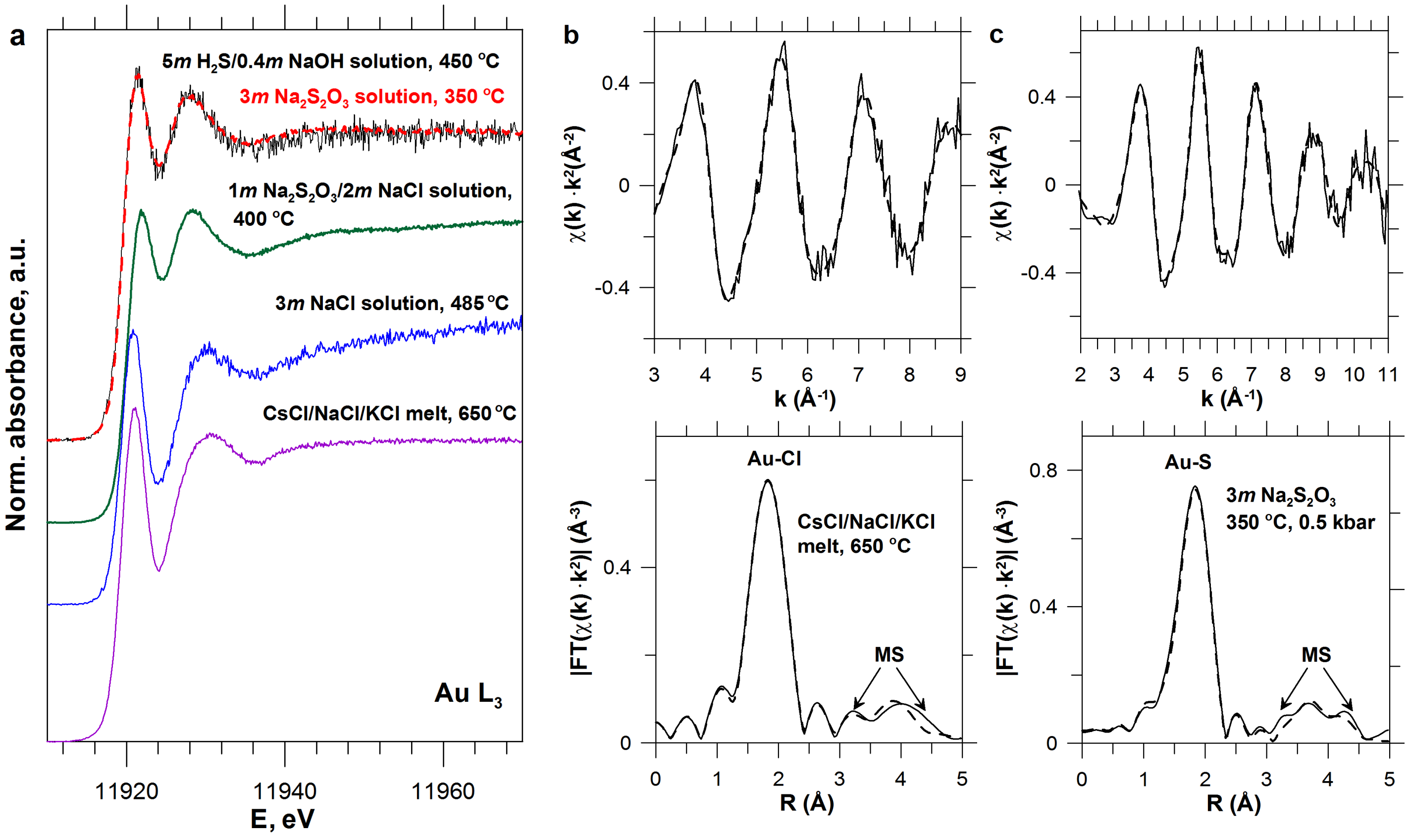

Figure 1. **(A)** - Au L_3-edge HERFD-XANES spectra of Au-bearing fluids; **(b)** - the k^2-weighted EXAFS spectra of Au in “dry” CsCl/NaCl/KCl eutectic mixture, 650 °C: *top* - background subtracted EXAFS spectra, *bottom* - preliminary fit of the Fourier Transform (not corrected for the phase shift), 2 atoms of Cl at 2.28±0.01 Å in the first coordination shell of Au. Thin lines show the experimental spectra, thick dashed curves - calculated spectra; **(c)** – the same for aqueous solution 3*m* $Na_2S_2O_3$ (decomposes with the formation of 2.8*m* SO_4^{2-} + 2.2*m* of H_2S), $t = 350°C$, $P \sim 0.5$ kbar, 2 atoms of S at 2.29±0.01 Å in the first coordination shell of Au. MS - multiple scattering features.

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