ESRF	**Experiment title:** Interrelationship between Fe speciation and P release during sulfidization of P containing Fe oxides	**Experiment number**: 26-01-1157
Beamline: BM26A	**Date of experiment**: from: 13 July, 2018 to: 16 July, 2018	**Date of report**: 18 June 2019
Shifts: 9	**Local contact(s)**: Dipanjan Banerjee	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Thilo Behrends (PI)*, Utrecht University

Case M. van Genuchten*, Utrecht University

Report:

1) Objectives. The objective of this experiment (26-01-1157) was to track the structural transformation of metastable Fe (oxyhdr)oxides during aging in solutions of different composition. We collected Fe K-edge XANES and EXAFS spectra for a matrix of experimental samples produced by exposing Fe oxides to varying the time of aging (from 1 hour to 1 year after synthesis) and the aging conditions, i.e. aerobic and anaerobic environments and presence or absence of oxyanions. In our previous DUBBLE experiments (26-01-1083), we used Fe K-edge EXAFS spectroscopy and iterative transformation factor analysis (ITFA) to determine the formation conditions of carbonate green rust and magnetite. Consequently, these synthesis conditions were followed to produce the initial Fe (oxyhydr)oxide phase. In this report, only Fe K-edge EXAFS spectra for a subset of experimental samples are given, but we note that EXAFS spectra for almost the entire proposed sample matrix were collected. These structural data will be combined with wet-chemical measurements of oxyanion uptake and/or release into solution and oxyanion speciation by X-ray absorption spectroscopy to resolve the impact of Fe phase transformation on the environmental fate of nutrients (phosphorous) and contaminants (arsenic)

2) Methods. Fe K-edge X-ray absorption spectra (XANES and EXAFS) of filtered suspensions were recorded in transmission mode out to k of 13 $Å^{-1}$ at the DUBBLE beamline (BM26A). Spectra were recorded at room temperature using ion chambers for measurements of I_0 and It. The X-ray beam diameter was approximately 1 (vertical) x 2 (horizontal) mm. The XANES region was measured with 0.3 eV steps, while step sizes of 0.05 $Å^{-1}$ were used for the EXAFS region. Two to 4 scans were collected for each sample depending on data quality. Reference Fe-bearing minerals, including lepidocrocite, green rust, magnetite, goethite, and 2-line ferrihydrite, were collected as part of our previous DUBBLE experiments (26-01-1083)

and will be used to analyse the data collected in the current experiment. Data reduction was performed with the SixPack software.

3) Results and Conclusions. Figure 1 shows the EXAFS spectra for samples of magnetite and green rust aged from 1 hour up to 1 year in anaerobic and aerobic conditions. When aged anaerobically, the magnetite synthesized in this work gains structural order over the first 6 weeks of aging. This conclusion is based on key features becoming more resolved in the EXAFS spectrum, particularly the beat feature near 5.3 $Å^{-1}$ (indicated by the * symbol), which increased in amplitude from a small shoulder initially to a well-defined oscillation after 1 year of aging. This trend was reproduced when magnetite was aged aerobically, with similar changes in the EXAFS spectra observed after only 1 hour. The major features of magnetite remained throughout the aerobic aging series, indicating that complete oxidation of magnetite to form lepidocrocite or another purely Fe(III) (oxyhydr)oxide did not occur.

Relative to magnetite, the green rust samples were less stable, displaying features in the EXAFS spectra consistent with substantial structural transformation during aging in both anaerobic and aerobic environments. In anaerobic conditions, the initial green rust transformed to magnetite after 1 year. However, the shape of the EXAFS oscillation centred near 5.3 $Å^{-1}$ in green rust aged anaerobically for 1 year indicates that the magnetite formed by green rust transformation is less ordered than the aged magnetite samples (anaerobic and aerobic). In aerobic conditions, the transformation of green rust was rapid, leading to EXAFS spectra with features indicative of lepidocrocite after 1 hour of aging. The lepidocrocite formed from green rust oxidation after 1 hour showed no signs of further structural transformation after several months of aerobic aging. Taken together, the magnetite and green rust aerobic and anaerobic aging series indicate different timescales of structural transformation depending on the initial and final Fe phase, with magnetite and lepidocrocite eventually favoured over green rust.

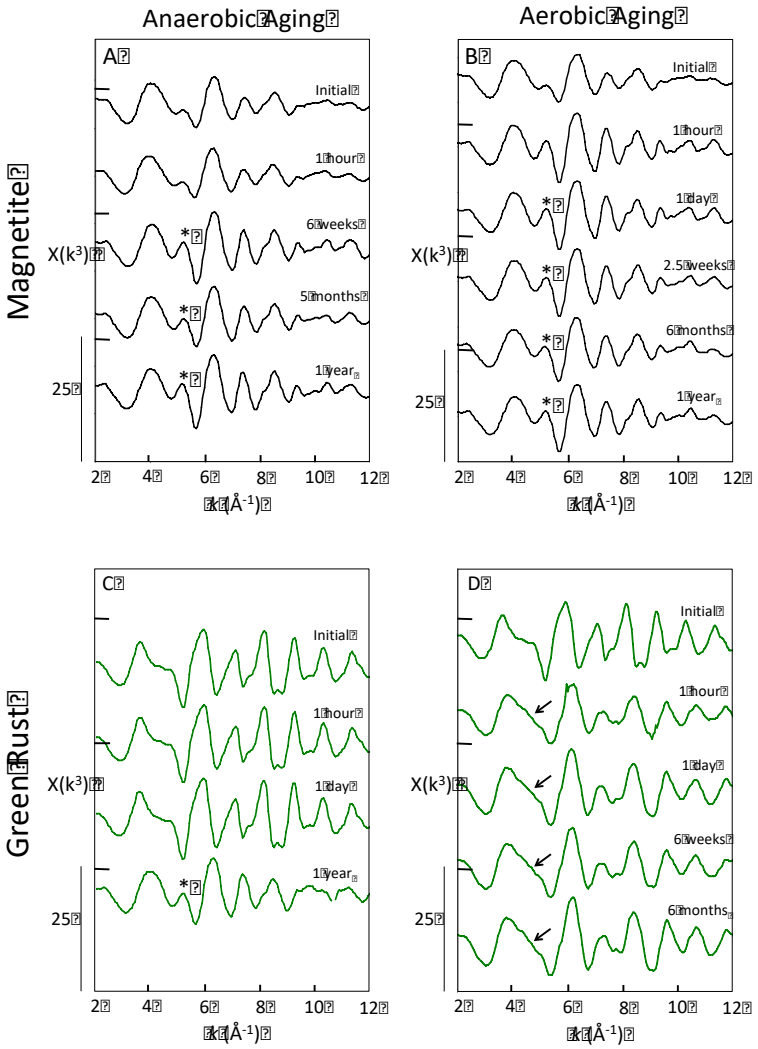

Figure 1: Fe K-edge EXAFS spectra of magnetite (top panels, A and B) and green rust (bottom panels, C and D) aged for different times in anaerobic (left panels, A and C) and aerobic (right panels, B and D) environments. The * symbol highlights spectral features indicative of crystalline magnetite, while the arrows show EXAFS features consistent with lepidocrocite.

4) Future Experiments. Based on these results, we plan to complete the Fe K-edge EXAFS data set for the aging series and investigate the speciation of oxyanions (phosphorous and arsenic) during the transformation of the Fe phase. A proposal to collect these data data has been accepted at the Stanford Synchrotron Radiation Lightsource (Menlo Park, USA).