



**Experiment title:** Transformation of phosphorus- and silicon-bearing iron oxides by reaction with dissolved ferrous iron

**Experiment number:**  
26-01-1123

<b>Beamline:</b> BM26A	<b>Date of experiment:</b> from: 25-08-2017 to: 29-08-2017	<b>Date of report:</b> 11-12-2017
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dipanjan Banerjee	<i>Received at ESRF:</i>

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**Report:**

During experiment 26-01-1123, we collected Fe EXAFS spectra from approximately 85 samples. In each case, a sub-sample equivalent to the Fe required for one absorption length was mixed with microcrystalline cellulose and pressed into pellets (7 mm diameter, ~1 mm thickness). All preparation steps and transport were performed under anoxic conditions, up to the moment where the pellets were attached to the sample holder and analyzed. Pellets were packed between 2 layers of Kapton tape (in a O<sub>2</sub>-free govebag) and Fe EXAFS spectra (6962 – 7862 eV) were collected at room temperature. The cryostat was not used; previous results (experimental report form 26-01-1090) showed negligible sample oxidation during an analysis run (up to 6 hours). Data reduction and fitting was performed with Athena, using reference spectra collected during this and previous experiments at ESRF.

One batch of samples (15) was from a lab-based incubation study, where synthetic ferrihydrite and lepidocrocite (Fe(III) minerals) with and without coprecipitated P or Si (shown to strongly impact mineral structure and reactivity) were exposed to iron-reducing bacteria in a seawater matrix. Previously obtained chemical results had clearly shown reduction of Fe(III) to Fe(II), but this was not reflected in the Fe EXAFS spectra; the samples were assumed to have been oxidized during sample treatment despite extensive measures taken to keep samples shielded from atmospheric oxygen.

The second batch of samples were subsamples from Fe mineral-doped diffusive gels (for technical details, see experimental report form 26-01-1090) that were deployed for ~ 4 weeks in natural Fe(II)-rich or H<sub>2</sub>S-rich porewater at two different sites (freshwater vs seawater) to investigate how coprecipitation of P and Si affected Fe mineral transformation under those two

regimes. In this experiment, duplicates were deployed at both sites for all Fe mineral-doped gels, and analyzed at ESRF. In the samples deployed in Fe(II)-rich porewater (chemical analysis had shown up to  $500 \mu\text{mol L}^{-1} \text{Fe}^{2+}$  during the period of deployment), there was hardly any transformation of poorly ordered ferrihydrite to more crystalline phases such as goethite, which is usually rapid due to catalysis by  $\text{Fe}^{2+}$ . These results were in stark contrast to previous experiments in Fe(II)-rich freshwater using similar Fe mineral-doped diffusive gels, which showed (through XRD analysis) substantial transformation of ferrihydrite to goethite over a 2-week period. The underlying reasons for this difference are currently under investigation.

The samples deployed in the sulfide-containing porewaters of the marine system showed significant sulfidation (i.e. transformation of ferrihydrite and lepidocrocite to iron sulfide ( $\text{FeS}$ )) at depth in the sediment. A major challenge was posed by the dynamic nature of this tidal system, which through physical processes (partial excavation of probes with gels) resulted in different vertical redox zonations (oxic – anoxic – sulfidic) in the gels, making comparison of different depth intervals between gels difficult. Importantly, the results from this experiment with duplicate gels suggest that spatial and vertical heterogeneity in the field override changes in sulfidation caused by altered ferrihydrite and lepidocrocite structure as a result of coprecipitation of P or Si.