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FeS Colloids – Formation and Mobilization Pathways in Natural Waters

Vincent Noël[a,*], Naresh Kumar[b,c,d], Kristin Boye[a], Lilia Barragan[a], Juan Lezama-Pacheco[e], Rosalie Chu[f], Nikola Tolic[f], Gordon E. Brown Jr.[a,b,d], John R. Bargar[a]

[a] *Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, 2575Sand Hill Road, Menlo Park, CA 94025, USA*

[b] *Department of Geological Sciences, School of Earth, Energy & Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA*

[c] *Department of Environmental Geosciences, Centre for Microbiology and Environmental Systems Science, University of Vienna, 1090 Vienna, AUSTRIA*

[d] *Center for Environmental Implications of NanoTechnology (CEINT), Duke University, P.O. Box 90287, Durham, NC 27708-0287, USA*

[e] *Department of Earth System Science, Stanford University, Stanford, CA 94305, USA*

[f] *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354, USA*

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*Corresponding author: Vincent Noël; e-mail: noel@slac.stanford.edu

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1) ADDITIONAL METHODOLOGY

FT-ICR-MS analyses. The chemical composition of natural organic carbon (NOC), water extractable organic carbon from grass collected at a DOE-managed former U ore processing facility at Riverton (Figure SI-1), water-soluble organic C was examined using a 12 Tesla Bruker SolariX Fourier-transform ion-cyclotron-resonance mass spectrometer (FT-ICR-MS) at the Environmental Molecular Sciences Laboratory (EMSL) based in Pacific Northwest National Laboratory. Extracts were diluted 50:50 (v/v) with LC–MS grade methanol less than 30 min before analysis to minimize potential esterification. Samples were injected directly into the mass spectrometer and the ion accumulation time was optimized for all samples.

A standard Bruker electrospray ionization (ESI) source was used to generate negatively charged molecular ions. Samples were introduced to the ESI source equipped with a fused silica tube (30 µm i.d.) through an Agilent 1200 series pump (Agilent Technologies) at a flow rate of 3.0 µl min^{-1}. Experimental settings followed previously established optimal parameterization: needle voltage +4.4 kV; Q1 set to m/z 50; heated resistively coated glass capillary operated at 180°C. All samples were run with instrument settings optimized by tuning for the IHSS Suwannee River fulvic acid standard. The instrument was externally calibrated weekly with a tuning solution from Agilent, which calibrates to a mass accuracy of <0.1 ppm and contains the following compounds: $C_2F_3O_2$, $C_6HF_9N_3O$, $C_{12}HF_{21}N_3O$, $C_{20}H_{18}F_{27}N_3O_8P_3$, and $C_{26}H_{18}F_{39}N_3O_8P_3$ with an m/z range of 112–1,333. Forty-four individual scans were averaged for each sample, and they were internally calibrated using an organic matter homologous series separated by 14 Da ($–CH_2$ groups). Mass measurement accuracy was typically within 1 ppm for singly charged ions across a broad m/z range (100–1,100). The mass resolution was ~350,000 at m/z 321. All observed ions in the spectra were singly charged, as confirmed by the 1.0034 Da spacing found between isotopic forms of the same molecule (between $^{12}C_n$ and $^{12}C_{n-1}$–$^{13}C_1$). DataAnalysis software (BrukerDaltonik version 4.2) was used to convert raw spectra to a list of peak locations applying FTMS peak picker with the absolute intensity threshold set to the default value of 100. To further reduce cumulative errors, all sample peak lists within a dataset were aligned to each other prior to formula assignment to eliminate possible mass shifts that would impact formula assignment.

Table SI-1. pH measurements in experiments; Fh: ferrihydrite; PAA: Polyacrylic Acid; NOC: Natural Organic Carbon

Sulfide/Fe ratio	Fh	Fh-PAA	Fh-NOC
0.05	6.89 7.24	6.91 7.24	6.98 7.21
0.1	6.93 7.28	6.94 7.26	7.04 7.18
0.5	7.03 7.39	7.06 7.39	7.08 7.29
2	7.13 7.41	7.11 7.43	7.15 7.33

Initial; Final (336h after sulfidation was induced)

2) CHARACTERIZATION OF SOURCE OF NATURAL ORGANIC CARBON

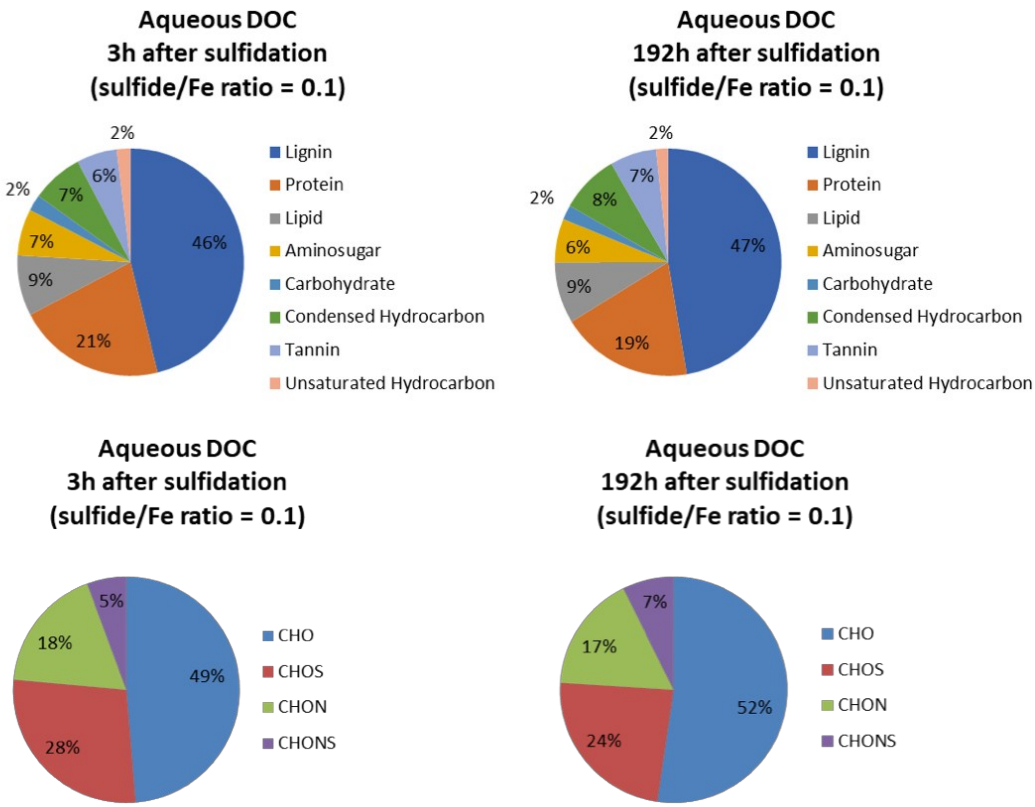


Figure SI-1. Relative distribution (%) of molecular class (top) and elemental formula (bottom) of organic compounds into the aqueous fraction from sulfidation of Fh-NOC (see §1) after the 3 first hours (left) and 192 first hours (right) of sulfidation was induced.

3) SELECTION OF THE CONCENTRATION OF ORGANIC COMPOUNDS RELATIVE TO FERRIHYDRITE

Kumar *et al.*[1] have previously shown differences in reactivity of Fe(III)-(oxyhydr)oxide nanoparticles with dissolved sulfides depending on the surface area and the degree of crystalinity of Fe(III)-(oxyhydr)oxide nanoparticles. Similarly, different Fe(III)-(oxyhydr)oxide nanoparticles could generate different colloids. The generation of Fe-colloids from sulfidation of goethite (Fe(III)O(OH)), other Fe(III)-(oxyhydr)oxide that is redox-sensitive and ubiquitous in surface and near-surface environments, will be compared with that of Fh sulfidation in an upcoming publication. To be consistent in our experimental approach, almost identical concentration of C was sorbed on to the fixed mass of Fe(III)-(oxyhydr)oxide nanoparticles. To determine the appropriate concentration of C to be sorbed, a series of batch tests were performed using varying concentrations of PAA for a 200 mg mass of Fh or goethite. (Figure SI-2). The maximum sorption of PAA is completed for 2115 mg/L of PAA added in a solution of 200mg of goethite (Figure SI-2a). Subsequently, 2115 mg/L of PAA have been added in a solution of 200mg of Fh, resulting in the sorption of the totality of PAA (Figure SI-2b). Thus, a ratio of 2115 mg C per 200g Fh, *i.e.* 10.6 (~11) mg C per g Fh was chosen for PAA.

Based on these batch experiments, we added 2115 mg/L of PAA to ferrihydrite to be able to have ~900 mg/L of PAA sorbed on 200 mg of ferrihydrite or goethite. the Fe(III)-(oxyhydr)oxides providing approx. ~200 mg C per gram of Fe(III)-(oxyhydr)oxide.

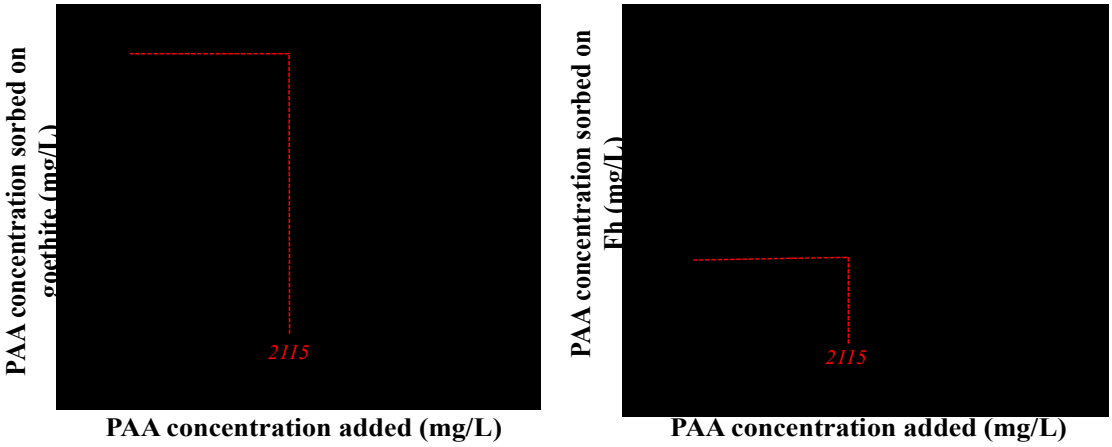


Figure SI-2. Sorbed dissolved organic carbon concentration in presence of 200mg of goethite (left) and ferrihydritre (right) as a function of added dissolved organic carbon concentration.

4) F_E OXIDATION STATE AND SPECIATION OF THE AQUEOUS FRACTION

4.1 Aqueous Fe(III) colorimetric analyzes

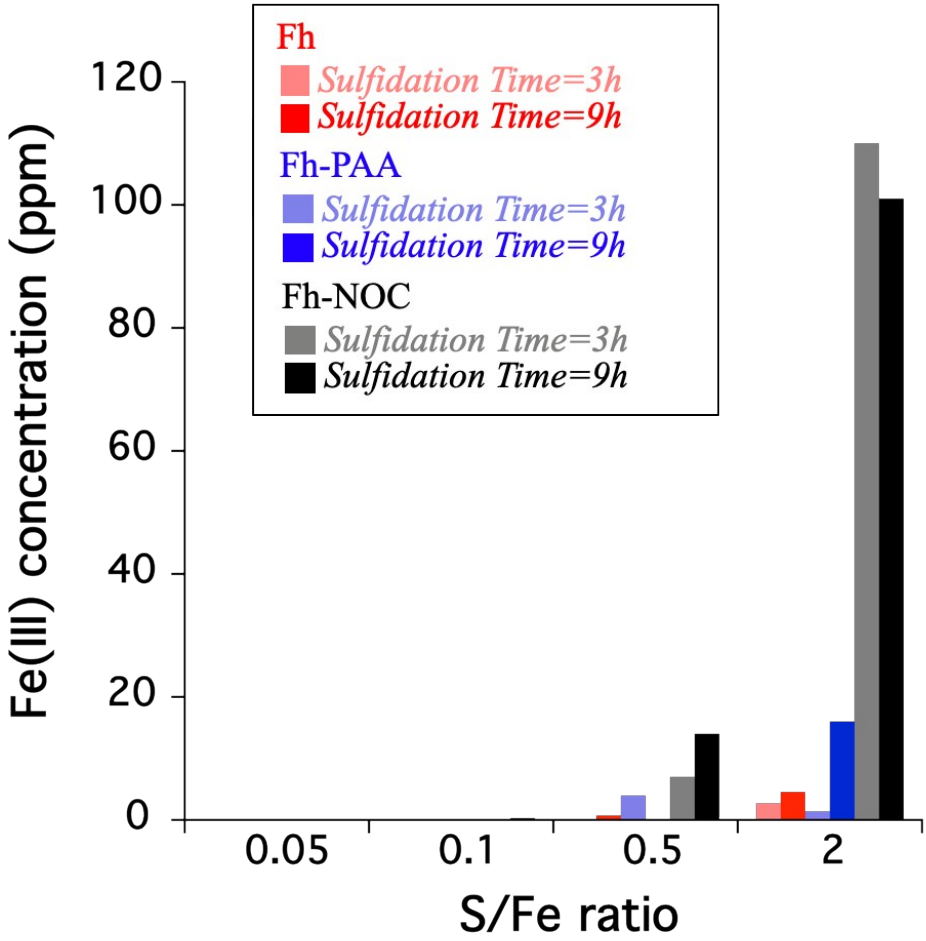


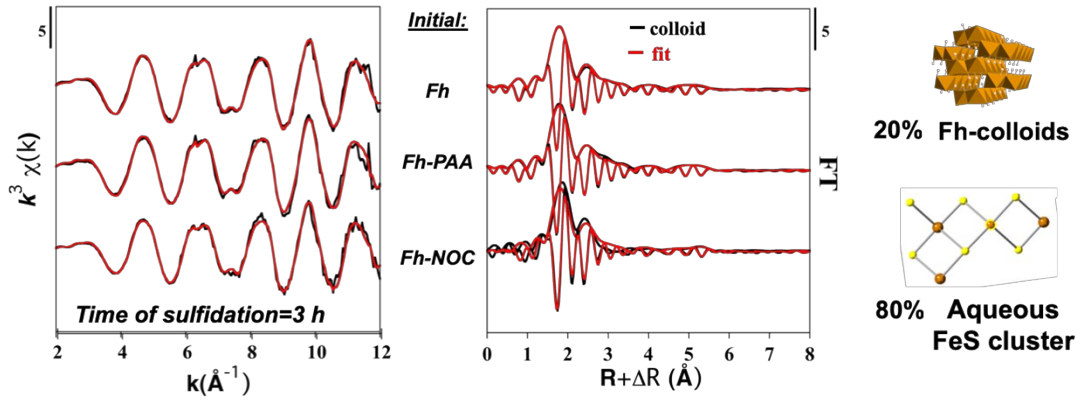
Figure SI-3. Dissolved Fe(III) concentration measured during sulfidation reactions of Fh, after 3 and 9h of reaction, as a function of different Sulfide/Fe ratios.

4.2 Fe speciation spectroscopic analysis

Table SI-2. Results of the Principal Component Analysis (PCA) of 12 bulk EXAFS spectra of the aqueous fraction (< 20 nm) collected after 3h, 24h, 48h, and 120h of Fh sulfidation in the presence and absence of organic compounds (PAA or natural organic carbon).

Component	Eingenvalue	Variance	Cum Var[a]
1	6.984109	0.997730	0.997730
2	0.007763	0.001109	0.998839
3	0.003264	0.000466	0.999305
4	0.002119	0.000303	0.999608
5	0.001852	0.000265	0.999872
6	0.000585	0.000084	0.999956
7	0.000309	0.000044	1

[a] Cumulative variance



Sample	Fh[1]	Aqueous FeS cluster from Fh sulfidation reaction (120h)	Rf* (10^{-2})
Fh after 3h of sulfidation	14	86	2.75
Fh-PAA after 3h of sulfidation	25	75	3.34
Fh-NOC after 3h of sulfidation	20	80	2.25

*Calculated as $\Sigma(k^3\chi_{exp}-k^3\chi_{fit})^2/\Sigma(k^3\chi_{exp})^2$

Figure SI-4. Molecular characterization of Fe in the aqueous fraction (< 20nm) from sulfidation of Fh, Fh-PAA, and Fh-NOC composites, at a sulfide/Fe ratio of 0.5 in a 0.1M NaCl-solution. Linear combination-least squares fitting of the EXAFS spectrum of the aqueous fraction collected 3 hours after sulfidation was initiated. The fits were performed using a Fh reference spectrum and the spectrum from Fe-colloids collected

after 120 hours of sulfidation reaction. The values of these best LC-LS fits normalized at 100% are reported in the table of the bottom.

Table SI-3. Results of shell-by-shell fitting of the EXAFS spectrum of Fh after sulfidation for 120 hours at a sulfide/Fe ratio of 0.5 in a 0.1M NaCl-solution.

	N	4**
Fe-S1	D (Å)	2.24(3)
	σ^2 (Å^2)	0.0020(3)
		1.8±0.3
Fe-Fe1		2.74(5)
		0.0027(3)
		1.0±0.5
Fe-Fe2		3.84(30)
		0.0047(6)
		2.3±1.2
Fe-S2		4.46(50)
		0.01**
		1.8±0.3
Fe-S-Fe (MS)		5.48(4)
		0.0055(6)

*S02=0.79+-0.03 **Denotes a fixed value

5) CHEMICAL COMPOSITION OF ARTIFICIAL GROUNDWATERS

Table SI-4. Chemical composition of artificial waters

Constituent	Alpine River (Composition of the Rhine River as it leaves the Alps)[1]	Alluvial groundwater, crested butte, CO (*personal communication*)	Alluvial groundwater Riverton, WY[2]	Seawater[3]
pH	7.02	7.3	7.5	7.1
	mM	mM	mM	mM
Ca	1.01	3.59	3.7	10
Na	2.5	1.17	10.4	469
Mg	0.29	2.26	18.5	52.8
Mn	-	-	0.03	-
K	0.03	9.72	0.5	10
Si	0.13	0.78	0.3	-
Fe	-	-	0.009	-
Cl^-	0.03	1.49	16.9	546
SO_4^{2-}	0.36	0.62	62.5	28.2
Bicarbonate	1.87	10.20		

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