

Speciation and thermodynamic properties of palladium chloride and bisulfide complexes: insights from experiments and *ab-initio* molecular dynamics simulations

YUAN MEI^{1,2}, T. M. SEWARD³, JOËL BRUGGER^{1,4},
STEPHEN J. BARNES² AND MARCO L. FIORENTINI⁵

¹School of Earth and Environmental Sciences, The University of Adelaide, Australia (yuan.mei@adelaide.edu.au)

²CSIRO Earth Science and Resource Engineering, Australia

³Victoria University of Wellington, New Zealand

⁴South Australian Museum, Australia

⁵CET/CCFS, The University of Western Australia, Perth, Australia

Characterising the speciation and solubility of platinum group elements (PGE) in hydrothermal fluids is useful in understanding the formation of PGE deposits, and for supporting the development of new exploration tools for high value magmatic nickel sulfide deposits, whose small footprints may be extended by hydrothermal remobilisation of PGE. A number of experimental studies have investigated Pd speciation and solubility in hydrothermal chloride solutions, with reasonable agreement over the nature and stability of Pd(II) chlorocomplexes (Barnes and Liu, 2012). In contrast, there are significant discrepancies among the available thermodynamic properties for the predominant Pd bisulfide species. This uncertainty severely hinders numerical modelling of PGE mobility in hydrothermal fluids.

Ab-initio molecular dynamics (MD) simulations were performed to investigate the stability of possible Pd-Cl and Pd-HS complexes in hydrothermal fluids. The simulations revealed the preference of four-fold square planar structures of both chloride and bisulfide complexes at high P,T (300 °C, 500 bar). We are building a geochemical model for Pd transport via thermodynamic integration (Mei *et al.*, 2013). The species geometry and thermodynamic properties derived from the MD simulations will be compared with the existing thermodynamic properties (Boily and Seward, 2005) and with new EXAFS measurement of Pd chloride complexes in hydrothermal brines up to 340 °C.

[1] Barnes and Liu (2012) *Ore Geol. Rev.*, **44**, 49–58. [2] Boily and Seward (2005) *Geochim. Cosmochim. Acta.*, **69**, 3773–3789 [3] Mei, Sherman, Liu, Brugger (2013) *Geochim. Cosmochim. Acta.*, **102**, 45–64.

Protein-silica interactions: The effect of lysozyme on the structure of amorphous silica

D.B. MEIER^{1*}, D.J. TOBLER², C.L. PEACOCK¹
AND L.G. BENNING¹

¹ School of Earth and Environment, University of Leeds, United Kingdom (*correspondence: eedbm@leeds.ac.uk)

² Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark

Amorphous silica is one of the two dominant biominerals in the world's oceans where it is precipitated by diatoms, radiolarians or siliceous sponges. Furthermore, in geothermal settings microorganisms can become quickly silicified through the precipitation of silica from under- or oversaturated geothermal waters. In both cases, the interaction between amorphous silica and cell internal or cell wall macromolecules, like proteins, are crucial for templating the siliceous structures or for enhancing microbial silicification [1, 2]. However, how and if proteins affect the structure, composition and morphology of amorphous silica at the molecular level is only poorly understood

Here, we quantified the effect a typical protein (lysozyme) has on the atomic structure and composition of amorphous silica that was precipitated from supersaturated aqueous solutions in the absence or presence of variable lysozyme concentrations (0 – 10'000 ppm).

Synchrotron-based pair distribution function (PDF) analyses showed only a minor change in the short range ordering (>15 Å) of amorphous silica precipitated in the presence of ≥ 1000 ppm lysozyme. This suggests limited structural interactions and hardly any incorporation of the lysozyme within the amorphous silica structure. Fourier Transform Infrared (FTIR) spectroscopic analyses however, indicate significant incorporation and surface interaction between lysozyme and amorphous silica at all lysozyme concentrations.

Further PDF and FTIR experiments are underway to test for artifacts and to confirm the findings reported above. Moreover, thermogravimetric analyses, X-ray diffraction, total carbon analyses and high resolution microscopy will help to quantify the ratio of incorporated to adsorbed protein contents, the water contents, and the morphology of amorphous silica as a function of protein content.

[1] Perry & Keeling-Tucker (2000), *Journal of Biological Inorganic Chemistry*, **5**, 537-550. [2] Tobler, Stefansson & Benning (2008), *Geobiology*, **6**, 481-502.