Understanding the composition and structure of ferrihydrite

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A growing body of evidence confirms a single phase model (SPM) suffices to explain the core (but perhaps not surface) atomic arrangement in inorganically and biologically derived 2- and 6-line varieties of ferrihydrite. The 50 years of effort expended on studying this material produced inconsistent results, probably due to variations in preparation, confusion due to over-fitting information poor (low Q, high incoherence) diffraction and x-ray absorption data with overly complex models, electron beam damage in TEM, etc. Careful large-batch synthesis of hydrogenous and deuterated samples and the use of several analytical probes on synthetic and natural samples provide a consistent picture: 1) there is no need to fit the data with a 3-phase model (TPM) – a SPM fits the PDF derived from the total elastic coherent neutron and x-ray scattering; 2) models claiming water contents of 10% or more, and citations of densities as rebuttal of the SPM that are based on samples that include non-structural water only removed after treatment to 215°C, are at odds with TGA/DSC/in situ scattering data that shows ~2 wt % structural water in ferrhydrite. The results of combined *in situ* high energy XRD/DSC are particularly revealing, since they show clearly ferrihydrite persists with about 2 wt % water up until transformation to hematite; 3) IR spectroscopy is fully consistent with result; 4) *In situ* PDF analysis indicates the ferrihydrite bulk structure remained intact up to the direct transition to crystalline hematite, with no intermediate phases, crystalline or amorphous, formed; 5) the recently proposed akdalaite-like ferrihydrite model has 2.2 wt.% H_2O-equivalent structural OH, and is consistent with these results. The TPM has an average formula close to FeOOH, containing 10 wt.% H_2O-equivalent structural OH, far more than suggested by our experiments. Based on the constraints set by the estimated water content and the PDF signatures, we examined possible anion packing types and local structural motifs in ferrihydrite, and demonstrate that ABAC is the only feasible packing type and that the peak at 3.45 Å in PDF provides indirect evidence for the presence of tetrahedral Fe.

Opportunities at light source and neutron facilities

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X-ray sources and pulsed neutron sources are getting brighter. In the case of x-ray sources peak brightness has risen increasing by several orders of magnitude in the last few years, spot sizes are approaching several nm and beam coherence is increasing. Although the gains in peak power in neutrons are modest by comparison, the coming on stream of SNS (and Japan and Europe sources eventually) in combination with Montel-like focusing optics will allow studies of smaller samples at more extreme and relevant environments at these sources as well. Together these developments in x-ray and neutron beam conditioning are opening up whole new areas of research in scattering, spectroscopy, and imaging studies of earth materials and processes that were not possible a decade ago. Increasingly the expectation is that the study of earth and planetary materials, and their analogues, will be carried out with selectable nm-μm-mm spatial resolution with < 1meV energy resolution and *in operando* – under the conditions simulating the pressure, temperature, humidity, and other environmental variables under which Earth, the planets (including gas giants and recently discovered exo-planets) operate. For example, at spallation and reactor sources the unique properties of the neutron will enable *in situ* studies using isotope specific imaging, contrast variation techniques, diffusion studies, derivation of partial structure factors for glasses along with already established studies of structure and dynamics for magnetic and hydrous materials, studied at older neutron sources for over 60 years. X-ray free electron lasers and next generation storage rings such as NSLS-II will provide opportunities for coherent imaging, diffraction microscopy, inelastic studies and a host of techniques previously regarded as 'pre-emergent' and exotic only a couple of years ago. Unprecedently small beams will allow imaging and spectroscopy, and possibly diffraction, from interfaces and small sample volumes. The impact of these latest-generation facilities on characterization of the chemistry and atomic arrangements in materials will be profound. In order to take full advantage of the opportunities afforded, earth scientists continue to design, build and operate new sample cells that simulate the conditions existing on Earth and planetary surfaces, and in their interiors.