EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

	Experiment title: Diagenesis and burial of hydrothermal iron in the deep sea	**Experiment number:** ES 1274
Beamline: BM23	**Date of experiment:** from: 3/3/23 to: 6/3/23	**Date of report:** 20/3/23
Shifts: 9	**Local contact(s):** Angelika Rose	*Received at ESRF:*

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Report:

During experiment ES 1274, we collected Fe K-edge EXAFS spectra of approximately 25 samples at beamline BM23. We brought two types of samples: (1) stacks of ~5x5-mm polyether-sulfone filter fragments with deep-sea particulate matter and (2) freeze-dried and ground sediment samples with varying Fe concentrations. At our home institute, the filter stacks were sealed in Kapton and transported to ESRF in N_2-filled, gas-tight containers. The sediment samples were brought untreated. At ESRF, in the BM23 lab, appropriate amounts of cellulose were added to prepare 5-mm-diameter pellets suitable for transmission mode (dilution of Fe-rich sediment with cellulose to obtain Fe edge jump 0.5 – 1 while keeping total absorption < 3) or fluorescence mode (Fe-poor samples, mimimal addition of cellulose to ~15 mg of sample to create robust pellet of ~0.5 mm thickness).

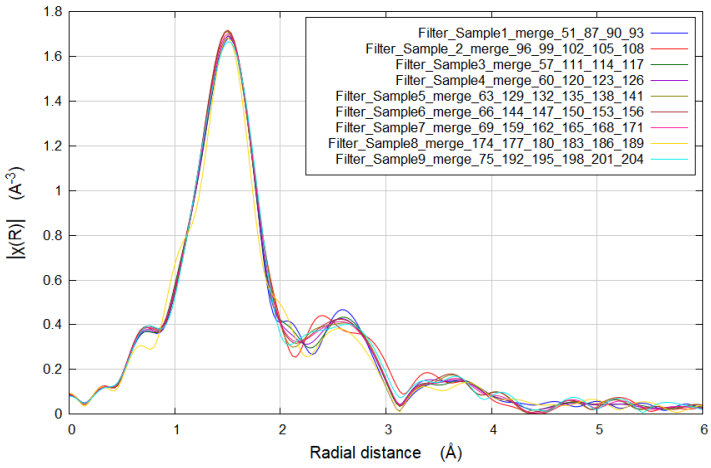

Fig. 1: Fourier-transformed spectra for water-column Fe particles

For filter stacks and pellets with dilute Fe-rich sediment, spectra were collected in transmission mode out to k = 12 with a

reference spectrum of Fe foil collected with each scan for drift correction. A first test run for all 9 filter stacks informed us on data quality, based on that 4 – 6 replicates were collected per sample. For the Fe-rich sediments analyzed in transmission mode, 3 replicates were collected. Data were of sufficient quality out to k ~10.

For 'concentrated' (i.e. minimal cellulose addition) pellets with relatively Fe-poor samples, spectra were collected in fluorescence mode with the sample holder rotated 45 degrees in y and a Vortex Si drift fluorescence detector positioned about 10 cm from the sample surface. Depending on data quality, 6 – 9 replicates were collected for each sample. Data were of sufficient quality out to k ~ 9. The setup at beamline BM23 was not suitable to obtain high-quality data for our most challenging samples in flueorescence mode (low Fe content, high $CaCO_3$ content). The thick samples did not allow for collection of useable Fe foil reference spectra; a separate Fe foil spectrum was collected after analysis of the last samples.

Spectra were aligned, normalized and merged at the beamline using Athena. The Fe K-edge EXAFS results showed suprisingly little variation, with a dominant signature of poorly-ordered Fe (oxyhydr)oxide (ferrihydrite) for all water-column and sediment samples – which cover timescales from hours (water column particulates) to hundreds or even thousands of years (buried sediment) after initial formation of the Fe species. The results support our theory that complexation of organic matter and/or silicon strongly retard crystallization of the Fe precipitates. We will attempt shell-by-shell fitting to verify signs of Fe-C or Fe-Si pairs, even though ideally data quality is higher out to k ~13 for this. Another challenge is to distinguish between poorly-ordered Fe(III) precipitates (ferrihydrite) and nano-crystalline pahses (e.g. nano-goethite), which can have similar short-range order.

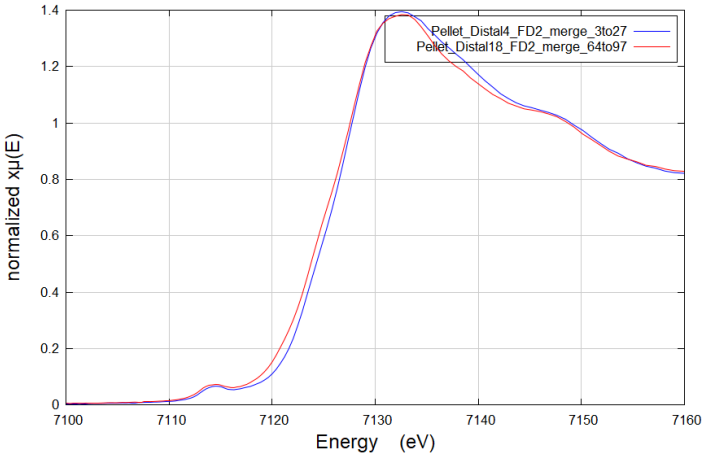

Fig. 2: Increasing contribution of Fe(II) – expressed as peak shift to lower energy – in sediment samples of increasing depth in the sediment (Distal4 = 2 cm, Distal 19 = 17 cm).

Investigation of the XANES region of samples compared to Fe(III) reference materials (ferrihydrite, goethite) revealed the presence of Fe(II), which fits with our chemical and TEM-EDX results, but any ferrous phases were not abundant enough to be apparent from preliminary linear combination fitting.

Overall, the collected data are useful in our quest to understand (lack of) iron mineral (trans)formation around hydrothermal vents in the deep sea. For analysis of water-column particles, Fe EXAFS in transmission mode using Kapton-sealed filter stacks worked well. We aim to explore such samples further in a new proposal submitted recently (ES 1359).