



	Experiment title: Characteristics and transformation of iron oxides containing adsorbed and incorporated phosphate and silicate	Experiment number: 26-01-1090
Beamline: BM26A	Date of experiment: from: 19-9-2016 to: 23-09-2016	Date of report: 18-10-2016
Shifts: 9	Local contact(s): Dipanjan Banerjee	<i>Received at ESRF:</i>

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Report:

Summary of approach

The goal of experiment 26-01-1090 was to elucidate the effects of P and Si incorporation into Fe(III) precipitates on the structural characteristics of the Fe(III) precipitates and their subsequent transformation during deployment in reducing sediments. Synthesis of ferrihydrite and lepidocrocite was done in the presence of varying amounts of P or Si (10/1 and 25/1 molar Fe/X ratio). A novel experimental approach was used, whereby the Fe precipitates were cast in porous diffusive gel patches (1 x w = 15 x 2 cm) that were vertically deployed in the sediment. The gels equilibrated with the porewater and the Fe(III) precipitates transformed by reaction with reduced porewater components. After deployment (2 weeks), the gels were sectioned into 4 pieces of ~3.75 cm each, which were dried and ground. A part of this 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) for bulk Fe XAS in transmission mode at BM26A (DUBBLE) of ESRF. 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 and Fe EXAFS spectra (6962 – 7862 eV) were collected at room temperature. The cryostat was not used, because analysis at room temperature of a pellet with highly reactive FeS showed no signs of oxidation during a 6-hour period in the experimental hutch. This was equivalent to the maximum time any pellet was exposed to air between transfer out of anoxic conditions to analysis at ESRF. Together with the samples from the gel deployment, we also analyzed pellets of the initial P- and Si-amended Fe(III) precipitates (the starting materials that were used in the gel preparations). In addition, sulfidic field sediments were taken to the lab, homogenized and a one-day deployment of Fe-doped diffusive gels was performed to compare to the field data (and minimize the role of sediment heterogeneity).

Results

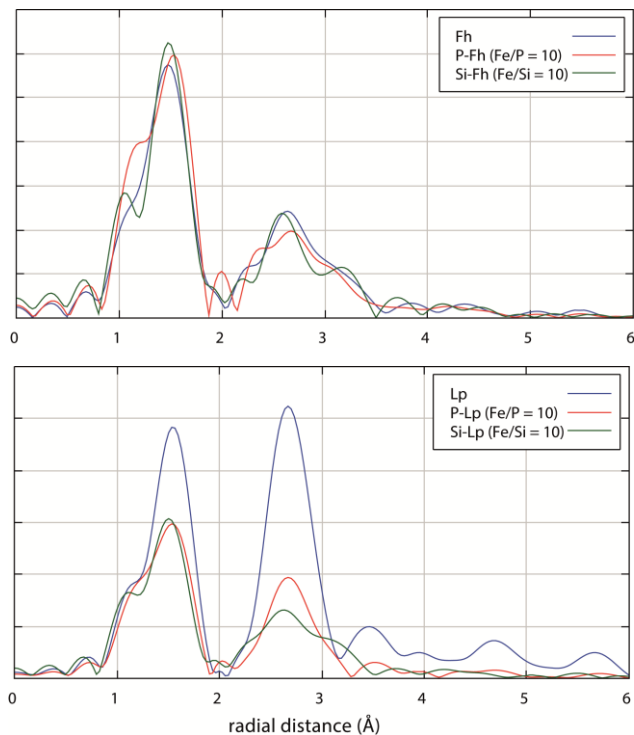


Figure 1. Radial distribution function (RDF) for synthetic unamended (blue) and P (red)- or Si (green)-amended Fh and Lp.

The presence of P or Si during Fe(III) precipitate synthesis strongly affected mineral structure in the case of Lp, but not Fh (**Fig. 1**). In case of lepidocrocite, this is due to P and Si interfering with bond formation between Fe octahedra (Fe-Fe bonds, the second large peak in the radial distribution function for Lp) and thus inhibiting development of the Lp structure.

The gel-based approach provided high-quality data (high signal-to-noise ratio) for the Fe minerals contained in the diffusive gels. As the method isolates the Fe precipitates from the sediment, no issues with the signal from background detrital Fe were encountered. The data revealed transformation of Fh into more stable Lp-type Fe(III) and sulfidization of Fh and Lp. Increasing sulfidization with increasing sediment depth is illustrated in **Fig. 2**, where the energy shift in the pre-edge peak and white line positions going from Fe(III) to Fe(II) is most apparent in the deepest sample (Fh_field_11.25-15).

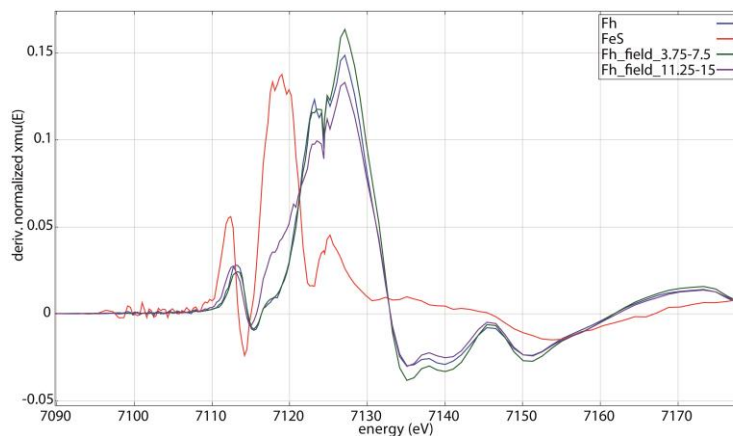


Figure 2. First derivative of normalized absorption against energy (XANES) for Fh (Fe(III), blue) and FeS (Fe(II), red) standards, and for Fh samples from the field deployed for two weeks at 3.75 – 7.5 cm (green) and 11.25 – 15 cm (purple) sediment depth.

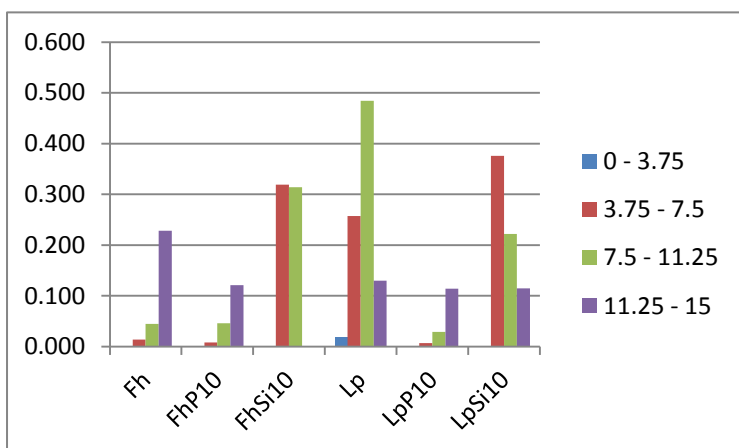


Figure 3. Fraction of Fh or Lp sulfidized during 2-week field deployment for the 4 investigated depth intervals. “10” indicates molar Fe/P or Fe/Si of 10 during mineral synthesis.

There were marked differences observed in degree of sulfidization of Fh and Lp, both with depth and between iron minerals (**Fig. 3**). In general, P-containing Fe(III) precipitates seem less sensitive to reductive transformation during the 2-week deployment in the field.

Currently, we are exploring the spatial and vertical heterogeneity in the field and its potential role in explaining the differences in transformation.