ESRF	Experiment title: The role of organics in gold transport: An investigation of gold speciation in organic liquids	Experiment number: ES-552
Beamline: BM30B	Date of experiment: from: 28.06.2017 to: 04.07.2017	Date of report : 12.09.2017
Shifts: 18	Local contact(s): Denis Testemale	Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

L. Crede^{1*}, K. Rempel¹, J. Brugger^{2*}, W. Liu^{3*}

¹Curtin University, Dept. of Applied Geology, Kent St, Bentley, Perth, Australia

²Monash University, School of Earth, Atmosphere and Environment, Rainforest Walk, Victoria, 3800 Australia

³CSIRO Earth Science and Resource Engineering, Clayton, Victoria, 3168 Australia

Report:

Introduction

New ore deposits are becoming increasingly difficult to discover, requiring better ore formation models. Organic matter is a common constituent of hydrothermal ore deposits, and is mostly interpreted as a reducing agent for the deposition of metals from hydrothermal ore fluids [2, 3]. However, experiments suggest that organic fluids such as petroleum may also act to dissolve and transport metals [1], a critical factor missing from current ore deposit models. The objective of this experiment was to determine the speciation and coordination structure of Au in organic liquids under hydrothermal conditions (25°C to 250°C, up to 600 bar), to provide a first assessment of Au dissolution and transport mechanisms in organic liquids, and to derive the fundamental data needed to determine whether organic fluids are able to transport metals under ore-forming conditions.

Eperiment

We performed XANES and EXAFS measurements in fluorescence mode (some exeptions with high Au concentrations where collected in transmission mode) at the Au L_{III} -edge on ndodecane (CH₃(CH₂)₁₀CH₃) and 1-dodecanethiol (CH₃(CH₂)₁₀CH₂SH) doped with Au(III)Cl or Au(I)Cl, and on partition experiments between each of the previous mentioned organic liquid and an acidified aqeous brine solution (pH=1.85; NaCl=10wt%) doped with Au(III)Cl (0.2 wt%), or water doped with Au(III)Cl. The partition experiments were conducted directly in the glassy carbon tubes, and as separate analyses of the aqueous and the organic liquid following a partition experiment between the two liquids in a beaker at 25°C. Temperature and pressures of the experiments ranged from 25°C to 200°C and 1 bar to 600bar. The main hydrocarbon standards analysed were n-dodecanethiol gold nanparticles (2%) in toluene and Sodiumaurothiomalate(I) hydrate (C₄H₃AuNa₂O₄S x XH₂O). XANES and some EXAFS of Au were collected successfully for some of the Au doped n-dodecane and 1-dodecanethiol, the seperatly sampled solutions of the partition experiment in the beaker, and from the partition experiments performed directly in the carbon tubes. XANES and EXAFS data are currently under analysis, but preliminary XANES data reduction shows that Au partitions from the aqueous phase into the n-dodecane in the form of Au^{III}. XANES spectra collected of Au dissolved in n-dodecanethiol and partitioned into n-dodecanethiol from the aqueous solution are identical with the data collected from the Sodiumaurothiomalate(I) hydrate indicating that Au^{III} is reduced to Au^I and bonds with the S in the n-dodecanethiols (Figure I). The XANES spectra of the aqueous phase sampled from the beaker partition experiments indicate that Au stays in solution as Au(III)Cl, when the aqueous phase is in contact with n-dodecane or 1dodecanethiol. In contrast, the Au^{III} was reduced to Au^I in the aqueous phase in the partition experiment within the glassy carbon tube. In both hydrocarbon solutions Au started to reduce to Au⁰ at temperatures $\geq 125^{\circ}$ C. As noted by other users [4], the reduction was often accelerated by the X-ray beam, as the Au⁰ intensity increased especially at the beam position. EXAFS data analysis will lead to determine Au-Au and Au-S distances and coordination numbers for all the investigated systems.



Figure I: A small selection of XANES spectra. Spectra 3 and 4 are from partition experiments in the glassy carbon tube.

References

[1] Emsbo et al. (2009), 10th Bien. SGA Meet., ed. by Williams, 99-101. [2] Giże (1999), Econ. Geol. Bull. Soc. 94, 963-965. [3] Giże et al. (2000), Rev. Econ. Geol. 9, 87-104. [4] Pokrovski et al. (2009), Chem Geol. 259, 17-29.