Structure and elasticity of hollandite at high pressures

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Hollandite ($KAlSi_3O_8$) is a high-pressure polymorph of potassium feldspar and has been believed to be the most abundant phase in the continental crustal material that are subducted to pressure and temperature conditions relevant for the mantle transition zone. They are possible reservoirs for large ion lithophile elements such as K, Na, Pb, Sr and are potential candidates to generate EMII geochemical signatures. Using first-principle simulations we investigate the energetics related with the high pressure phase transformation Results of compression for the hollandite phase are well represented by a third order Birch-Murnaghan finite strain expression with K_0 = 207 GPa, K^t_0 = 4.5 and V_0 = 233.12 Å^3. Our static (0 K) calculation predict tetragonal to monoclinic transformation at 34 GPa, which compares well with 22 GPa observed in experiments (300 K).

Calculated elastic constants for tetragonal hollandite show significant anisotropy, with $C_{11} < C_{33}$ at all pressure conditions. Elastic constant C_{11} and C_{66} show softening at pressures greater than 50 GPa, outside the stability region of the tetragonal phase.

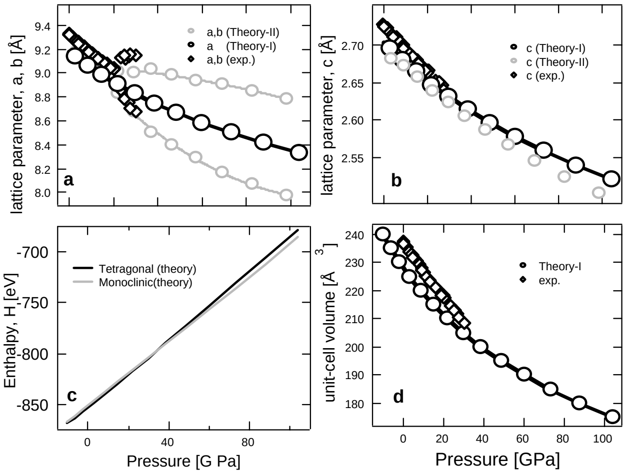

Figure 1: a) Lattice parameters a and b; b) enthalpy of tetragonal and monoclinic phases; c) lattice parameter c; d) volume vs pressure. Theory-I and II refers to tetrahonal and monoclinic structure, exp. Refers to experimental data by [1].

[1] Ferroir *et al.* (2006). *Am. Mineral.*, **91,** 327-332.

Cu(II) sorption to *Bacillus subtilis* and bacteriogenic ferrihydrite: Insights from XAS spectroscopy

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Accurately predicting the fate and mobility of geogenic chemicals in natural biogeochemical systems requires thermodynamic models capable of describing their scavenging onto key mineral phases. Models require a molecular-level understanding of the mineral surfaces and the sorption complexes formed. For Cu(II), sorption to Fe (hydr)oxides is a key control on oxic soil and groundwater Cu concentrations and, as such, we require detailed knowledge of Cu sorption to the dominant reactive Fe (hydr)oxide phases present in freshwater systems. In addition to abiotic Fe (hydr)oxides, nanocrystalline bacteriogenic Fe (hydr)oxides are abundant in surface and groundwaters and increasingly recognised as perhaps the primary reactive Fe (hydr)oxide in freshwater systems. Comprised of poorly ordered Fe (hydr)oxide intermixed with intact and fragmented bacterial cells, bacteriogenic Fe (hydr)oxides have different nanostructure and physiochemical characteristics compared to abiotic Fe (hydr)oxide analogues. These differences imply abiotic laboratory Fe (hydr)oxides may not be a correct model system for natural bacteriogenic phases, potentially affecting our ability to predict Cu concentrations in complex biogeochemical systems.

We have synthesised 2 line ferrihydrite in the presence of the common soil bacterium *B. subtilis* to produce bacteriogenic ferrihydrite. Sorption of Cu(II) to abiotic ferrihydrite, *B. subtilis* and bacteriogenic ferrihydrite was measured under controlled atmospheric conditions from pH 2.5–8. Cu surface complexes in each sorption system and over the entire pH range were determined using EXAFS spectroscopy.

Sorption edge experiments for bacteriogenic ferrihydrite show significant elevated Cu sorption in the mid to low pH regime (<pH6) compared to abiotic ferrihydrite. EXAFS indicates Cu sorption on bacteriogenic ferrihydrite results from inner-sphere Cu complexation by carboxyl functional groups on the residual bacterial fraction and inner-sphere bidentate Cu complexation by Fe-OH groups at the ferrihydrite surface.

Sorption experiments, EXAFS results and implications of our results for accurate prediction of Cu fate and mobility in freshwater systems will be discussed.