

Gold-sulfur complexes in crustal fluids: insights from first-principles molecular dynamics simulations

VOLKER HAIGIS^{1*}, ROMAIN JONCHÈRE²,
GUILLAUME FERLAT², A. MARCO SAIITA²,
ARI P. SEITSONEN³ AND RODOLPHE VUILLEUMIER¹

¹École normale supérieure, Department of Chemistry, UMR 8640 CNRS-ENS-UPMC, 24 rue Lhomond, 75005 Paris, France (*correspondence: volker.haigis@ens.fr)

²UPMC, IMPMC, UMR 7590 CNRS-IPGP-UPMC, 4 place Jussieu, 75005 Paris, France

³Institut für Chemie der Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Sulfur is one of the major ligands of gold in fluids of the Earth's crust and thus has a strong influence on gold solubility and transport to ore deposits. A detailed understanding of these processes requires knowledge as to which of the various known sulfur species are actually available in crustal fluids for complexation with gold. In a recent Raman study, Pokrovski and Dubrovinsky [1] found that at the relevant conditions, S_3^- might be more abundant than competing sulfur-bearing ligands of gold, which are dominant at near-ambient conditions. Therefore, S_3^- might play an essential role in the mobilization of gold in crustal fluids if it is able to form stable complexes with the metal.

We investigated different gold-sulfur complexes in water, including AuS_3^- , with first-principles molecular dynamics simulations, based on density functional theory. We compare the extended x-ray absorption fine structure (EXAFS) derived from our simulations to recent experimental data [2], which allows us to identify the experimentally detected species. The geometry and vibrational properties of various solvated gold-sulfur complexes are investigated, and we rationalize them in terms of their electronic structure. Furthermore, we discuss the influence of redox conditions on the speciation of gold-sulfur complexes. From a methodological point of view, we show how computer simulations can assist the interpretation of experimental data by elucidating the structure and dynamics of solvated species at the atomic level.

[1] G. S. Pokrovski and L. S. Dubrovinsky (2011), *Science* **331**, 1052-1054 [2] G. S. Pokrovski *et al* (2009), *Geochim. Cosmochim. Acta* **73**, 5406-5427