

First in situ XAFS determination of gold solubility and speciation in sulfur-rich hydrothermal solutions

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The solubility and atomic structure of Au(I) in NaOH-S-H₂O, and S-H₂O fluids have been simultaneously determined at 200-450°C and 0.3-0.6 kb by X-ray absorption spectroscopy at Au L₃-edge using a new glassy-carbon cell inserted in a high-pressure vessel equipped with Be windows. *In NaOH-S-H₂O fluids at near neutral pH*, both XANES and EXAFS spectra are consistent with the presence of 2 S atoms at an average distance of 2.29±0.01 Å in linear AuS₂ units. These parameters values remain constant within errors in the investigated T-P range. Both aqueous gold structural parameters and Au solubilities measured in this study are consistent with the dominance of Au(I) hydrosulphide complexes, Au(SH)₂⁻, in neutral to alkaline sulfide bearing solutions over investigated conditions (200-450 °C, 0.3-0.6 kb; 0.3<ΣS<4 mol/kg).

In S-H₂O fluids at pH~2 (300 to 400°C, 0.6 kb), XANES and EXAFS spectra are very similar to those in near-neutral solutions and largely dominated by a first-shell contribution from 2 S atoms at 2.29±0.01 Å. However, these structural parameters and the high Au concentrations measured at these conditions (10⁻³ and 5·10⁻⁴ m(Au) at 300 and 400 °C, respectively) are not consistent with the neutral mono-hydrosulphide complex, AuHS⁰, which is believed to be the dominant Au species in S-bearing acid solutions. In particular, our ab initio calculations of optimized structures of AuHS⁰ predict a two-fold linear coordination of Au to a SH⁻ ligand and a water molecule with an Au-O distance of 2.19 Å, inconsistent with our EXAFS spectra. Both EXAFS spectra and Au measured solubility suggest the formation of the neutral Au(H₂S)HS⁰ complex, in agreement with this species stability constants deduced from gold solubility measurements in H₂S-SO₄ solutions. Ab initio calculations of Au(H₂S)HS optimized structures predict a linear Au-S₂ geometry with Au-SH₂ and Au-SH distances of 2.40 and 2.32 Å, a distance splitting that could not be detected by EXAFS within statistical errors. However, because of high SO₂(aq) concentrations in our experiments at acid pH, formation of sulfite or mixed sulfide-sulfite gold species cannot be completely excluded.

This study illustrates the perspectives offered by XAFS spectroscopy coupled with quantum chemical calculations in determining metal solubility and speciation in high T-P geological fluids.