Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information for

Influence of Time and Ageing Conditions on the Properties of Ferrihydrite

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CONTENT

Methods of ferrihydrite synthesis under different atmosphere

Ferrihydrite synthesis. Ferrihydrite (Fh) was synthesized according to procedures described in the main text, except that separate batches of Fh were synthesized in normal atmosphere (aerobic) and inside an anaerobic glovebox (anaerobic). Briefly, a solution of 100 mM $FeCl_3 \cdot 6H_2O$ was prepared in deionized water and stirred. Care was taken to minimize contamination of NaOH with carbonate. To do this, a solution of 50% NaOH was prepared and allowed to stand to precipitate less soluble Na_2CO_3. This solution was filtered using a 0.45 µm polypropylene syringe filter prior to dilution to approximately 2 M and 0.2 M NaOH. New dilutions of NaOH were prepared each day for use from freshly dispensed deionized water. Fh was precipitated from $FeCl_3$ solution by adding 2 M NaOH dropwise until pH 5.0 and 0.2 M NaOH until pH 7.0 to 7.2 was reached. The Fh suspension was centrifuged and washed three times with deionized water and stored as a suspension of ~200 mM Fe (~20 g/L). This procedure was repeated in an anaerobic glovebox with 95% N_2/5% H_2 atmosphere maintained to <5 ppm O_2 with a Pt O_2 removing catalyst. Washing was done inside the anaerobic glovebox with N_2-sparged deionized water.

Methods for Total Inorganic Carbon Analysis.

Total inorganic carbon measurements. The total inorganic carbon concentration (TIC = dissolved carbon dioxide and carbonate species) was measured using the TIC apparatus of a Shimadzu TOC-V instrument and a liquid autosampler. Aliquots of ferrihydrite suspensions were placed in EPA VOA vials and sealed with parafilm and analyzed immediately after preparation. The whole ferrihydrite suspension TIC was measured by injection of 250 to 500 µL aliquots, depending on assumed TIC concentration, into a 25% v/v phosphoric acid solution in deionized water. During the sparging and measurement of TIC the ferrihydrites were observed to dissolve into the phosphoric acid solution. TIC concentrations were standardized with dilutions of a 1,000 mg/L TIC bicarbonate-carbonate buffer (500 mg/L of $NaHCO_3$ and 500 mg/L Na_2CO_3) with a standard curve to 20 mg/L TIC. Blanks were acidified with 500 µL 0.1M HCl and sparged with 99.999% N_2 gas. Diluent solutions were first sparged with 99.999% N_2 gas to remove dissolved CO_2. Analysis of a batch of air synthesized and air aged ferrihydrite was done to quantify analytical variability (1σ) due to the non-standard measurement of TIC of suspended particles. Analysis of six aliquots of the suspension yielded TIC of 0.82 ± 0.0077 mmole C L^{-1} suggesting that the variability in the measurement is due to batch-to-batch variability rather than instrumental variability.

Differences in suspension TIC were evaluated using two-factor ANOVA with replication in Microsoft Excel as a function of both synthesis condition and aging condition. Data at one day and approximately two weeks were taken together given little difference in TIC over this time period (**Table S1**).

TIC removal and pH change during sparging. The loss of TIC and change in pH of a suspension of ferrihydrite was measured by sparging 20 mL of ferrihydrite suspension with 150 mL/min of 99.999% N_2 gas. The pH was monitored for 260 minutes and aliquots of the initial suspension and final suspension were used for TIC measurement.

Synthesis condition	Aging condition	Batch	Aging time (days)	pH	Suspension TIC (mmoles C L^{-1})
Air	Air	1	1	4.72	1.36
		1	16	4.81	1.12
		1	42	5.37	1.42
Air	Air	2	1	4.71	0.54
		2	12	4.67	0.56
Air	Air	3	41	-	0.82 ± 0.008†
Air	Glovebox	1	1	4.92	1.36
		1	15	5.30	0.80
		1	41	5.12	0.89
Air	Glovebox	2	0	4.46	0.94
		2	9	4.41	0.92
Glovebox	Glovebox	1	9	5.12	0.33
		1	34	5.05	0.44
Glovebox	Glovebox	2	2	4.73	0.33
		2	13	4.78	0.35
Glovebox	Air	1	8	5.46	0.45
		1	33	5.50	0.55
Glovebox	Air	2	2	4.70	0.27
		2	11	5.01	0.41

Table S1: Effect of synthesis and aging conditions on total suspension inorganic carbon (TIC) in ferrihydrite suspensions. †Analysis of a third batch of air synthesized and air aged ferrihydrite was done to quantify analytical variability (1σ) due to the non-standard measurement of suspended Fh particles with TIC analysis.

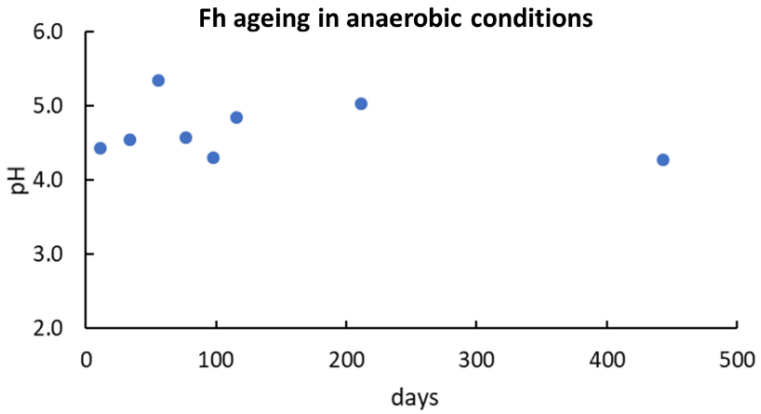

Figure S1: Time-evolution of the pH as function of Fh ageing under anaerobic conditions.

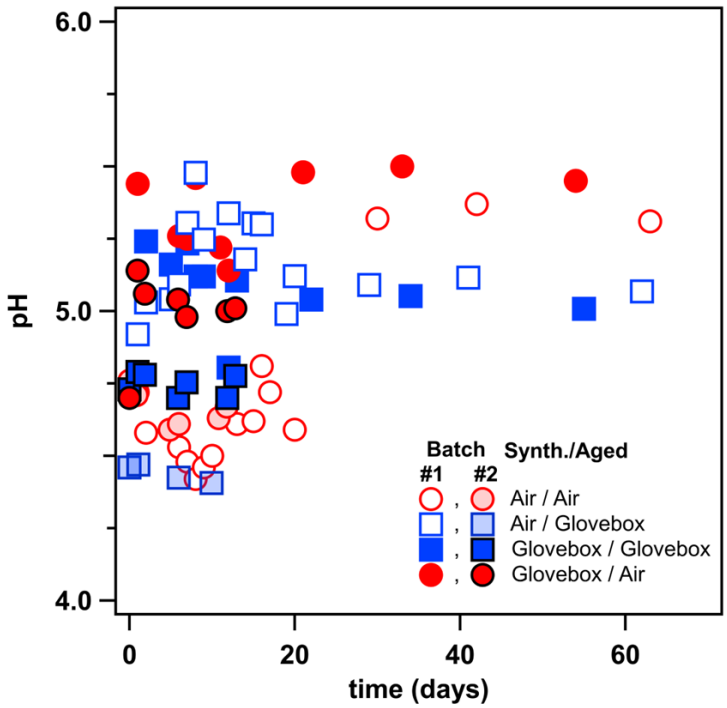

Figure S2: Measured pH of ferrihydrite suspensions of ~20 g/L ferrihydrite as a function of time, synthesis conditions, and aging conditions. The difference in marker types of open markers and light shading and filled markers and black borders representing Batch 1 and Batch 2, respectively. Air/Air denotes that the ferrihydrite was synthesized in air and aged in air, Air/Glovebox denotes that the ferrihydrite was synthesized in air and aged inside an anoxic glovebox with 93% N_2/7% H_2 atmosphere with <1 ppm O_2.

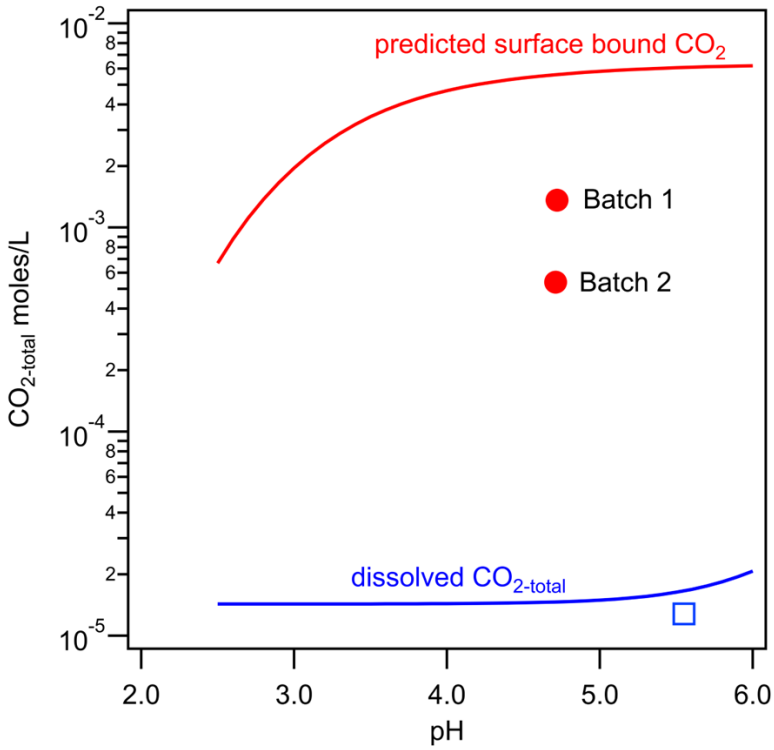

Figure S3: Dissolved and surface-bound CO_2 species calculated for 420 ppm CO_2 and 20 g/L ferrihydrite loadings. Calculations were done in Visual MINTEQ using the Dzombak and Morel Double Layer Model[1] and surface complexation data from Zachara *et al.*[2] and Appelo *et al.*[3] Red markers reflect the measured TIC for air synthesized-air aged ferrihydrite batches (Table S1), and the blue marker represents the pH and TIC content of air-saturated water measured in the laboratory.

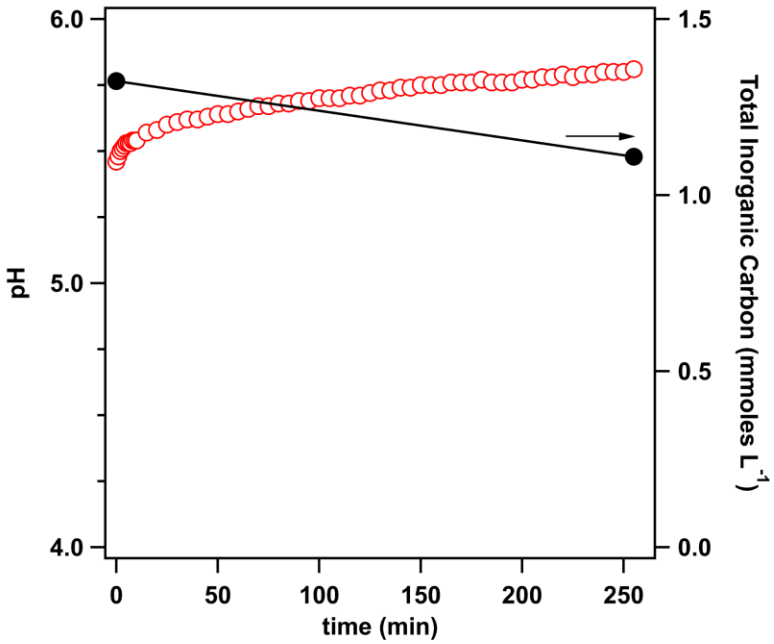

Figure S4: pH and TIC content of 20 g/L ferrihydrite suspension during sparging with 99.999% N_2 gas over three hours.

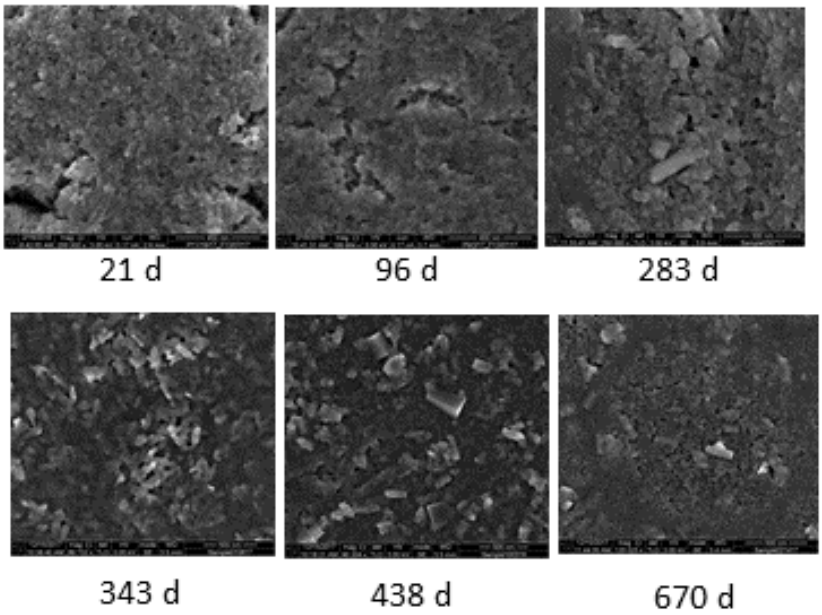

Figure S5: SEM images of Fh ageing synthesized in aerobic and aged in anaerobic conditions.

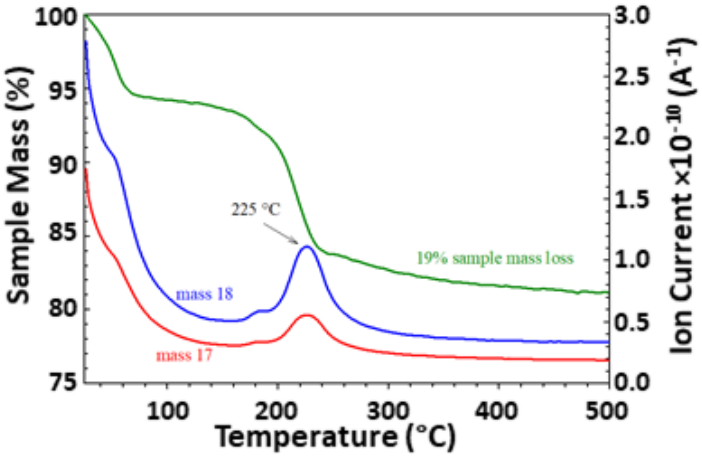

Figure S6: TGA-MS results for the reference goethite sample.

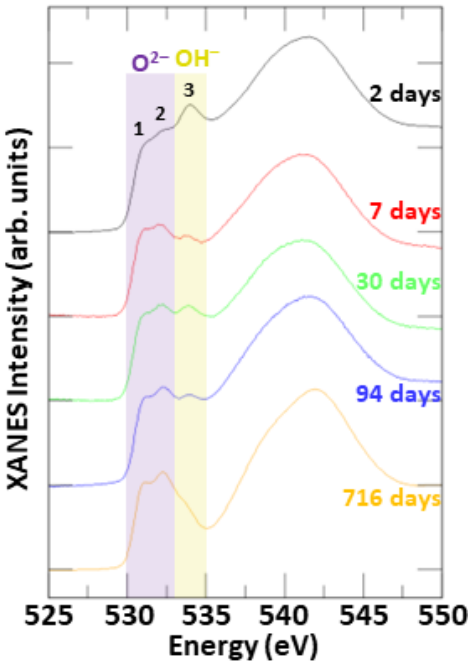

Figure S7: O K-edge spectra of Fh synthesized in aerobic and aged in anaerobic conditions as function of ageing. The energy regions associated to OH^- and O^{2-} have been highlighted.

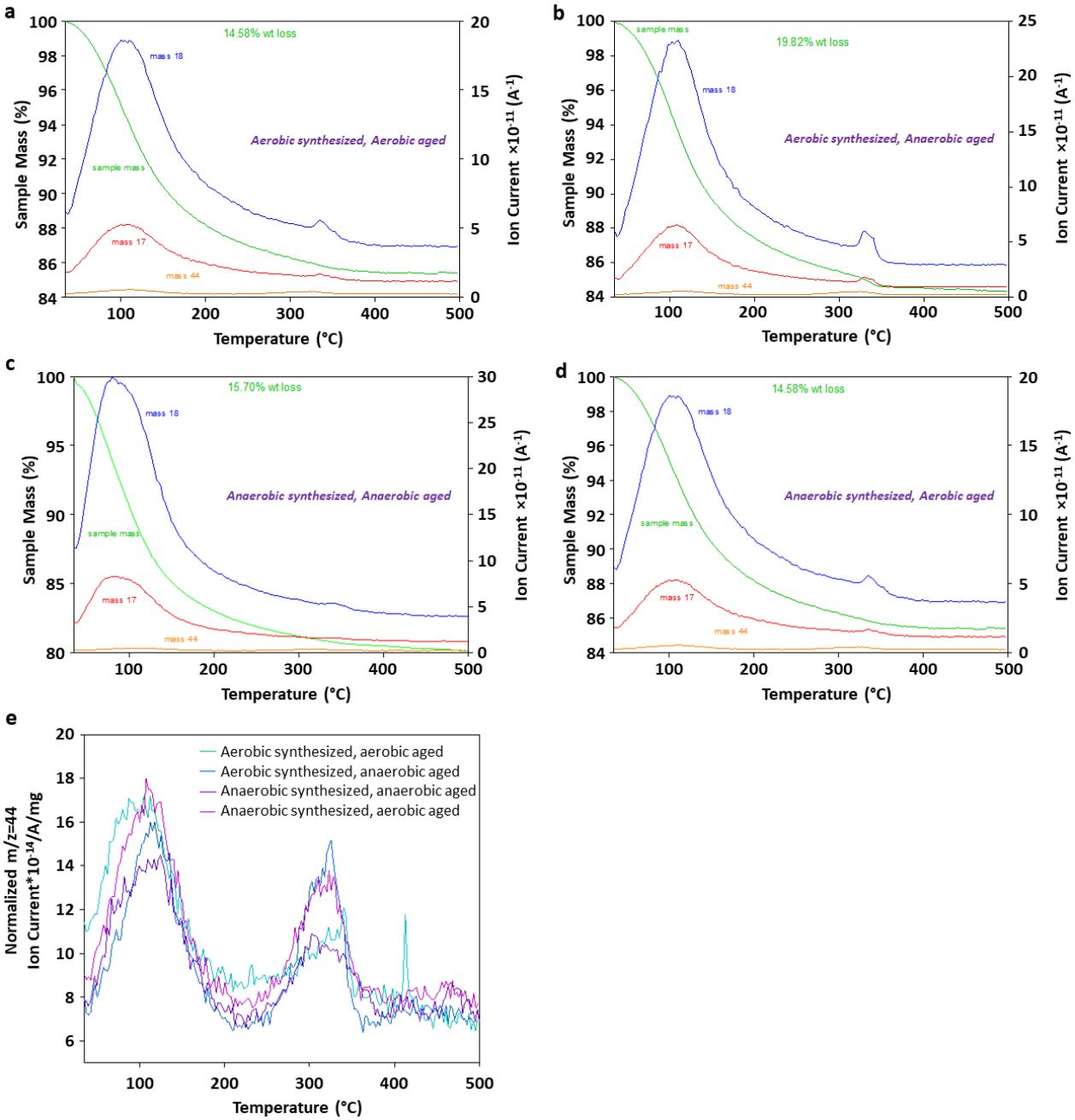

Figure S8: (a-d) TGA-MS measurements conducted on (~7-14 days old) Fh samples that were synthesized and aged in four combinations of aerobic and anaerobic environments. (e) Measure of CO_2 incorporation for the four combinations of aerobic and anaerobic environments.

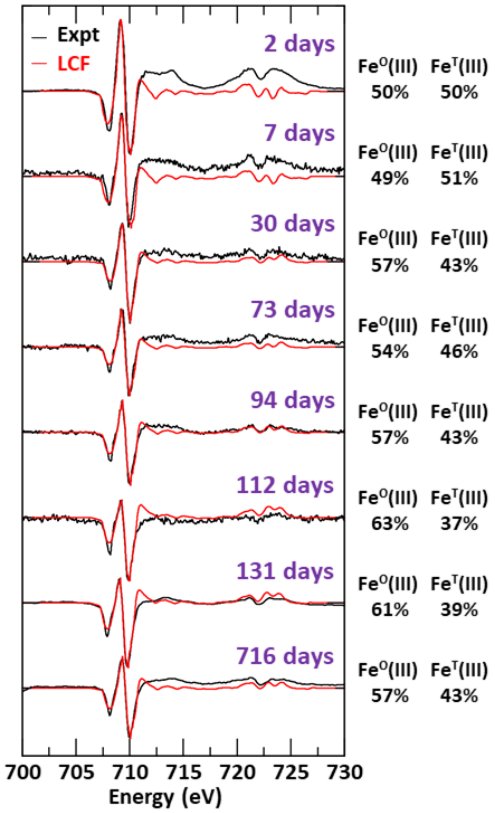

Figure S9: Linear combination fits (LCF) of experimental Fe $L_{2,3}$-edges XMCD spectra of Fh samples synthesized in aerobic and aged in anaerobic conditions as function of time. The linear combination fits used two ligand field multiplets calculated Fe(III) components, octahedral and tetrahedral, labelled as Fe^{O}(III) and Fe^{T}(III) respectively.

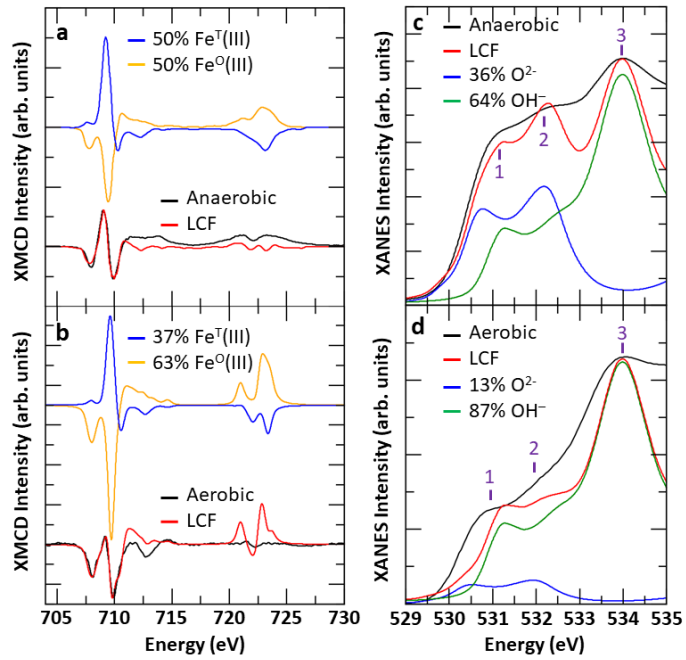

Figure S10: Linear combination fits (LCF) of (a, b) Fe $L_{2,3}$-edges XMCD and (c, d) O K-edge XANES of fresh Fh samples synthesized in aerobic conditions and aged in (a, c) anaerobic and (b, d) aerobic conditions.

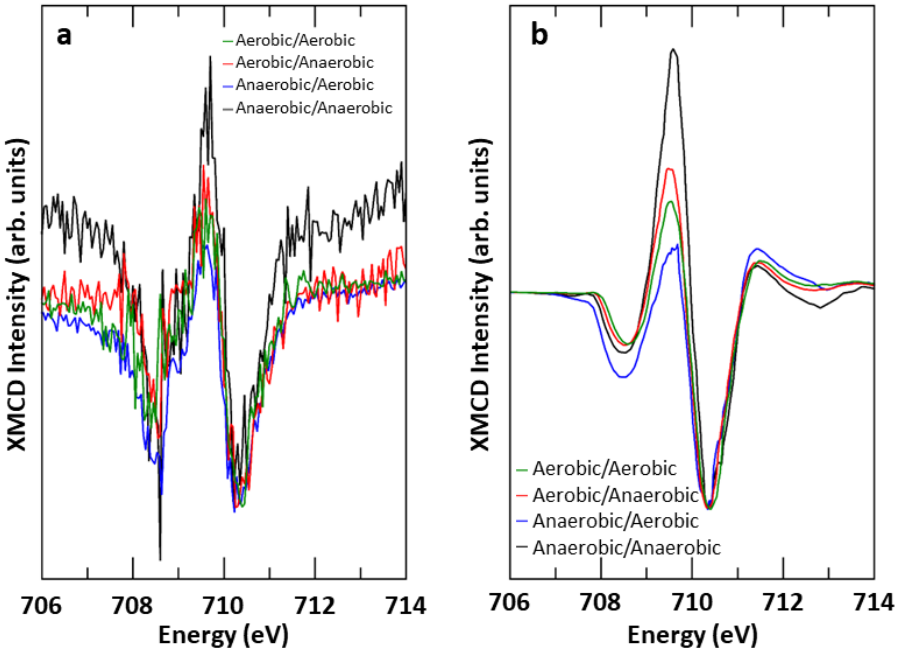

Figure S11: (a) Experimental Fe L-edge XMCD spectra and (b) corresponding linear combination fits for fresh (2 days old) Fh samples synthesized in either aerobic and anaerobic conditions and aged in either aerobic and anaerobic conditions.

References:

1. Dzombak, D. A.; Morel, F. M. M. Surface Complexation Modeling: Hydrous Ferric Oxide. *John Wiley & Sons: New York* **1990**, p 393.
2. Zachara, J. M.; Girvin, D. C.; Schmidt, R. L.; Resch, C. T. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. *Environ. Sci. Technol.* **1987**, *21*, 589-594.
3. Appelo, C. A. J.; Van der Weiden, M. J. J.; Tournassat, C.; Charlet, L. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* **2002**, *36*, 3096-3103.