

Sorption of Hg(II) by nanocrystalline mackinawite (tetragonal FeS)

SHARON BONE^{1*}, KIDEOK KWON², JOHN BARGAR³
AND GARRISON SPOSITO¹

¹Environmental Science, Policy and Management, UC Berkeley (*correspondance: shbone@berkeley.edu) (gsposito@berkeley.edu)

²Earth Sciences Division, Lawrence Berkeley National Laboratory (kkwon@lbl.gov)

³Molecular Environmental & Interface Science, Stanford Synchrotron Radiation Light Source (bargar@slac.stanford.edu)

Mercury is transformed to the biomagnifying species monomethyl mercury by sulphate reducing bacteria in anoxic sediments. The iron sulphide mineral, mackinawite (FeS_(s)), can limit Hg(II) bioavailability by sequestering Hg in the solid phase or by reducing it to volatile Hg (0). We use a combination of extended X-ray absorption fine structure (EXAFS) spectroscopy, density functional theory (DFT) geometry optimization and X-ray diffraction (XRD) to examine the speciation of Hg sorbed by FeS_(s) as a function of Hg concentration, pH, and reaction time. Analysis of the Hg L_{III}-edge EXAFS spectra indicates that Hg exists in multiple coordination environments upon sorption by FeS_(s), including a metacinnabar (HgS_(s))-like phase and a component that we have tentatively identified as surface bound Hg. We use DFT geometry optimization to clarify the coordination environment of the putative surface complex and our preliminary results indicate that Fe-bound Hg is energetically favoured relative to S-bound Hg, as we had previously hypothesized. Lastly, Hg L_{III}-edge EXAFS spectra indicate Hg (0) forms in the presence of FeS_(s), while spectroscopic and diffraction analysis of FeS_(s) leads us to hypothesize that Hg(II) reduction results in the formation of surface-bound Fe^{III}. This research demonstrates that Hg(II) interacts with FeS_(s) through multiple mechanisms, leading to the production of both sorbed and volatile Hg species, which vary in their reactivity and bioavailability in Hg-polluted sulphidic waters.

Inhibited water diffusion and inhomogeneities in glassy atmospheric aerosol proxies

D.L. BONES¹, D.M. LIENHARD^{1,2}, U.K. KRIEGER² AND J.P. REID¹

¹School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom

²Institute for Atmospheric and Climate Science, ETH Zürich, Zürich, Switzerland

Atmospheric aerosol particles are typically complex mixtures of organic and inorganic species with correspondingly complex behaviours in changing humidity regimes. We investigate the formation of glassy or highly viscous phases in aqueous sugar aerosols such as sucrose and levoglucosan and aerosols of mixtures of sugars and inorganic compounds. It has recently been recognised that many aerosols exist as highly viscous solutions or as amorphous glasses, rather than a crystalline state, over a wide range of relative humidities (Virtanen, *et al.* 2010).

We use optical tweezers to trap single aerosol particles, exploiting subtle changes in the Raman spectra to deduce the size changes due to water uptake and evaporation from aqueous particles exposed to varying RH. We compare the experimental data with a kinetic model of diffusional limited size change.

Changes in size are dramatically hindered at low RH, with time scales approaching 10000s, for both increasing and decreasing RH regimes. The shift in resonance modes suggests initial formation of a layer of water on the surface of the glassy particle and subsequent establishment of a steep concentration gradient within.

[1] Virtanen A. *et al.*, (2010) *Nature*, **467**, 824– 827.