Gold-sulfur complexes in geological fluids studied by means of molecular dynamics simulations

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The mobility of metals in fluids of the Earth's crust and precipitation of metals in ore forming processes depend strongly on the speciation of the metal cations in the fluids. In the case of gold, complexes with sulfur and, to a lesser extent, chlorine are thought to play a dominant role in Au mobilization and deposition. In particular, current speciation models focus on hydrogen sulfide (HS^-) as the most important ligand for gold [1]. However, this picture may be challenged by the discovery that the radical ion S_3^- is a stable sulfur species in aqueous solution at elevated pressures and temperatures [2]. It is therefore a new candidate for the formation of complexes with gold (and similar metals) in hydrothermal fluids.

Here, we present results of first-principles molecular dynamics simulations of various gold-sulfur complexes in water at hydrothermal conditions. From a structural point of view, these simulations demonstrate, in combination with experimental EXAFS data, that gold is coordinated by two sulfur ligands in a quasi-linear arrangement. Furthermore, using constrained dynamics, we calculated the free energy of ligand-exchange reactions and found that gold has similar affinities for HS^- and S_3^-. Since S_3^- dominates over HS^- in most S-rich acidic to neutral fluids at elevated temperatures [2], S_3^- may indeed be a major carrier of gold in geological fluids.

[1] Seward (1973), *Geochim. Cosmochim. Acta* **37**, 379-399

[2] Pokrovski and Dubessy (2015), *Earth Planet. Sci. Lett.* **411**, 298-309