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

Supporting Information

for

Sulfidation Mechanisms of Fe(III)-(oxyhydr)oxide Nanoparticles: A Spectroscopic Study

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Figure S1: X-ray diffractogram of unreacted ferrihydrite (2-Line), goethite, and hematite nanoparticles

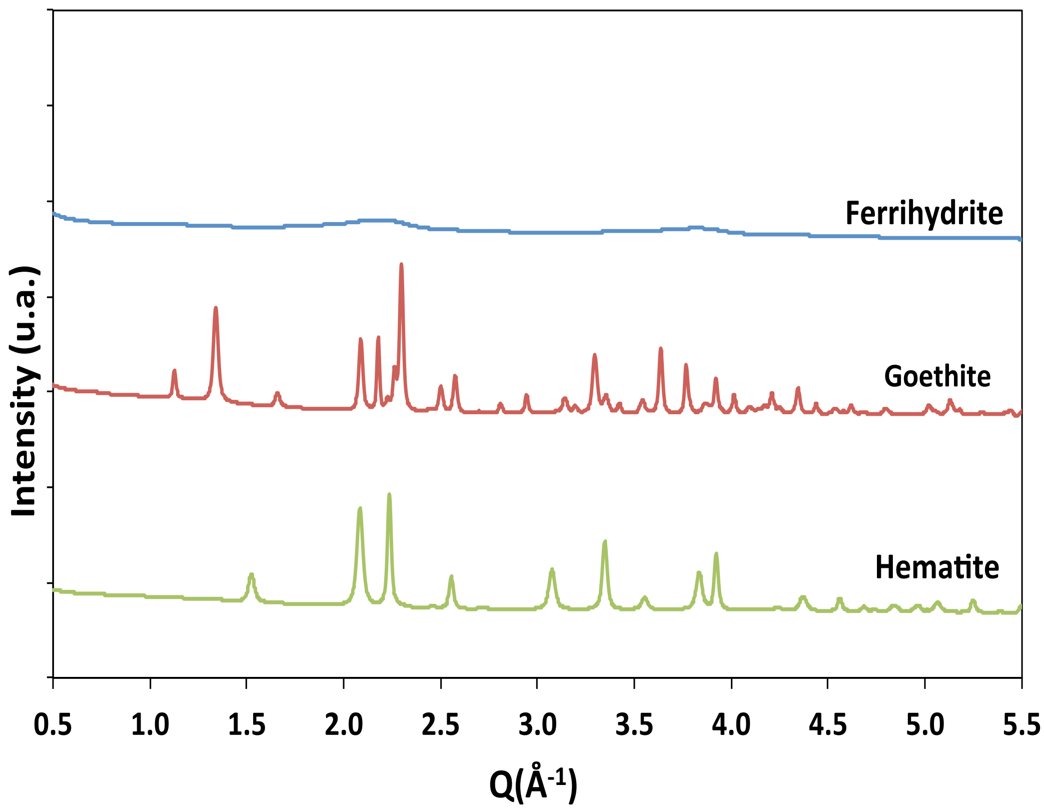


Figure S-2: **Reconstruction of the whole set of experimental EXAFS spectra from the reaction of ferrihydrite with dissolved sulfide at various S/Fe ratios with (a) the first, (b) the two first, (c) the three first, and (d) the four first components extracted by the PCA procedure. Black and red lines correspond, respectively, to experimental and reconstructed data.**

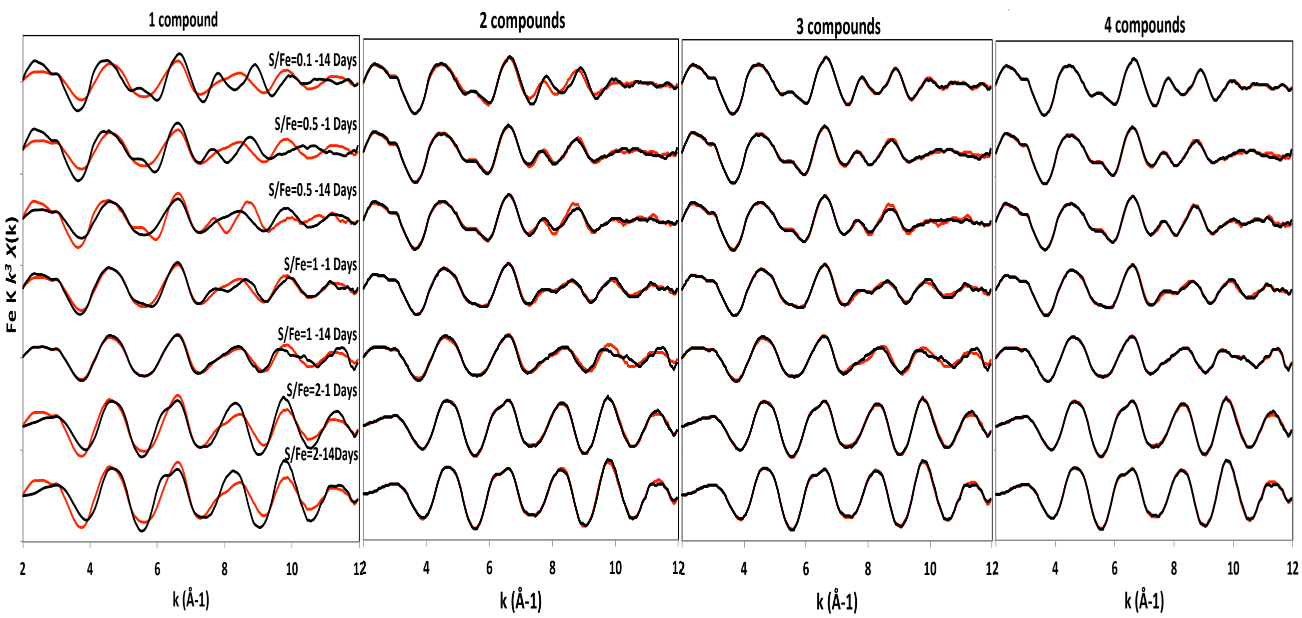


Figure S3. Variance derived from Principal Component Analysis (PCA) of 24 bulk S-*K*-edge XANES spectra

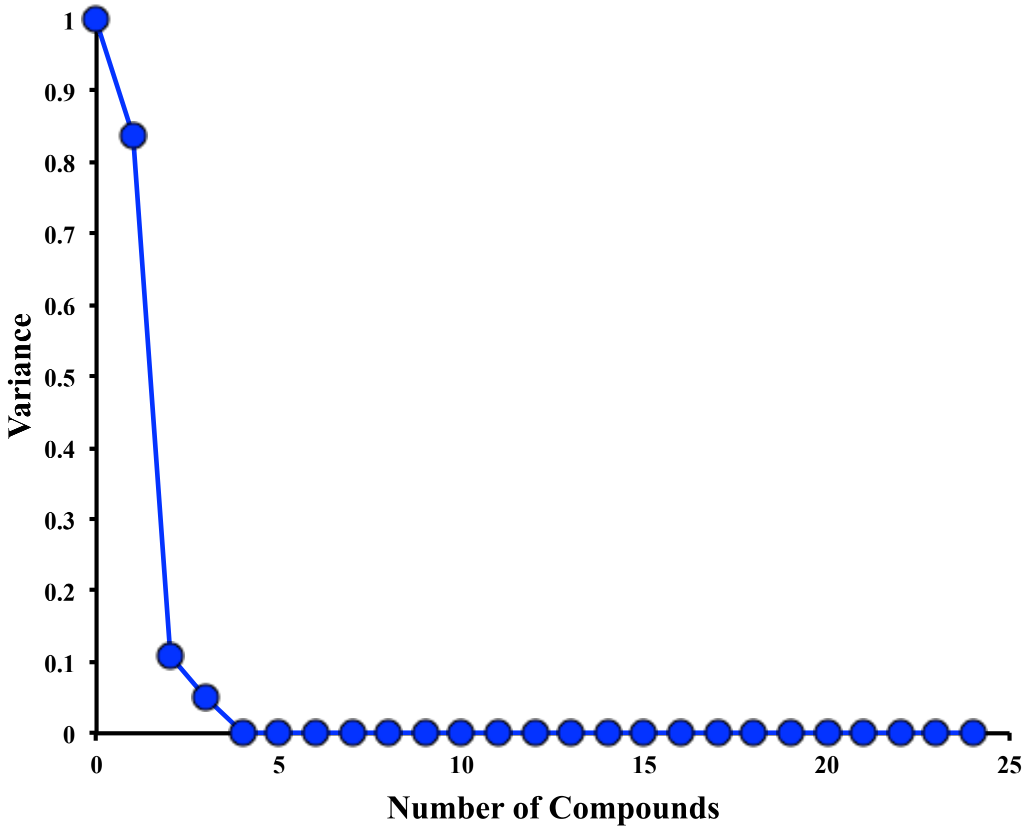


Table S1. **Results of the Principal Component Analysis (PCA) performed on the Fe-*K*-edge EXAFS spectra from the reaction of ferrihydrite with dissolved sulfide at various S/Fe ratios**

Component	**Eingenvalue**	**Variance**	**Cumulative variance**	**Indicator Function**
1	46.439	0.755	0.755	0.15517
2	13.658	0.222	0.978	0.01462
3	0.701	0.011	0.989	0.01311
4	0.373	0.006	0.995	0.01231
5	0.176	0.002	0.998	0.0134
6	0.072	0.001	0.999	0.0262
7	0.021	0	1	NA

Table S2: Results of Target Transformation performed on the Fe-*K*-edge EXAFS spectra from various model compounds using the first three principal components obtained by PCA (Tabe S1).

Reeference	$NSSR_{TT}^{(1)}$	R Value	SPOIL
Ferrihydrite initial	25.5191	0.02219	0
Ferrihydrite- 6L	62.63707	0.03574	0
Ferrihydrite-2L	67.12988	0.0394	0
Schwertmannite	164.62148	0.07419	0
Goethite Initial	328.86008	0.14468	0
Oxidized Mackinawite	222.42799	0.27627	0.3826
Pre-oxidized Mackinawite	798.79697	0.27627	0.3826
Magnetite	853.39351	0.36241	1.345
Pyrite	2351.01149	0.38527	1.0646
$FeCl_3$	1068.38247	0.39783	0.39783
Pyrrhotite	1031.45748	0.54252	0.54252
Mackinawite	1835.49505	0.61896	0.63213
Lepidocrosite	2790.36652	0.77665	0.6119
Marcasite	3376.84199	0.6863	1.1151
Green Rust (SO_4)	895.94946	0.79698	1.9875
Greigite	916.16537	0.83186	0.3488
Troillite	821.82264	0.89005	0.5186
FeO	2052.2323	0.89013	2.1396
$FeSO_4$	1823.4491	0.94838	1.2127

SPOIL classification (Malinowski 1978): 0-1.5, excellent, 1.5-3 good, 3-4.5, fair; 4.5-6 acceptable; and >6, unacceptable reference.
NSSR- Normalized Sum of Squared Residual (NSSR= $\sum(k^3 \chi Target - k^3 \chi_{Transform})^2 / \sum(k^3 \chi_{Target})^2$)

Figure S-3: (A) S-*K*-edge XANES spectra of reference sulfur compounds (B) S-*K*-edge XANES spectra of reference iron sulfide compounds. All measurements were taken using the same experimental setup at BL 4-3 at the Stanford Synchrotron Radiation Lightsource (SSRL).

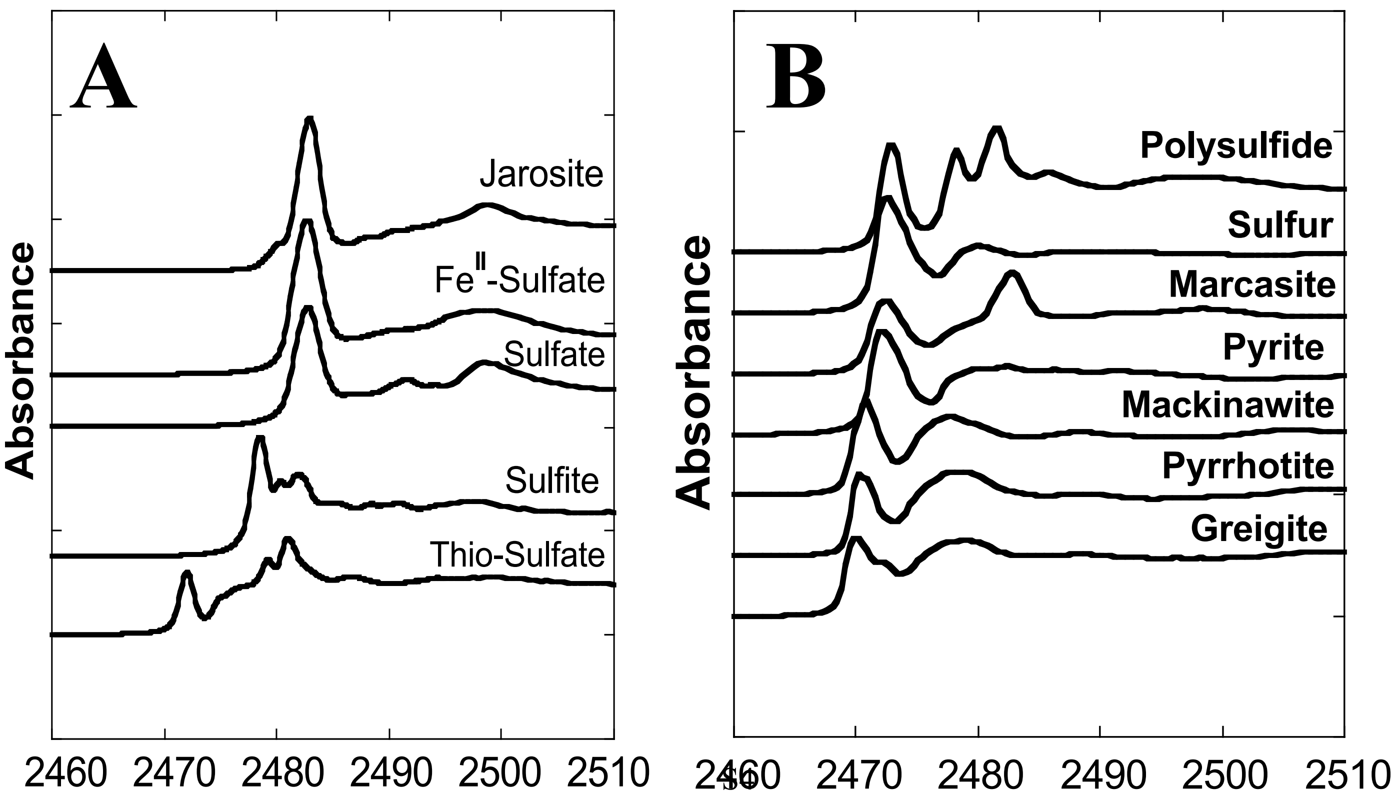
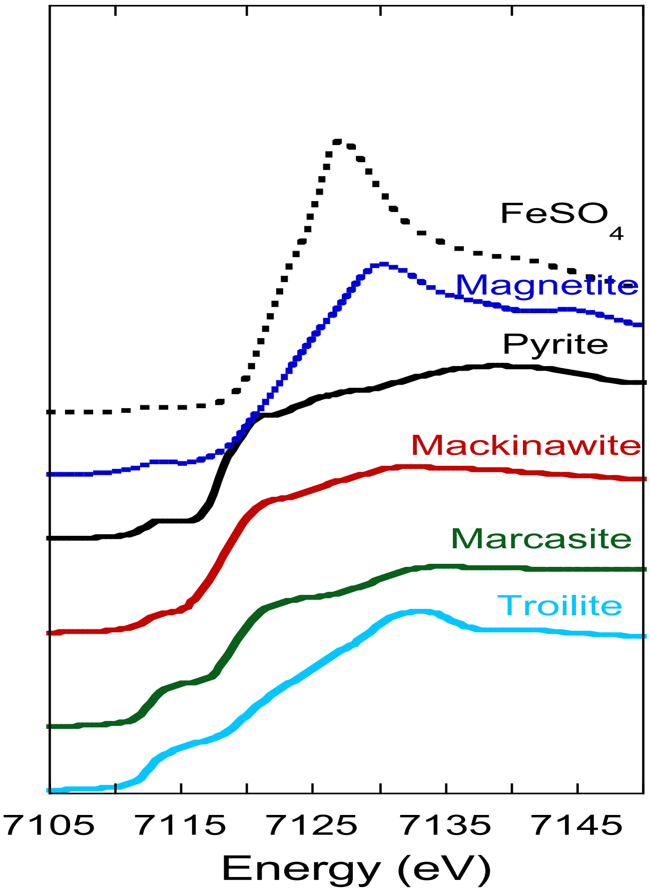


Figure S-4. Fe-*K*-edge XANES spectra of iron-containing reference compounds collected at BL 7-3 of SSRL at 10K using a LHe cryostat.



Model Compounds for X-Ray absorption spectroscopy analysis (XAS)

Model compounds for S-*K*-edge XAS analysis:

Spectra of reference compounds were collected at beamline 4-3 at SSRL using the same experimental setup as the sulfidized Fe(III)-(oxyhydr)oxide nanoparticle samples. Reference compounds included: SO_4^{2-} as Na_2SO_4; thiosulfate as $Na_2S_2O_3$, sulfite as Na_2O_3S; iron disulfides as pyrite FeS_2 (synthesized as described in Ikagou *et al.* 2015), iron monosulfide, a laboratory synthesized mackinawite (as described in Ikagou *et al.* 2015), and elemental sulfur (from the Stanford mineral collection). Phase purity of the synthesized compounds (mackinawite and pyrite) and elemental sulfur was determined by x-ray diffraction analysis prior to XAS analysis.

Model compounds for Fe-*K*-edge XAS analysis:

Fe *K*-edge XAS spectra of initial compounds (*i.e.* ferrihydrite, goethite, and hematite nanoparticles synthesized for this study) were also used as reference compounds for LCF. Fe-sulfide reference spectra for mackinawite and pyrite were taken from the same synthesized samples as for S-*K*-edge. All other Fe-*K*-edge XAS spectra were from our reference data collection as described in detail by Noel *et al.*, 2017.

Figure S5: Derivatives of (A) ferrihydrite (B) goethite and (C) hematite XAS spectra. Ferrihydrite (A) shows a clear transition suggesting new species formation at a S/Fe ratio > 0.5. Goethite and hematite do not show significant changes.

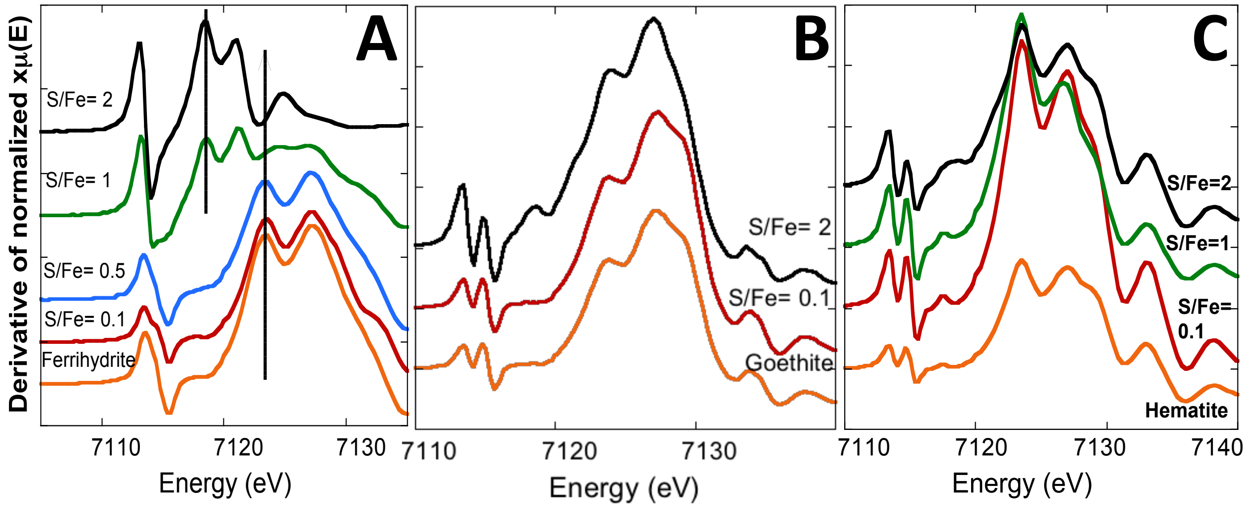


Table S3: PCA analysis and Target Transfer analysis for S-K-edge EXAFS

Compound	Eigen	Var	Cum Var[a]	IND[b]
Comp1	4.91	0.836	0.836	0.00027
Comp2	0.636	0.108	0.944	0.00012
Comp3	0.292	0.049	0.994	7.98e-06
Comp4	0.011	0.001	0.996	6.28e-06
Comp5	0.009	0.001	0.997	3.79e-06
Comp6	0.004	0.000	0.998	2.60e-06
Comp7	0.002	0.000	0.999	1.80e-06
Comp8	0.001	0.000	0.999	1.46e-06
Comp9	0.001	0.000	0.999	1.14e-06
Comp10	0.000	0.000	0.999	8.31e-07
Comp11	0.000	6.30e-05	0.999	7.95e-07
Comp12	0.000	4.98e-05	0.999	7.73e-07
Comp13	0.000	4.17e-05	0.999	7.42e-07
Comp14	0.000	3.48e-05	0.999	6.83e-07
Comp15	0.000	2.60e-05	0.999	6.29e-07
Comp16	0.000	1.93e-05	0.999	5.64e-07
Comp17	6.69e-05	1.13e-05	0.999	5.95e-07
Comp18	4.62e-05	7.88e-06	0.999	7.00e-07
Comp19	4.01e-05	6.83e-06	0.999	8.38e-07
Comp20	3.69e-05	6.28e-06	0.999	9.03e-07
Comp21	1.84e-05	3.14e-06	0.999	1.42e-06
Comp22	1.48e-05	2.52e-06	0.999	2.94e-06
Comp23	1.30e-05	2.22e-06	0.999	1.03e-05
Comp24	1.03e-05	1.75e-06	1.0	NA

Table S4. Target testing of reference spectra using the first four components obtained by PCA (S3). The model compounds yielding SPOIL values below 6 but higher than 0.15 were not considered as possible components. Minimally oxidized mackinawite: synthetic FeS exposed to sub-stoichiometric amounts of weak oxidants or Fe^{3+}.

Reference compounds	Chi Sq	R[a]	SPOIL
Elemental Sulfur	1.72329	0.01825	2.5121
Minimally Ox.Mack	3.88869	0.05622	5.8684
Polysulfides	8.03231	0.05507	5.8101
Thiosulfate	5.84479	0.06604	2.2190
Jarosite	5.31753	0.07522	5.3523
Greigite	5.31753	0.07522	8.3523
Pyrite	7.02439	0.07710	9.5132
Na Sulfite	29.1777	0.08974	6.0348
Marcarssite	8.96939	0.10088	10.4628
Pyrrothite	10.74290	0.12983	7.7034
FeII Sulfate	49.01836	0.14212	9.7999
Troilite	11.17527	0.14511	6.3461
Arcanite	35.33255	0.15164	5.3014
Na Sulfate	39.95255	0.17229	14.1728
Malenterite	27.99072	0.18425	5.8153
Mackinawite	15.67636	0.20129	8.8299
Rhomboclase	26.80198	0.20491	7.0944

K2SO4	169.98442	0.23460	4.3631
Anhydrite	193.39713	0.24200	3.0616
Quenstedtite	30.26299	0.26925	8.7005

[a] $R_{TT} = \Sigma\, (k^3\chi_{exp} - k^3\chi_{model})^2 / \Sigma\, (k^3\chi_{model})^2$

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Figure S6: Background-subtracted and k^3- weighted Fe-*K*-edge EXAFS spectra of ferrihydrite, goethite, and hematite at different S/Fe ratios

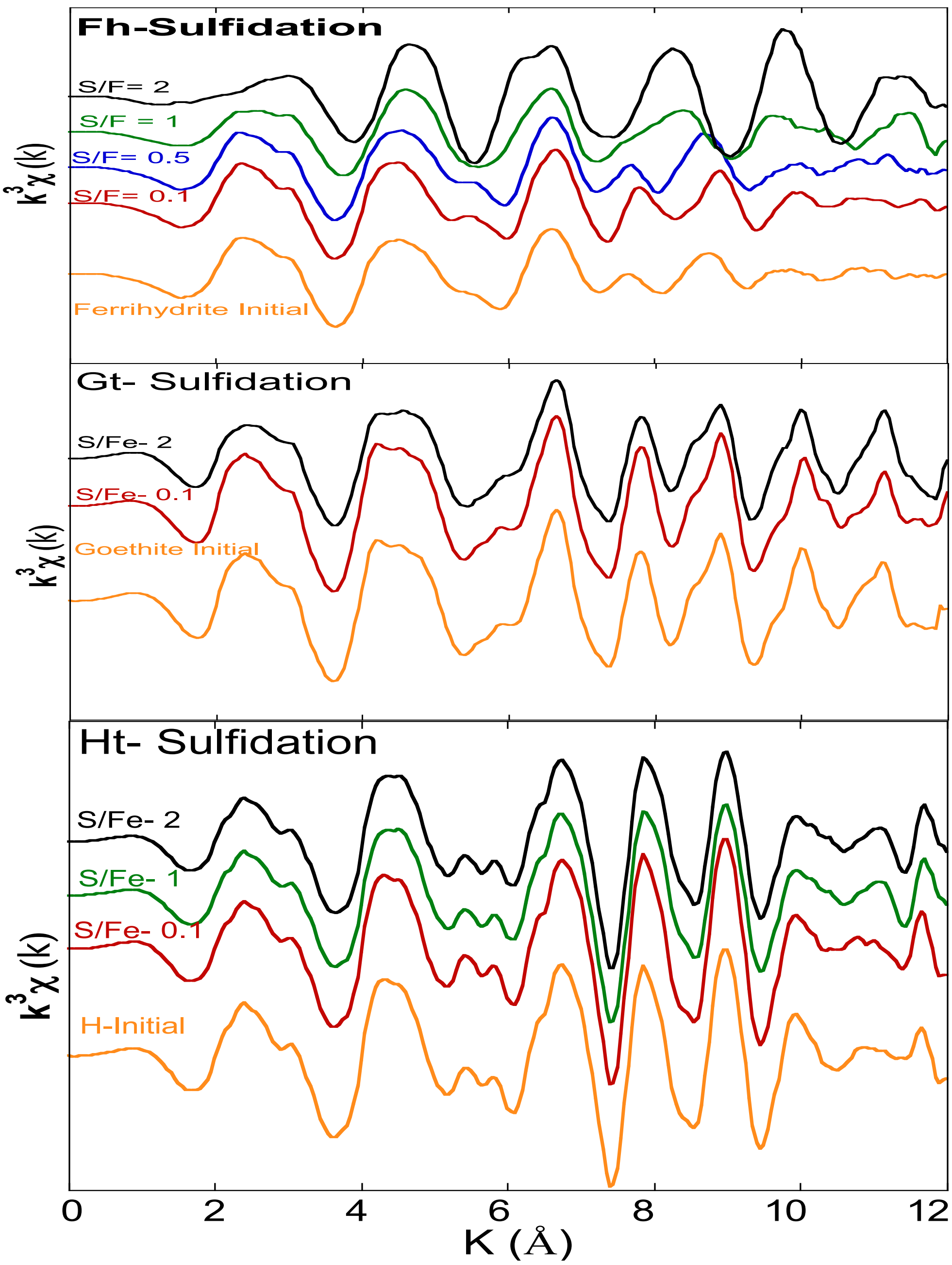


Table S5: Results of linear combination fitting (LCF) for Fe *K*-edge XANES spectra of ferrihydrite, goethite, and hematite nanoparticles at different S/Fe ratios following reaction with dissolved sulfide.

S/Fe ratio	Ferrihydrite	Goethite	Hematite
0.1	Ferrihydrite- 102% R-factor- $9.57\ 10^{-5}$ Reduced Chi-square $2.76\ 10^{-5}$	Goethite- 99 % Total- 99% R-factor- $1.72\ 10^{-5}$ Reduced Chi-square $5.5\ 10^{-6}$	Hematite- 101% Total- 101% R-factor- $1.04\ 10^{-4}$ Reduced Chi-square $2.8\ 10^{-4}$
0.5	Ferrihydrite- 94% Mackinawite- 4% Total – 98% R-factor- $4.01\ 10^{-5}$ Reduced Chi-square $1.12\ 10^{-5}$	Goethite- 97% Total- 97% R-factor- $7.3\ 10^{-4}$ Reduced Chi-square $8.2\ 10^{-5}$	Hematite- 97% Total- 97% R-factor- $6.24\ 10^{-5}$ Reduced Chi-square $1.4\ 10^{-5}$
1	Ferrihydrite- 47% Mackinawite- 49% Total – 96% R-factor- $6.24\ 10^{-5}$ Reduced Chi-square $1.4\ 10^{-5}$	Goethite- Mackinawite- Total- R-factor- $6.24\ 10^{-5}$ Reduced Chi-square $1.4\ 10^{-5}$	Hematite- 91% Mackinawite- 11% Total- 102% R-factor- $5.41\ 10^{-4}$ Reduced Chi-square $1.4\ 10^{-4}$
2	Mackinawite- 100% R-factor- $3.24\ 10^{-5}$ Reduced Chi-square $6.14\ 10^{-5}$	Goethite- Mackinawite- Total- R-factor- $7.02\ 10^{-4}$ Reduced Chi-square $2.07\ 10^{-4}$	Hematite- 82% Mackinawite- 21% Total- 103% R-factor- $2.09\ 10^{-4}$ Reduced Chi-square $5.59\ 10^{-5}$

Table S6: Results of linear combination fits (LCF) for S-*K*-edge XANES spectra following reaction of ferrihydrite, goethite, and hematite nanoparticles with dissolved sulfide at different S/Fe ratios.

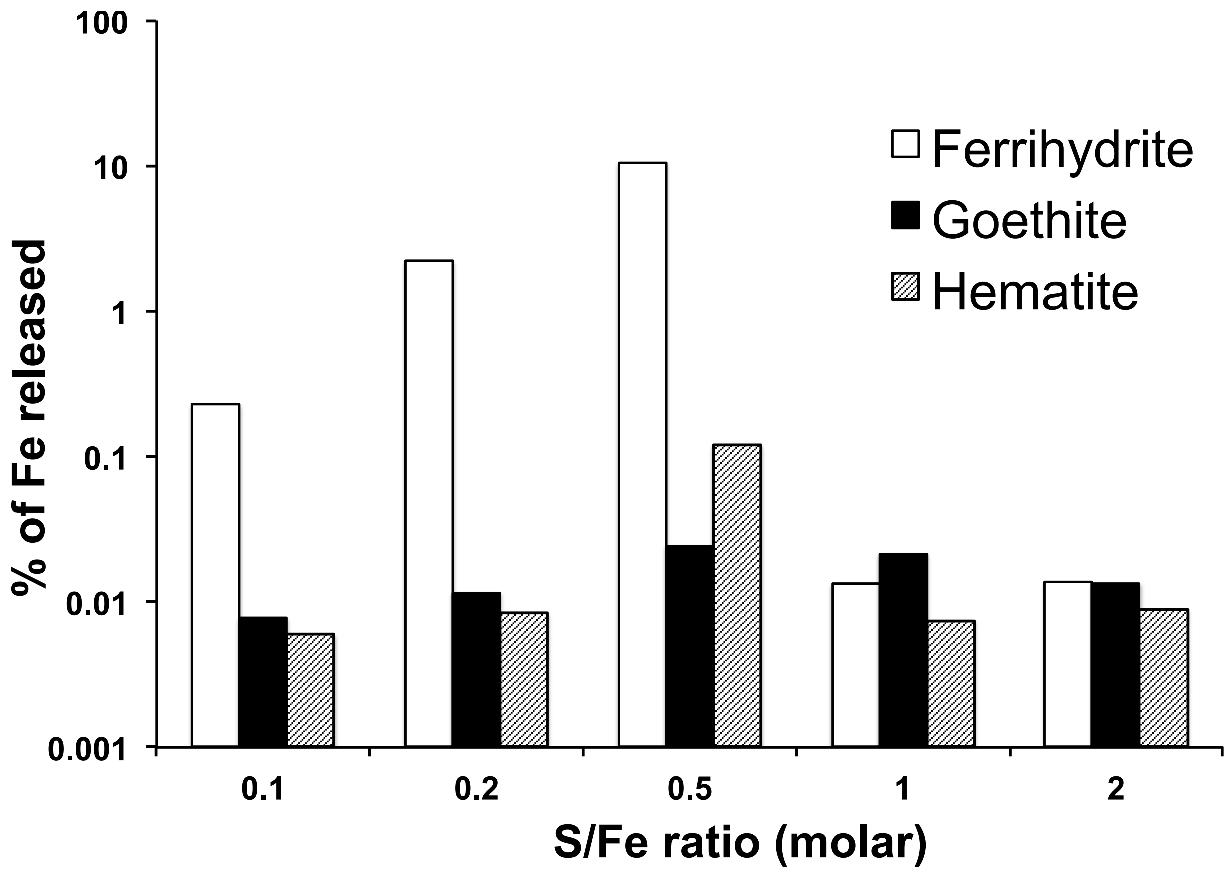
S/Fe ratio	Ferrihydrite		Goethite		Hematite	
0.1	Mackinawite-	0	Mackinawite-	0	Mackinawite-	0
	Sulfur (S^0) –	96	Sulfur (S^0) –	20.2	Sulfur (S^0) –	45.4
	Polysulfide -	4	Polysulfide -	62	Polysulfide -	3
	Thiosulfate -	0	Thiosulfate -	4.4	Thiosulfate -	42.6
	Sulfate -	0	Sulfate -	13.4	Sulfate -	9
	R-factor-	0.0652689	R-factor-	0.068611	R-factor-	0.0356345
	Reduced Chi-square	0.0243348	Reduced Chi-square	0.0280754	Reduced Chi-square	0.0124224
0.5	Mackinawite-	0	Mackinawite-	0	Mackinawite-	0
	Sulfur (S^0) –	80.3	Sulfur (S^0) –	41	Sulfur (S^0) –	63
	Polysulfide -	12	Polysulfide -	2	Polysulfide -	2
	Thiosulfate -	7.3	Thiosulfate -	57	Thiosulfate -	35
	Sulfate -	0	Sulfate -	0	Sulfate -	0
	R-factor-	0.0400926	R-factor-	0.0146188	R-factor-	0.015799
	Reduced Chi-square	0.0113898	Reduced Chi-square	0.0046066	Reduced Chi-square	0.0047396
1	Mackinawite-	68	Mackinawite-	55.9	Mackinawite-	62.3
	Sulfur (S^0) –	11.8	Sulfur (S^0) –	29.7	Sulfur (S^0) –	14
	Polysulfide -	20	Polysulfide -	0	Polysulfide -	8
	Thiosulfate -	0	Thiosulfate -	14.4	Thiosulfate -	15.7
	Sulfate -	0	Sulfate -	0	Sulfate -	0
	R-factor-	0.0026806	R-factor-	0.0082647	R-factor-	0.025799
	Reduced Chi-square	0.0004932	Reduced Chi-square	0.0016948	Reduced Chi-square	0.0047396
2	Mackinawite-	87.8	Mackinawite-	64.4	Mackinawite-	74
	Sulfur (S^0) –	8.1	Sulfur (S^0) –	9.4	Sulfur (S^0) –	10
	Polysulfide -	4.1	Polysulfide -	0	Polysulfide -	5
	Thiosulfate -	0	Thiosulfate -	26.2	Thiosulfate -	11
	Sulfate -	0	Sulfate -	0	Sulfate -	0
	R-factor-	0.002932	R-factor-	0.005848	R-factor-	0.0029376
	Reduced Chi-square	0.0005922	Reduced Chi-square	0.0012109	Reduced Chi-square	0.00017924

<u>Fe-Dissolution rates</u>:- R (mol.m^2.day^{-1})

$$R = \frac{d[Fe^{2+}{}_{aq}]}{\mathrm{A}\,dt}$$

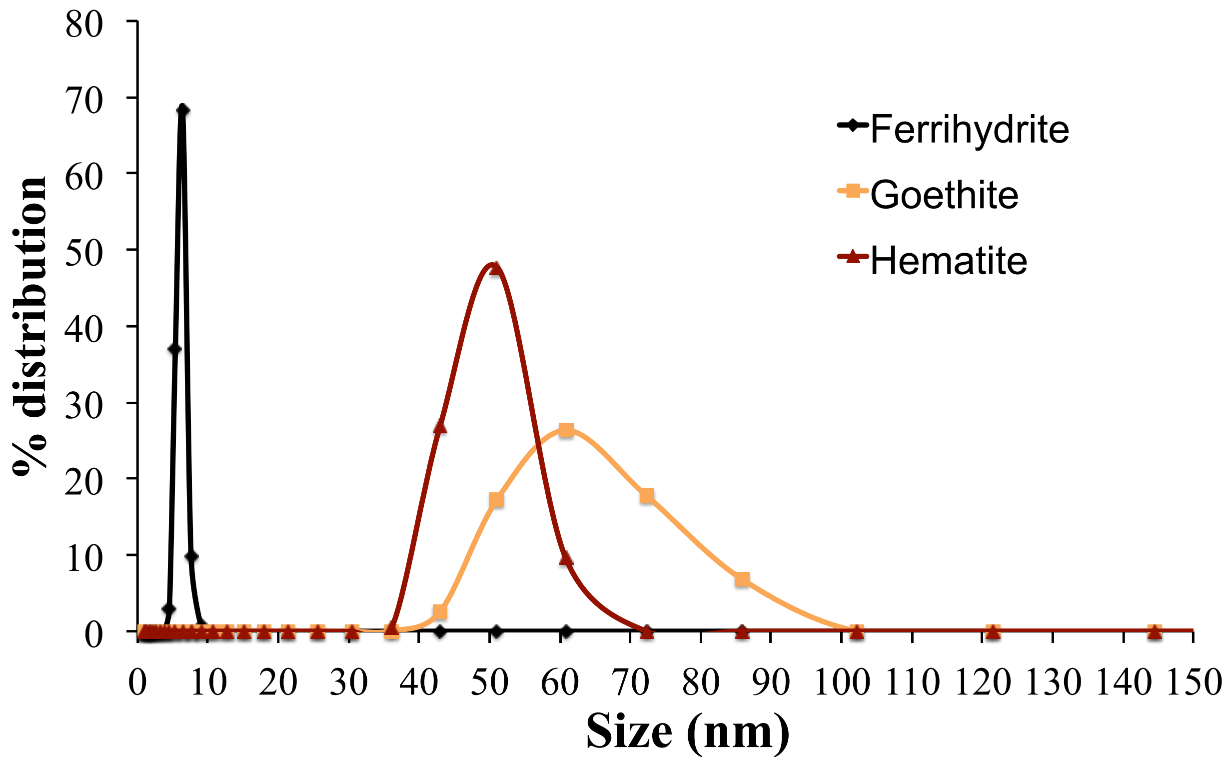
Where 'A' is available surface area in the experimental vial and 't' is the time
'A' was calculated based on the mass of Fe(III)-(oxyhydr)oxides per liter solution used in the experimental vial normalized by the surface area per gram.
't'- is time in days

Figure S7: Percentage of Fe released as Fe(II) from the reactions Fe(III)-(oxyhydr)oxide nanoparticles with dissolved sulfide at different S/Fe ratios.



The above figure shows the Fe(II) measured in the experimental vials during the reaction of ferrihydrite, goethite, and hematite with dissolved sulfides. It is important to note here that these concentrations are the dissolved concentrations measured in solution and do not necessarily represent the total amount of Fe that was released during reductive dissolution of Fe(III)-(oxyhydr)oxides. It is plausible that part of the Fe(II) released might also sorb on the surface of Fe(III)-(oxyhydr)oxide nanoparticles. Hence, these concentrations underestimate the total Fe(II) released. However, the mechanism and the trends remain the same. In this study, we did not try to extract or quantify the sorbed Fe(II) on Fe(III)-(oxyhydr)oxide nanoparticle surfaces.

Figure S8: Particle size measurements by DLS



Particle size measurements were performed using dynamic light scattering (DLS) on a Malvern Zetasizer Nano-ZS (Malvern Instruments, Malvern, UK). A dilute suspension of Fe(III)-(oxyhydr)oxide nanoparticles was prepared (100 mgL^{-1}) in milliQ water with 100 mM NaCl (the aggregation was too fast at higher concentrations). Samples were exposed to a sonicator for a few minutes to break up the aggregates, if any, before the particle size measurements. Samples were measured in disposable polystyrene cuvettes at room temp. (25±2 ºC). The following assumptions were made for the analysis: the solution viscosity was assumed to be that of water, the solution refractive index for the blank was that of water (1.33); the refractive indices for the suspensions were as follows: ferrihydrite (2.32), goethite (2.17), and hematite (3.01). Data were acquired in automatic mode, and the results were assumed satisfactory when the software "data quality report" indicated "good quality" of the data obtained. The size distribution shown here is in terms of volume. The broader peak for the goethite size measurements is perhaps due to the fact that the particles are not spherical in shape but rather are rod shaped.

Experimental Protocols:

200 mg of Fe(III)-(oxyhydr)oxide particles were added to 20 ml of N_2 flushed milliQ water with 100 mM NaCl in 25 mL glass vials. The vials were sonicated for 5 minutes before adding the relevant volume of sulfide solution (from 0.5M stock solution, prepared using Na-sulfide nonahydrate ($Na_2S.9H_2O$)) into the vials. pH was adjusted to pH 7 ± 0.2 with HCl/KOH inside the glove bag. Vials were shaken vigorously for the first 30 minutes of mixing and then at a constant pace (40 RPM) for rest of the reaction. Samples were retrieved at different time points using a disposable syringe inside a N_2 filled glove bag.

Table S7: pH measurements in experiments

S/Fe ratio	Ferrihydrite	Goethite	Hematite
0.1	6.93 7.28	6.82 7.19	7.06 7.23
0.2	6.89 7.34	6.92 7.30	6.87 7.19
0.5	7.03 7.39	6.98 7.36	7.10 7.27
1.0	7.08 7.43	7.04 7.32	6.98 7.21
2.0	7.13 7.41	7.07 7.33	7.09 7.28

Initial; Final (14 days)

Reference:

Noel, V., Boye, K., Kukkadapu, R.K., Bone, S., Pacheco, J.S.L., Cardarelli, E., Janot, N., Fendorf, S., Williams, K.H., Bargar, J.R. (2017) Understanding controls on redox processes in floodplain sediments of the upper Colorado River Basin. *Science of The Total Environment* **603-604**, 663-675.