Geophysical Research Abstracts
Vol. 18, EGU2016-10933, 2016
EGU General Assembly 2016

Hard X-ray total scattering study on the structure of Si-dopped ferric oxyhydroxides and products of their transformation

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Here we report the results of a detailed structural investigation, using synchrotron-based pair distribution function analyses (PDF) and high-resolution X-ray diffraction (HR-XRD), on a series of Si-bearing synthetic analogues of ferrihydrite with a range of Si/Fe ratio relevant to geological environments and on products of their thermal transformation. Hard X-ray total scattering data suitable for PDF analyses have been collected at the PDF-dedicated beamline 11-ID-B and the HR-XRD data at beamline 11-BM of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL).

Ferrihydrite is a poorly crystalline, nano-sized hydrous ferric oxyhydroxide with a nominal/ideal formula $Fe_5HO_8 \bullet 4H_2O$. Its chemical composition however, can vary significantly and the atomic structure is yet to be fully understood despite multitude of structural studies undertaken over the past two decades (Michel et al., 2007; Manceau, 2009). One of the most commonly discussed and still unsettled contention points regarding the structural arrangements of ferrihydrite is related to the presence or absence of tetraherdally coordinated iron(III) within its structure. The majority of experimental work carried out to date focused on pure, synthetic ferrihydrite analogues with chemical composition close to ideal/nominal. This approach is clearly a significant oversimplification of natural ferrihydrite which always contains substantial amounts of admixtures, with Si, C, P, As, Ca, S and Al being the most common. One of the most important and the most commonly encountered impurities is Si, in the form of silicate ion that has strong affinity for ferrihydrite. SiO_2content in natural ferrihydrites can vary substantially but generally falls with the range of 2.6-31.5 wt% (Cismasu et al., 2011). In certain environments however, such as modern seafloor hydrothermal vents, higher Si/Fe ratios (up to ca. 3) have been reported (Sun et al., 2013). The results of previous reports indicate that silicate ions not only cause decrease in sample crystallinity, inhibits particle growth, modifies morphology, magnetic ordering and solubility but also strongly affect its surface atomic arrangement. Small amount of silica in ferrihydrite increases its stability with respect to transformation into Si-hematite and cristobalite. Structural properties of substituted synthetic ferrihydrite have received increased scientific attention. This study sheds more light on the structural effect of Si in both, ferrihydrite and its annealed products .

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