Kinetics of phosphate adsorption on goethite in seawater

Jia-Zhong Zhang *, and Charles Fischer

Ocean Chemistry Division, Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, Miami, Florida 33149, USA jia-zhong.zhang@noaa.gov (* presenting author)

The adsorption kinetics of phosphate on goethite was studied at low concentrations of both adsorbent and adsorbate to adequately measure the initial rate of decreasing phosphate concentration in solution. Phosphate sortion desplayed a two-step process. A rapid decrease in phosphate concentration was observed during the first few minutes, which was followed by a slow decrease over hours and days. Batch experimental data were fitted with a model of film-diffusion at particle-water interface for the fast process and a intra-particle/pore diffusion model for the slow process.

Batch adsorption experiments were performed at different concentrations of goethite and phosphate, as well as a range of temperatures and salinities in pH 7.9 seawater. The rate of adsorption increased with increasing concentrations of either goethite or initial phosphate concentration. At a given goethite and phosphate concentrations, the rate of adsorption increased linearly with increasing temperature from 5 to 45°C. The rate of adsorption also increased with decreasing salinity from 36 to 18 A more rapid increase was observed at salinities below 18.

Phosphate adsorption rates were similar both in seawater and artificial seawater. Comparison of rates in different seasalt solutions was used to reveal the effect of individual ions on the adsorption rate. The rate decreased exponentially with an increasing bicarbonate concentration at a constant pH 7.9. At seawater pH and total dissolved inorganic carbon concentration (2mM), the rates were constant in NaCl solution with concentrations ranging from 0.1-0.7M. This suggests that the initial rate is independent of ionic strength. The addition of SO_4^{2-} to the NaCl solution decreased the rate. In contrast, the rate was increased with the addition of Ca^{2+} or Mg^{2+} to the NaCl solution. Adding Ca^{2+}, Mg^{2+} and SO_4^{2-} together at the seawater ratio diminished the acceleration effects of Ca^{2+} or Mg^{2+}. This is likely due to the formation of ion pairs of $CaSO_4$ and $MgSO_4$ which reduced the free ion concentrations. For anions in seawater, the capacity for rate reduction was in an order of $HCO_3^- > SO_4^{2-} > Cl^-$. For cations, the order for capacity of rate acceleration was $Ca^{2+} > Mg^{2+} > Na^+$.

In-situ determination of crystal structure of (Mg,Fe)SiO₃

Li Zhang[1*], Wenge Yang[2], Yue Meng[3], Lin Wang[2], Qiao-Shi Zeng[4], Wendy L. Mao [4,5] and Ho-kwang Mao[1]

[1] Geophysical Laboratory, Carnegie Institution of Washington, Washington DC, USA, lzhang@ciw.edu
[2] High Pressure Synergetic Consortium, Geophysical Laboratory, Carnegie Institution of Washington, Argonne IL, USA
[3] High Pressure Collaborative Access Team, Geophysical Laboratory, Carnegie Institution of Washington, Argonne IL, USA
[4] Geological and Environmental Sciences, Stanford University, Stanford CA, USA
[5] Photon Science and Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, USA

$(Mg,Fe)SiO_3$ silicate is believed to be the principal mineral in Earth's lower mantle. Precise measurements of structural transitions and associated changes in composition of $(Mg,Fe)SiO_3$ at the high pressure (P) and temperature (T) conditions within Earth's lower mantle are required to interpret the seismic observations.

The $(Mg_{1-x},Fe_x)SiO_3$ (x=0.15 and 0.4) orthopyroxene starting materials were compressed to 60-130 GPa in separate symmetric diamond anvil cells and heated by the double-sided YLF laser system at the beamline 16 ID-B of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The crystal structure of the $(Mg_{1-x},Fe_x)SiO_3$ phase was studied as a function of pressure and temperature, in comparison with the known *Pbnm* orthorhombic structure. The structural details of the micron-size $(Mg,Fe)SiO_3$ crystals at high pressure were determined by the combined *in-situ* powder X-ray diffraction (XRD) and single-crystal XRD techniques. The unit-cell parameters were obtained from powder XRD measurements. The orientation matrix of individual micron-size crystal was determined in a polycrystalline sample with a focused 5×10 µm monochromatic X-ray beam. All possible reflections were then predicted with tuning diffraction angle and intensity of each reflection was measured for structure solution.
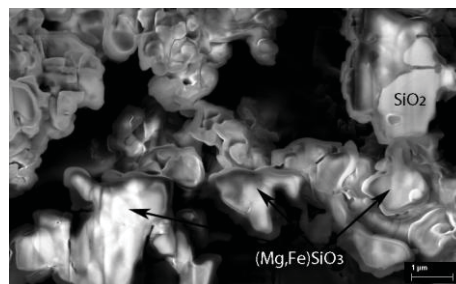
Figure 1: Cross-section of recovered $(Mg,Fe)SiO_3$ and SiO_2 in $(Mg_{0.6},Fe_{0.4})SiO_3$ from 85 GPa and 2500 K in Neon media.

The recovered samples were prepared by FIB (focused ion beam) for chemical analysis. $(Mg,Fe)SiO_3$, $(Mg,Fe)O$, SiO_2 and metallic Fe were selectively present in the recovered product, depending on temperature profile and starting composition.

The structural information of $(Mg,Fe)SiO_3$ silicate and associated changes in chemical composition at high *P-T* conditions is used to build a reliable mineralogical model for the lower mantle in consistent with the seismic observations.