Supporting Information

Fe(II)-catalyzed transformation of organic matter-ferrihydrite coprecipitates: A closer look using Fe isotopes

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Supporting Information Content:
Number of pages: 22
Number of figures: 13
Number of tables: 7

Table S1. Properties of different natural organic matter compiled from IHSS website (reference 1) unless otherwise noted.

Sources	C (%)	Carboxyl [b] (%)	Phenolic[b] (%)	Aromatic[c] (%)	Aliphatic[c] (%)
Suwannee River Fulvic Acid[a]	52.3	11.2	2.8	22	35
Suwannee River NOM	50.7	11.2	2.5	23	27
Elliot Soil Humic Acid[a]	59.5	8.3	1.9	41	27
Pahokee Peat Humic Acid	56.4	9.0	1.9	47	19
Pahokee Peat Fulvic Acid[d]	51.3	10.6	5.4	40.4	17.1

a. humic acid and fulvic acid are operationally defined based on their solubility at different pH ranges;
b. Measured by titration using 0.1 M NaOH. Carboxyl is the charge density (meq/g C) at pH 8.0; Phenolic is two times the change in charge density (meq/g C) between pH 8 and pH 10;
c. Analyzed from NMR peak area percentages. d. Pahokee Peat Fulvic Acid data is from reference 2.

Table S2. Summary of Fe(II) experimental results with OM-Fh coprecipitates

OC Source	C/Fe Nominal	C/Fe TOC[a]	Solid C Content (%)[b]	Fe(II) Initial (µmol)	Fe(II) Sorbed (µmol)	End Minerals[c]
PPHA	1.6	1.6	17.7	31.1	20.4	G
ESHA	1.6	1.6	17.7	30.6	20.3	G
SRFA	1.6	1.1	11.3	32.7	19.7	Fh
PPFA				31.5	22.5	Fh
	1.6	1.4	15.9	58.1	27.6	Fh
				88.7	30.1	Fh
SRNOM				30.5/30.11	16.7/19.4[d]	Fh
	1.6	1.2	13.9	59.7	26.4	Fh
				81.9	26.8	Fh

a. C/Fe ratio calculated from C content measured by TOC analyzer and total Fe content measured by dissolution and quantification with 1,10-phenanthroline;
b. Calculated from C/Fe ratio, ferrihydrite was calculated as FeOOH;
c. G = goethite; Fh = ferrihydrite.
d. Two different batches of SRNOM-Fh (C/Fe = 1.2) used in ET and AE study, In ET study, 16.7 µmol Fe(II) was sorbed; In AE study, we have slightly more Fe(II) sorbed.

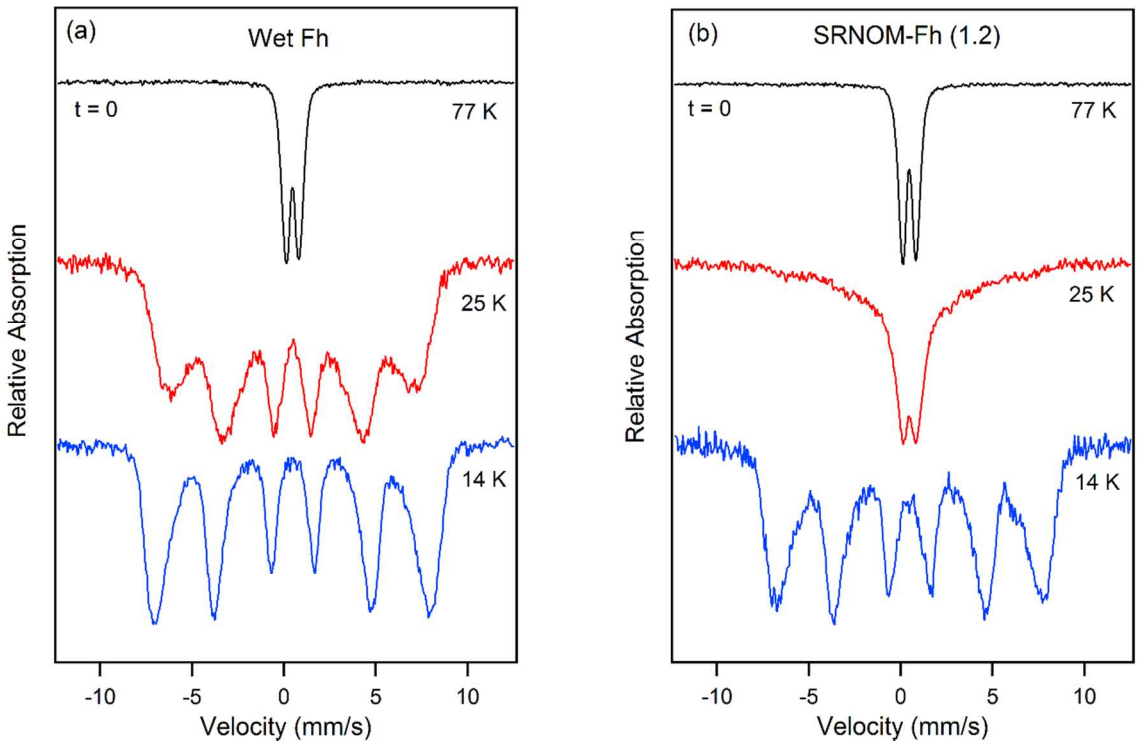


Figure S1. Mössbauer temperature profile of (a) wet Fh and (b) SRNOM-Fh (C/Fe = 1.2) coprecipitate.

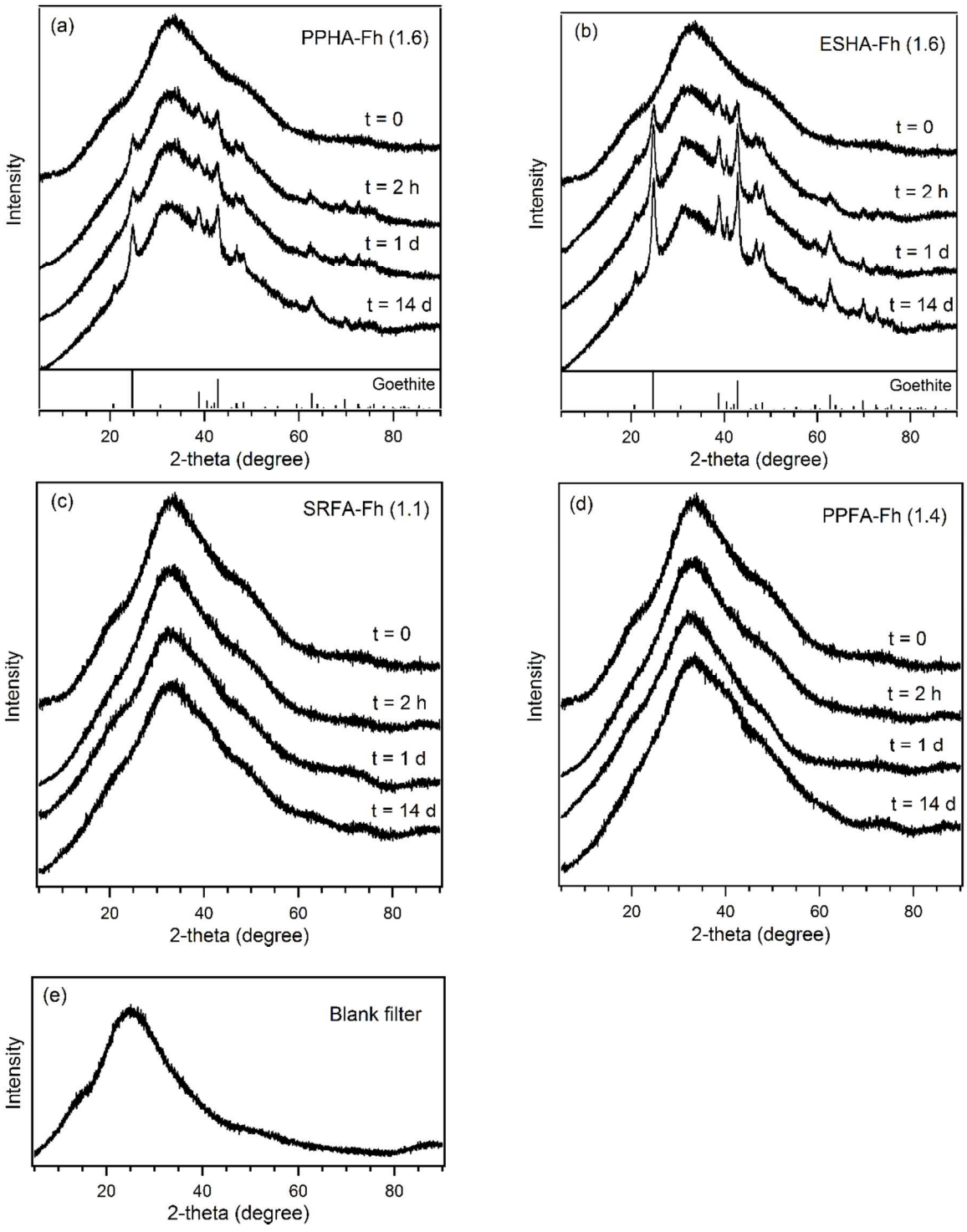


Figure S2. X-ray diffraction of (a) PPHA-Fh (C/Fe = 1.6), (b) ESHA-Fh (C/Fe = 1.6), (c) SRFA-Fh (C/Fe = 1.1) and (d) PPFA-Fh (C/Fe = 1.4) reacted with 2 mM Fe(II) in 10 mM PIPES (pH 7.0) over 14 days. Solids were collected and characterized with 0.22 μm glass fiber filter (e). Measurement was conducted at step width 0.02 at 30 kV and 15 mA. The identical peaks of secondary Fe mineral in (a) and (b) are consistent with goethite and the intensity of peaks increased over time.

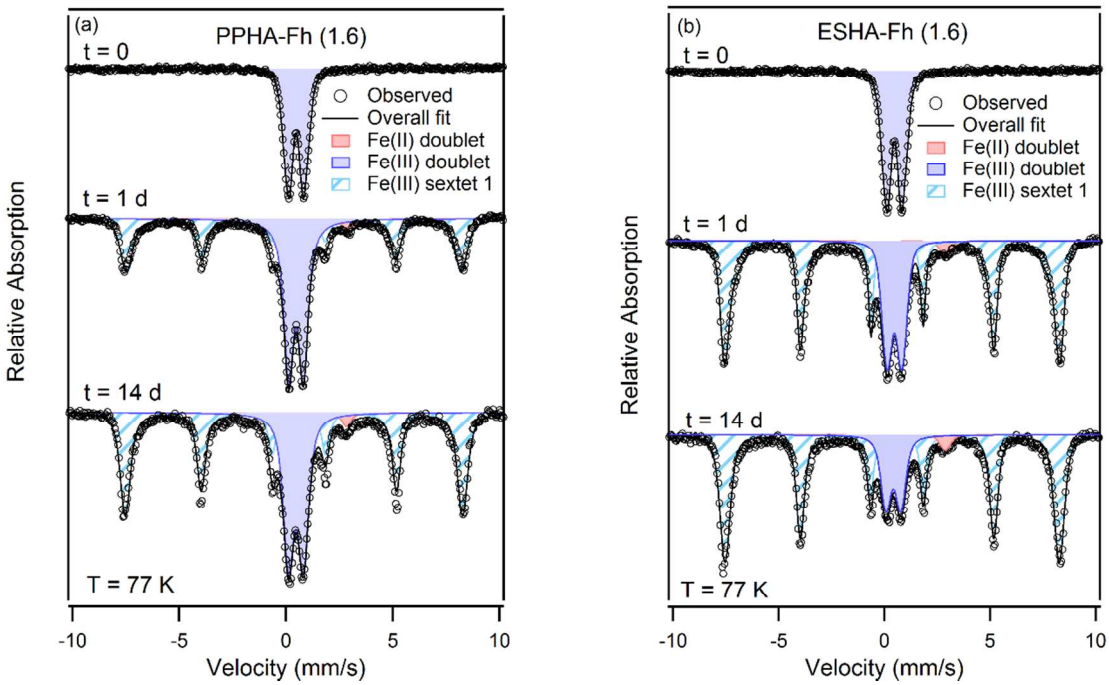


Figure S3. Mössbauer spectra and fitting of (a) PPHA-Fh (C/Fe = 1.6) (b) ESHA-Fh (C/Fe = 1.6) reacted with 2 mM ^{NA}Fe(II) over time. The spectra were fitted using one sextet and two doublets with Recoil. Based on XRD result (Figure S2) and Recoil fitting report, in PPHA-Fh (C/Fe = 1.6), there are 44.23% of goethite and 51.70% of ferrihydrite in 1 day sample, and 56.52% of goethite and 39.94% of ferrihydrite in 14 days sample; in ESHA-Fh(C/Fe = 1.6), there are 67.33% of goethite and 28.91% of ferrihydrite in 1 day sample, and 72.05% of goethite and 19.69% of ferrihydrite in 14 days sample. Detailed fitting parameters were listed in Table S3.

Table S3. Mössbauer spectral parameters derived from fitting samples in Figure S3.

OM-Fh	Reaction time (day)	Component	Relative area (%)	Center shift, CS (mm/s)	QS or 2ε [b] (mm/s)	σ(Δ)[c] (mm/s)	Hyperfine field, H (Tesla)	χ_v^2
PPHA-Fh (1.6)	0	Fe(III) doublet	100	0.47	0.76	0.35		1.6
	1	Fe(II) doublet	4.07(.47)	1.28	3.17	0.38		2.9
		Fe(III) doublet	51.70(.46)	0.46	0.69	0.15		
		Goethite	44.23(.45)	0.48	-0.22	48.63	0.94	
	14	Fe(II) doublet	3.54(.34)	1.13	3.39	0.13		2.4
		Fe(III) doublet	39.94(.43)	0.46	0.70	0.25		
		Goethite	56.52(.44)	0.48	-0.23	48.98	0.73	
ESHA-Fh (1.6)	0	Fe(III) doublet	100	0.47	0.76	0.33		1.6
	1	Fe(II) doublet	3.76(.33)	1.28	3.19	0.41		2.9
		Fe(III) doublet	28.91(.29)	0.47	0.71	0.12		
		Goethite	67.33(.36)	0.48	-0.23	48.23	2.16	
	14	Fe(II) doublet	8.27(.74)	1.26	3.92	2.21		3.1
		Fe(III) doublet	19.69(.39)	0.42	0.7	0.29		
		Goethite	72.05(.68)	0.48	-0.22	49.04	0.97	

a value in parenthesis reflects the error (1σ) in determination of the relative area for each component
b QS = quadrupole splitting; 2ε = quadrupole shift parameter in sextet
c σ(Δ) = standard deviation of quadrupole splitting component

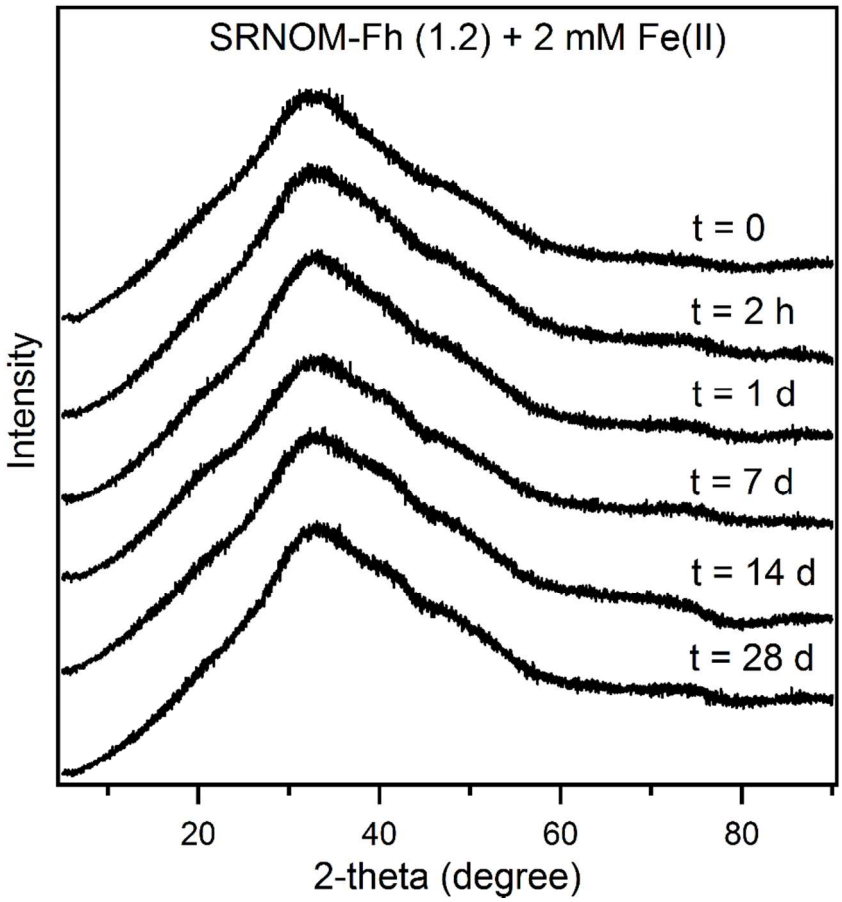


Figure S4. X-ray diffraction of SRNOM-Fh (1.2) reacted with 2 mM Fe(II) over time in PIPES buffer, pH 7.0. Solids were collected and characterized on the 0.22 μm glass filter. No mineral transformation was observed over 28 days.

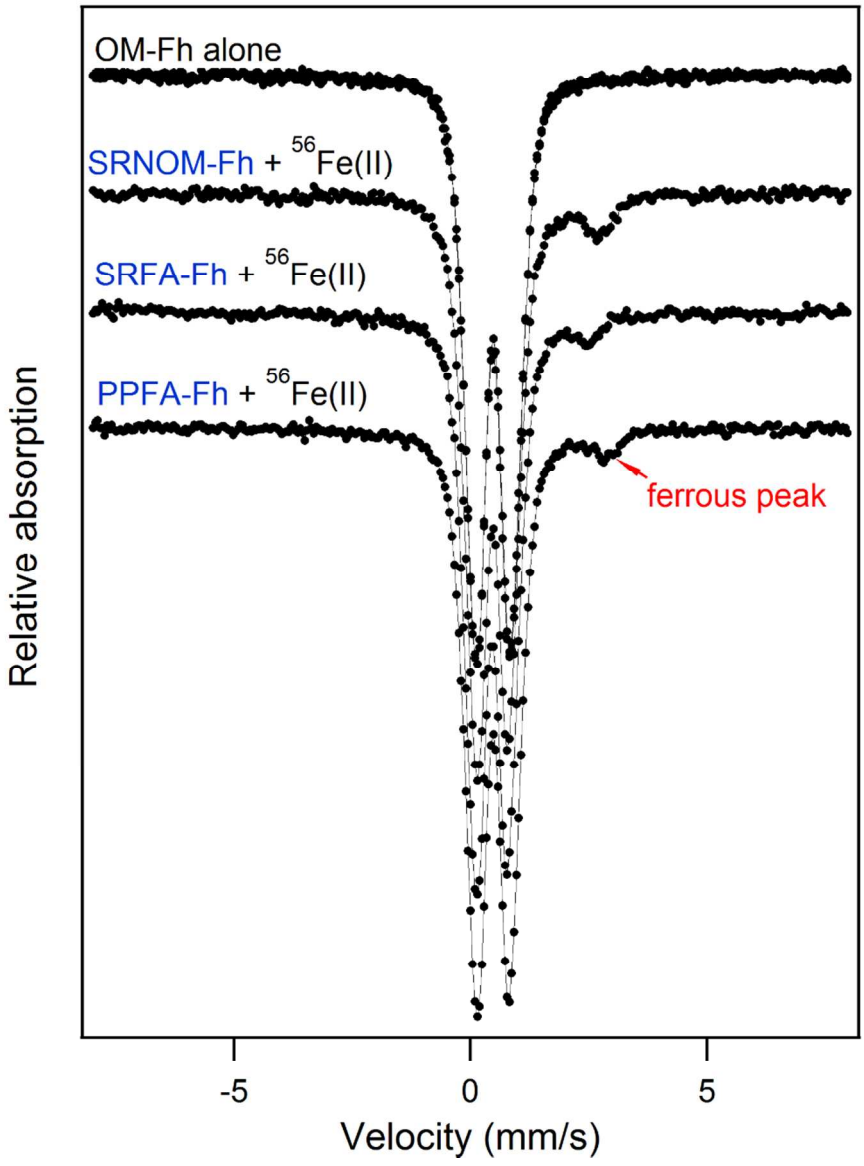


Figure S5. ^{57}Fe Mössbauer spectra of various OM-Fh coprecipitates (10 mM Fe(III)) reacted with 2 mM ^{56}Fe(II) in 10 mM PIPES buffer (pH 7.0) over 1 day. Spectra were collected at 77 K. A ferrous peak emerged in reacted OM-Fh coprecipitates.

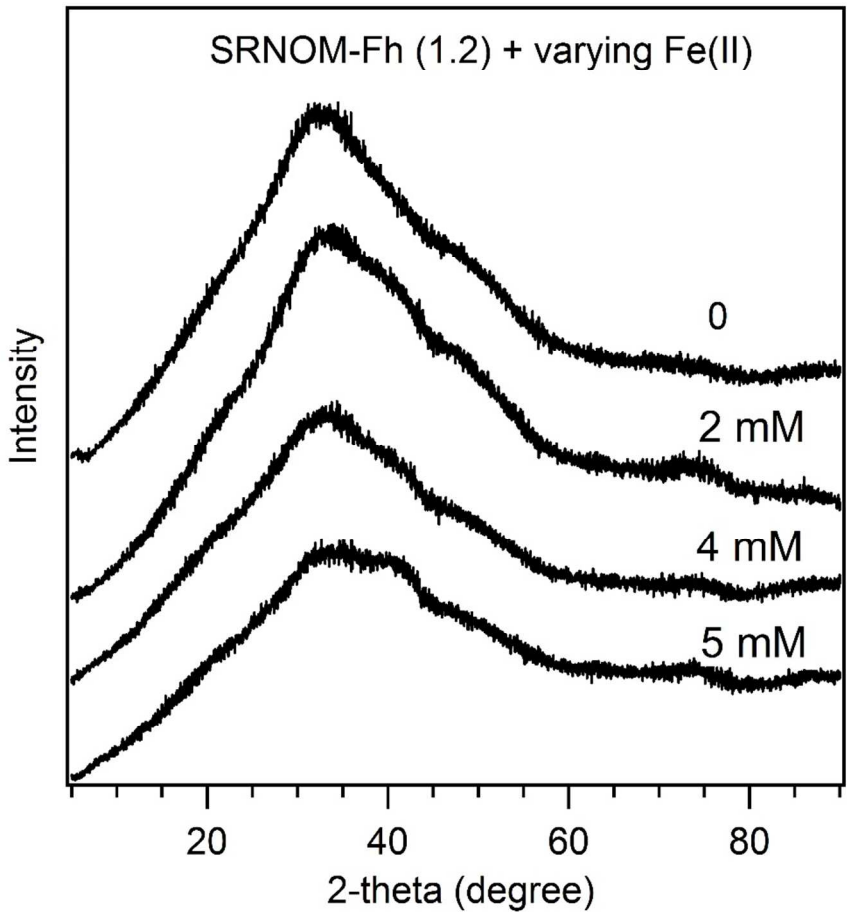


Figure S6. X-ray diffraction of reacted SRNOM-Fh (C/Fe = 1.2) with various Fe(II) concentration. Same solids as measured in Figure 3.

Table S4. Mössbauer spectral parameters derived from fitting SRNOM-Fh (C/Fe = 1.2) samples reacted with different amount of Fe(II) (same samples as Figure 2).

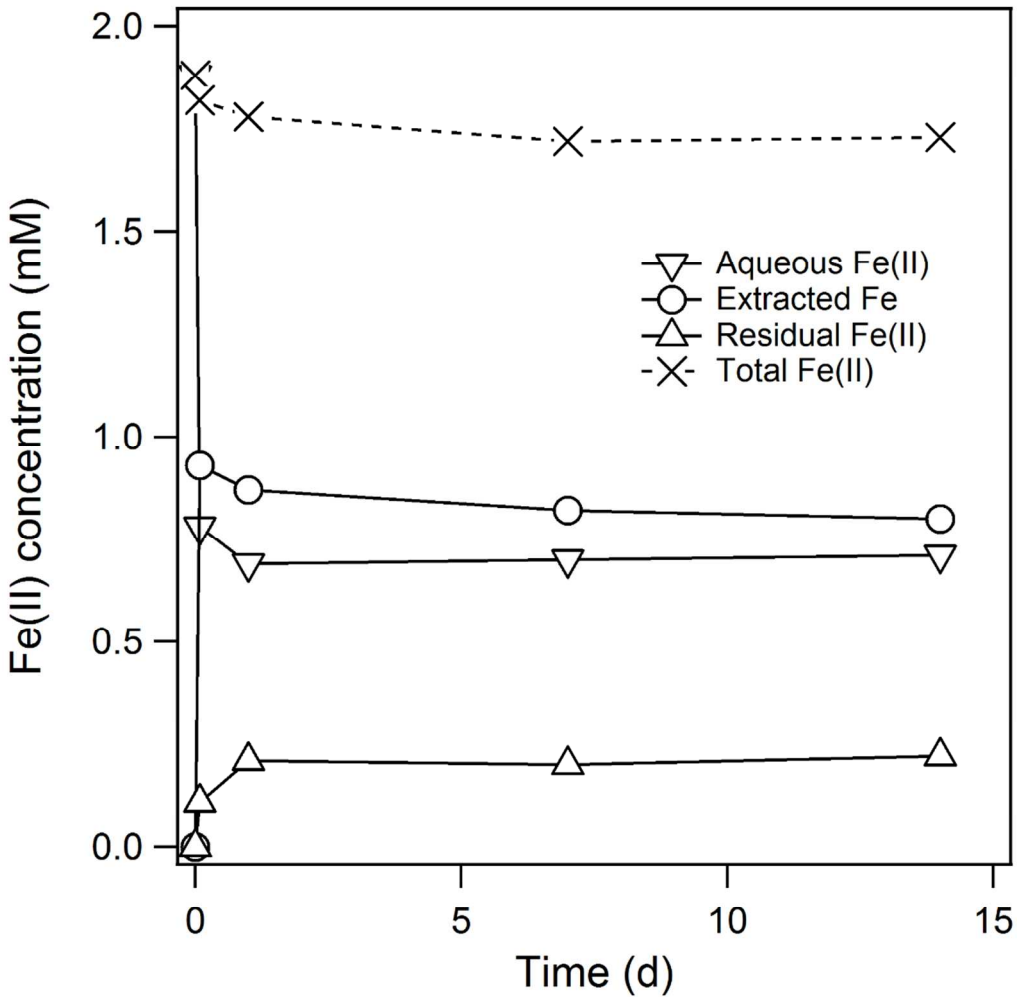
Initial Fe(II) (mM)	**Component**	**Relative area (%)**	**Center shift, CS (mm/s)**	**Quadrupole splitting, QS or 2ε [b] (mm/s)**	**σ(Δ)[c] (mm/s)**	χ_v^2
2	Fe(II) doublet	12.02(.62)	1.16	3.0	0.89	1.82
	Fe(III) doublet	87.98(.62)	0.47	0.70	0.33	
4	Fe(II) doublet	14.56(.81)	1.21	2.90	0.70	1.42
	Fe(III) doublet	85.44(.61)	0.46	0.68	0.33	
5	Fe(II) doublet	17.29(.53)	1.12	2.90	0.90	2.24
	Fe(III) doublet	82.71(.53)	0.45	0.68	0.34	

a value in parenthesis reflects the error (1σ) in determination of the relative area for each component
b 2ε = quadrupole shift parameter in sextet
c σ(Δ) = standard deviation of quadrupole splitting component

Table S5. Summary of Fe isotope data during reactions between aqueous Fe(II) and SRNOM-Fh coprecipitate (C/Fe = 1.2) at pH 7.0.

Time (d)	Aqueous				Extract[a]				Solid			
	Fe(II) (μmole)	$f^{57}Fe$	$f^{56}Fe$	$f^{54}Fe$	Fe(II) (μmole)	$f^{57}Fe$	$f^{56}Fe$	$f^{54}Fe$	Fe (μmole)	$f^{57}Fe$	$f^{56}Fe$	$f^{54}Fe$
0	30.11(0.42)	0.95(0.006)	0.026(0.006)	0.001(0)	NA	NA	NA	NA	152.7(3.41)	0.02(0)	0.92(0.001)	0.055(0)
0.083	11.72(1.0)	0.42(0.007)	0.53(0.007)	0.028(0)	13.9(0.66)	0.38(0.016)	0.57(0.015)	0.03(0.001)	139.04(6.02)	0.13(0.002)	0.82(0.002)	0.043(0)
1	10.36(0.10)	0.30(0.002)	0.65(0.002)	0.034(0)	13.0(0.25)	0.29(0.002)	0.67(0.003)	0.035(0)	145.75(8.78)	0.16(0.001)	0.79(0.001)	0.042(0)
7	10.45(0.48)	0.19(0.002)	0.75(0.001)	0.046(0)	12.32(0.34)	0.19(0.002)	0.76(0.002)	0.046(0)	139.43(4.37)	0.17(0.005)	0.78(0.005)	0.048(0)
14	10.68(0.91)	0.19(0.001)	0.75(0.001)	0.046(0)	11.94 (0.50)	0.19(0.002)	0.76(0.002)	0.046(0)	132.83(2.59)	0.18(0.002)	0.78(0.002)	0.048(0.001)

a. Around 80% of sorbed Fe(II) was extracted by this extraction method, less than 3% of Fe in the extraction was Fe(III).



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106 **Figure S7.** Fe(II) distribution in each phase during Fe(II) reaction with SRNOM-Fh (C/Fe = 1.2).

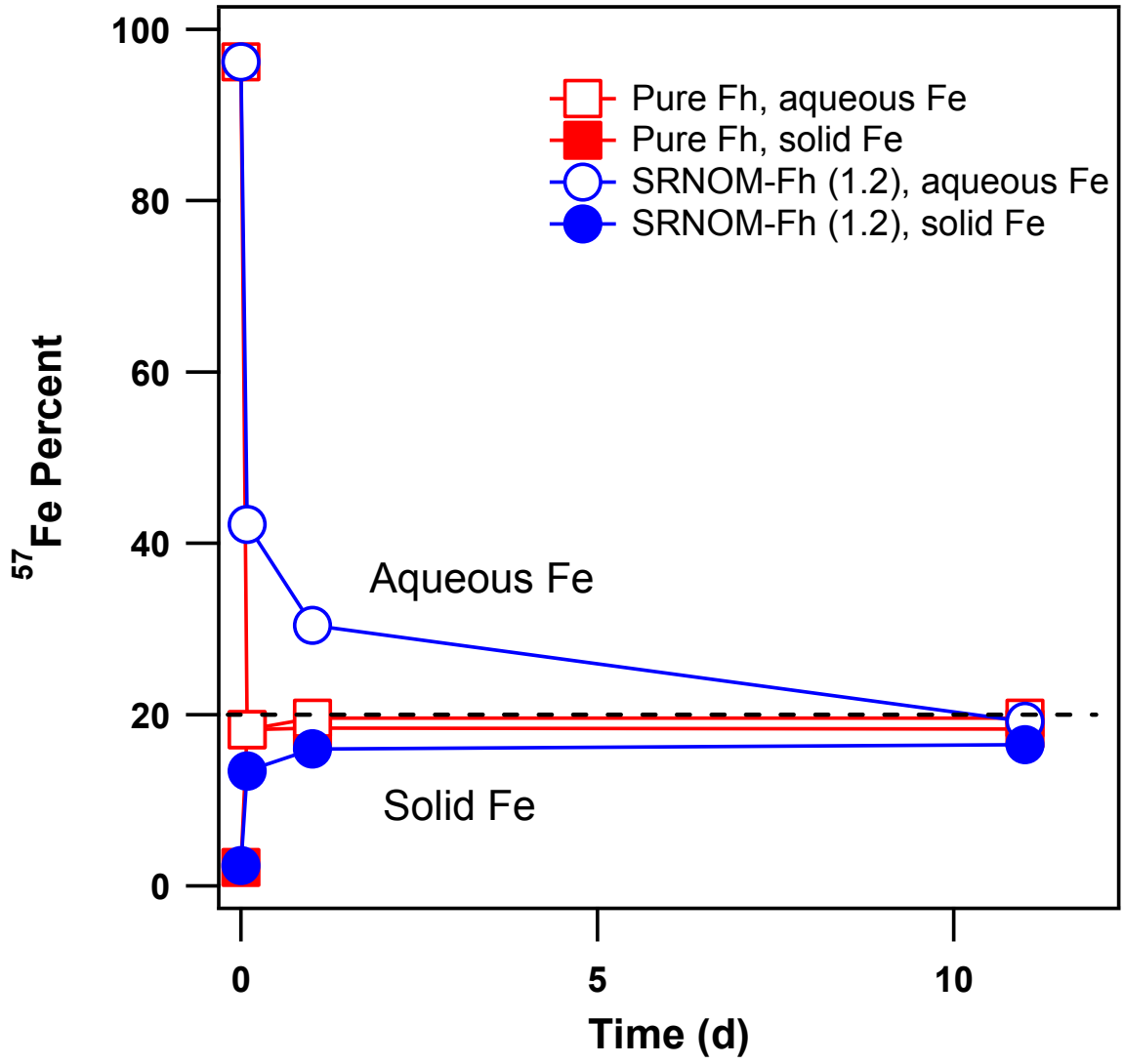


Figure S8. Measured ^{57}Fe percentage of aqueous Fe(II) and residual solid Fe over time when 2 mM ^{57}Fe(II) was reacted with wet ferrihydrite and SRNOM-Fh (C/Fe = 1.2) synthesized with naturally abundant Fe. Dash line represents the completely mixed ^{57}Fe percent value in pure Fh reactors.

Table S6. Fe mass and isotope composition in each fraction during the sequential extraction to SRNOM-Fh (C/Fe ratio 1.2) reacted with ^{57}Fe(II) over different time.

Fe(II) treated time (d)	Fraction	Fe(II) (μmol)	Fe(III) (μmol)	Total Fe (μmol)	^{57}Fe percent (%)	^{57}Fe mass (μmol)	Sum of ^{57}Fe mass (μmol)	Percent of Fe mass recovered (%)
0	aqueous	30.9(0.3)	-	_-	94.6(0.3)	29.2	32.9	98.1
	extract 1	0	11.2	11.2(0.3)	2.6(0.03)	0.3		
	extract 2	0	20.2	20.2(0.1)	2.6(0.03)	0.5		
	extract 3	0	28.4	28.4(0.3)	2.6(0.005)	0.7		
	extract 4	0	28.4	28.4(0.2)	2.6(0.003)	0.7		
	extract 5	0	19.9	19.9(0.1)	2.6(0.01)	0.5		
	residual	0	32.9	32.9(0.1)	2.6(0.02)	0.8		
0.08	aqueous	13.6(0.2)	-	-	33.6(0.1)	4.6	34.3	96.9
	extract 1	15.2(0.3)	8.5	23.7(0.3)	31.6(0.2)	7.5		
	extract 2	0.6(0.1)	15	15.6(0.1)	23.4(0.1)	3.7		
	extract 3	0.1(0.3)	25.3	25.4(0.3)	18.7(0.1)	4.7		
	extract 4	0.4(1.3)	24.6	25(1.3)	16.6(0.1)	4.2		
	extract 5	0(0.3)	16.1	16.1(0.3)	15.6(0.04)	2.5		
	residual	1.9(0.8)	47.1	49(0.8)	14.7(0.1)	7.2		
1	aqueous	13.1(0.3)	-	-	25.8(0.1)	3.4	32.2	93.8
	extract 1	13.5(0.2)	9	22.5(0.8)	25.4(0.03)	5.7		
	extract 2	0.5(0.1)	9.5	10(0.5)	22.1(0.1)	2.2		
	extract 3	0.8(0.7)	16.3	17.1(0.7)	19.6(0.03)	3.4		
	extract 4	0.4(0.04)	23.6	24(1.6)	18.2(0.1)	4.4		
	extract 5	0.1(0.06)	10.4	10.5(0.2)	17.2(0.5)	1.8		
	residual	3.2(0.1)	62.3	65.5(1.2)	17.3(0.03)	11.3		
7	aqueous	12.9(0.4)	-	-	22.2(0.04)	2.9	30.1	92.8
	extract 1	13.4(0.4)	6.1	19.5(0.6)	22.3(0.2)	4.3		
	extract 2	1.5(0.04)	11	12.5(0.7)	20.3(0.05)	2.5		
	extract 3	0.1(0.1)	6	6.1(0.2)	19.3(0.1)	1.2		
	extract 4	0.2(0.2)	6.9	7.1(0.3)	18.6(0.1)	1.3		
	extract 5	0.1(0.1)	8.3	8.4(0.1)	18(0.4)	1.5		
	residual	2.3(0.1)	87.7	90(0.6)	18.2(0.2)	16.4		
14	aqueous	12.4(0.1)	-	-	20.2(0.1)	2.5	29.9	93.6
	extract 1	13.2(0.3)	6.1	19.3(0.4)	19.9(0.1)	3.8		
	extract 2	0.3(0.1)	5.2	5.5(0.5)	18.3(1.1)	1.0		
	extract 3	0.2(0.03)	9.2	9.4(0.1)	18(0.1)	1.7		
	extract 4	0.1(0.06)	10.4	10.5(1.1)	16.9(0.5)	1.8		
	extract 5	0.1(0.04)	10.7	10.8(0.3)	16.9(0.1)	1.8		
	residual	2.8(0.2)	92.6	95.4(2.8)	18.1(0.1)	17.3		

Calculation of percent Fe exchange

To calculate the percent of ferrihydrite exchange with aqueous Fe(II), we measured the Fe mass of Fe(II) ($N_{Fe(II)}$) and ferrihydrite (N_{Fh}) in the reactor and calculated the percent of ^{57}Fe in initial Fe(II) ($fFe(II)^{i}_{aq}$) and ferrihydrite (fFh^{i}). The ^{57}Fe percent in aqueous Fe(II) at different time ($fFe(II)^{t}$) was also calculated, then we used the following non-linear equation[3] to calculate the percent of ferrihydrite that was exchanged with aqueous Fe(II):

$$Percent\ of\ ferrihydrite\ exchanged = \frac{N_{Fe(II)} \times (fFe(II)^{i}_{aq} - fFe(II)^{t})}{N_{Fh} \times (fFe(II)^{t} - fFh^{i})}$$

This equation was based on the homogeneous model that assume recrystallized ferrihydrite would involve further exchange with aqueous Fe(II) and reach a homogeneous isotope distribution in the recrystallized ferrihydrite.[3, 4] Considering the heterogeneous Fe isotope distribution in the Fe(II)-treated solid over short time, we only calculated the percent of ferrihydrite exchanged at 14 days where we observed a nearly homogeneous Fe isotope distribution. Over 14 days reaction, there was 85 ± 3 % ferrihydrite in the coprecipitate exchanged with aqueous Fe(II). All the numbers used in this calculation can be found in Table S5 and the detailed calculation example can be found in our previous publication.[3]

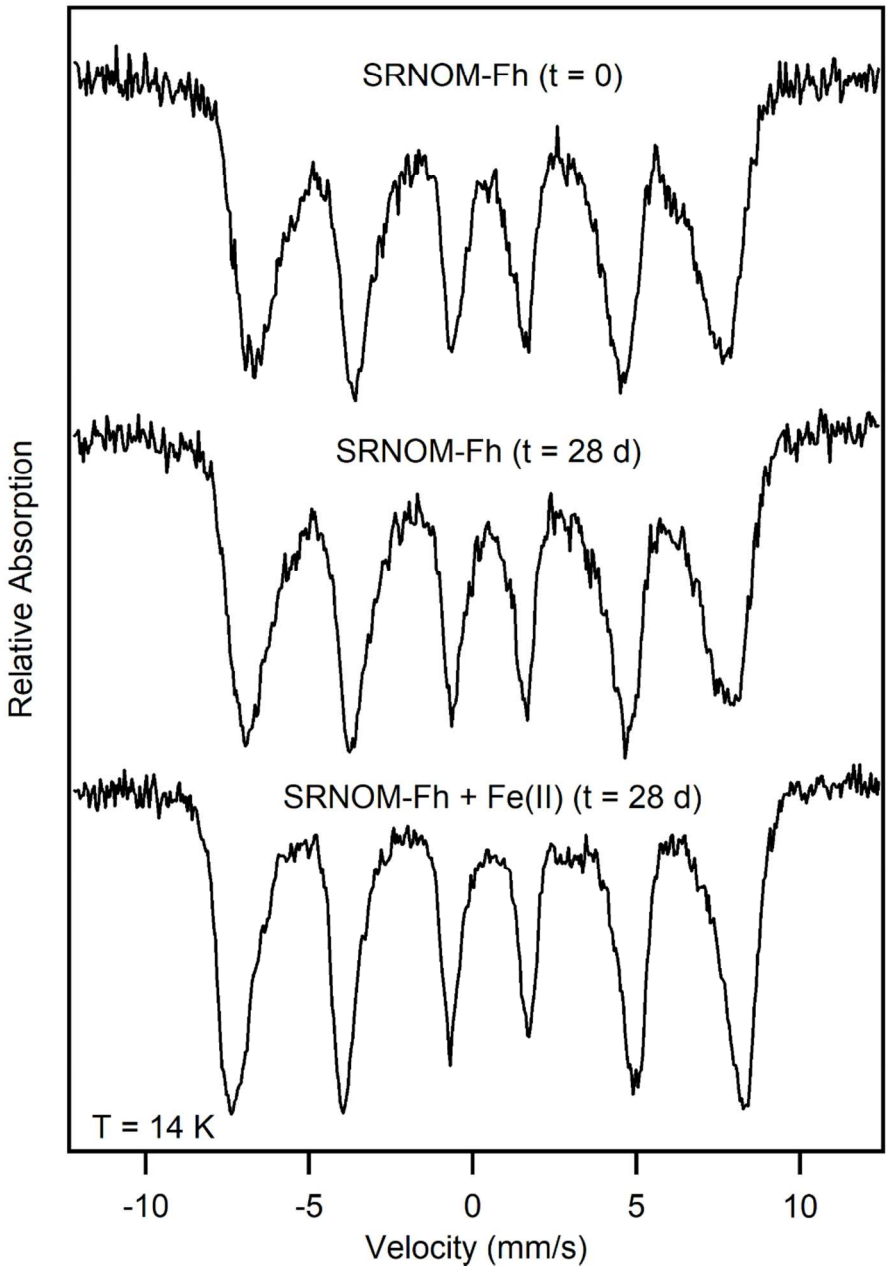
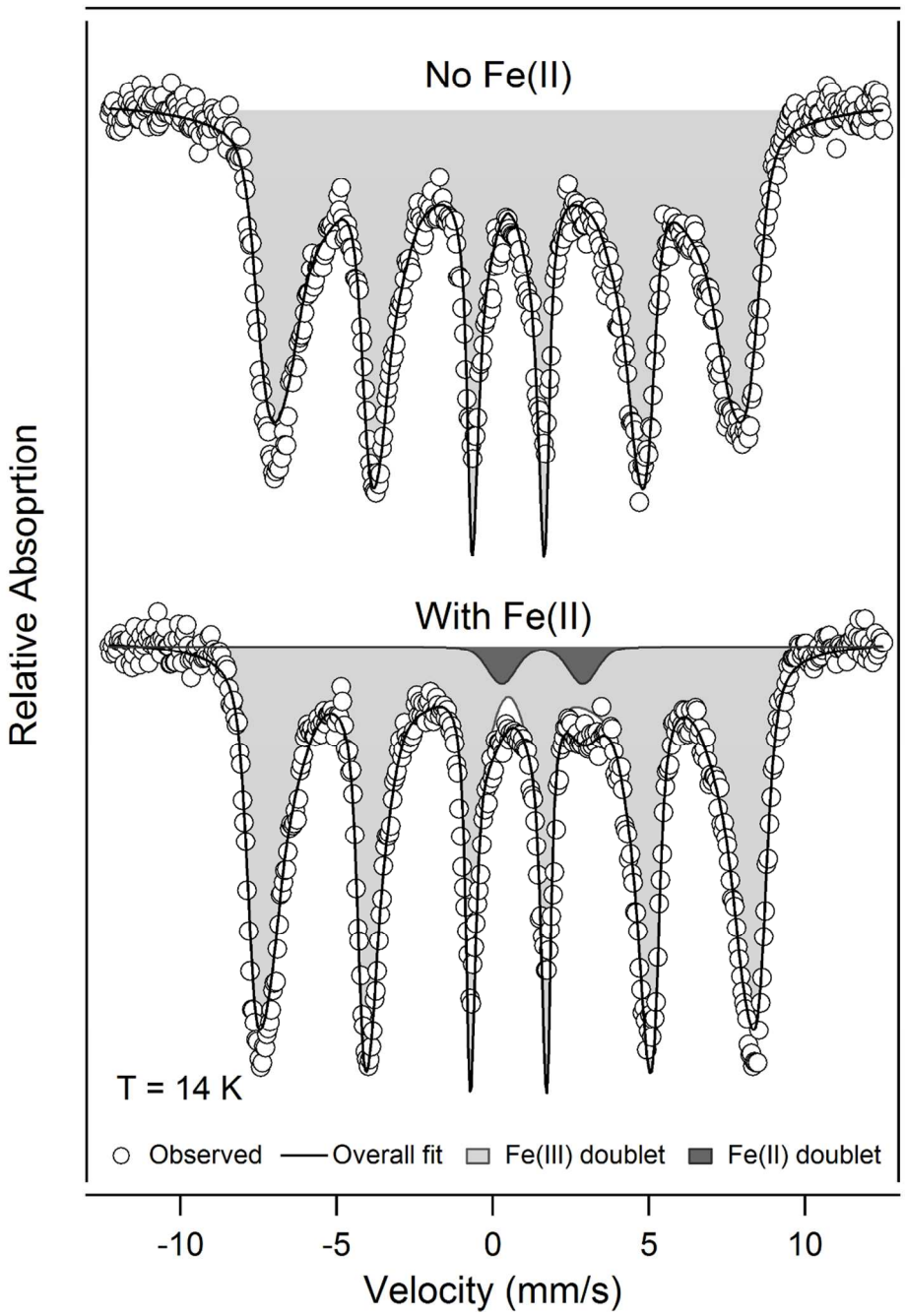


Figure S9. Mössbauer spectra of SRNOM-Fh (C/Fe = 1.2) with or without Fe(II) over 28 days at 14 K.



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139 Figure S10. Mössbauer spectra fitting of SRNOM-Fh (C/Fe = 1.2) aged with or without Fe(II)
140 over 28 days.

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Table S7. Mössbauer parameters derived from fitting spectra in Figure S10.

Sample			<CS>[a] (mm/s)	<QS>[b] (mm/s)	<H>[c] (T)	std(H) (T) or std(QS) (mms^{-1})[d]	Area (%)	χ_v^2
Aged SRNOM-Fh (1.2)	With Fe(II)	Fe(II) Doublet	1.59	2.60	-	0.81	2.92	3.16
		Fe(III) Sextet	0.48	-0.02	43.30	10.71	97.08	
	No Fe(II)	Fe(III) Sextet	0.48	-0.01	39.28	12.54	100	1.71

[a] Center shift.
[b] Quadrupole splitting for doublets and quadrupole shift parameter for sextets.
[c] Hyperfine field.
[d] Standard deviation of the Voigt profile for the hyperfine field or quadrupole splitting parameters.

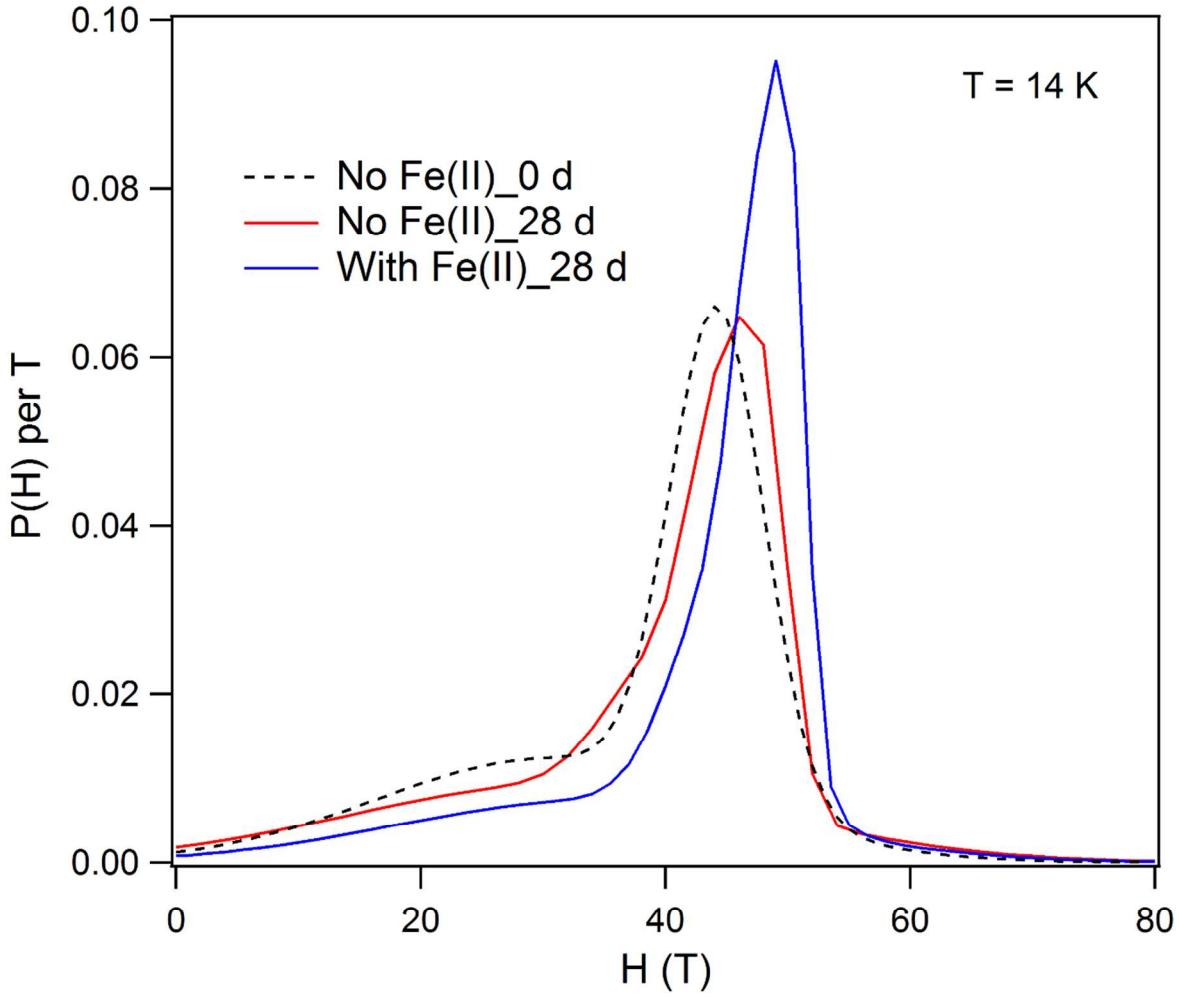


Figure S11. Hyperfine field distribution of SRNOM-Fh (C/Fe = 1.2) with or without Fe(II) at 14 K.

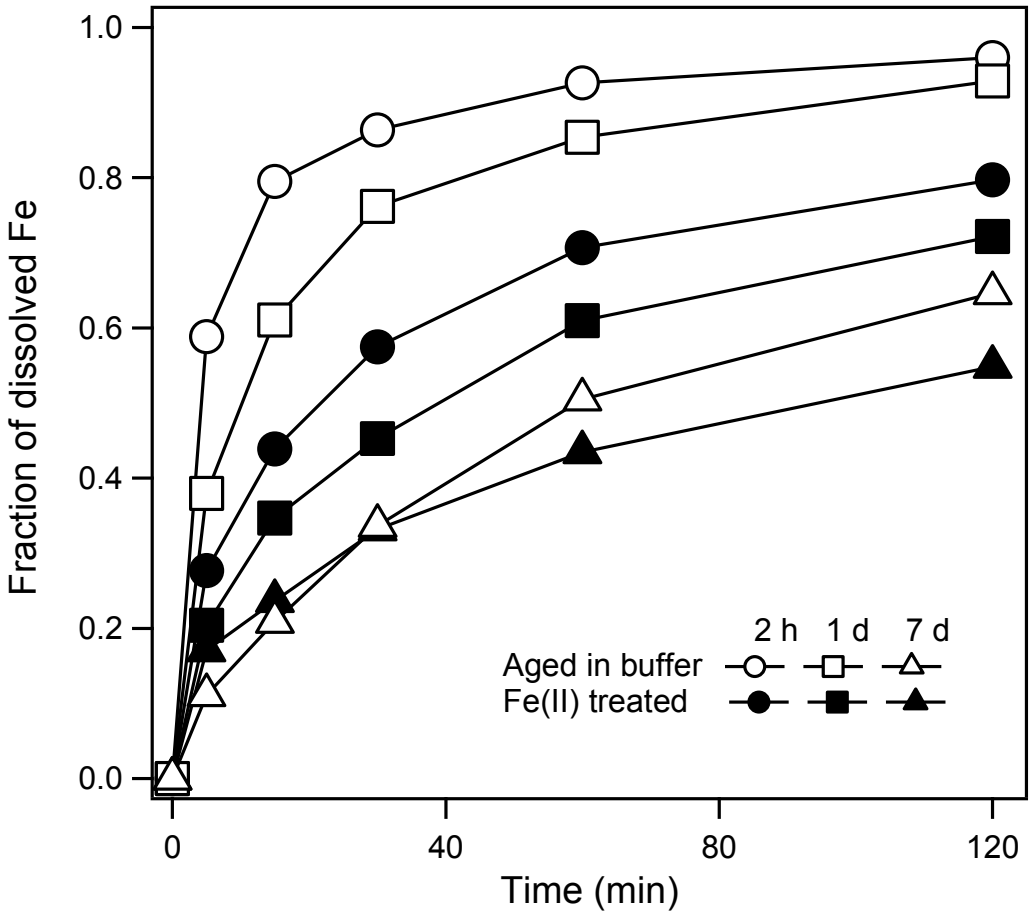
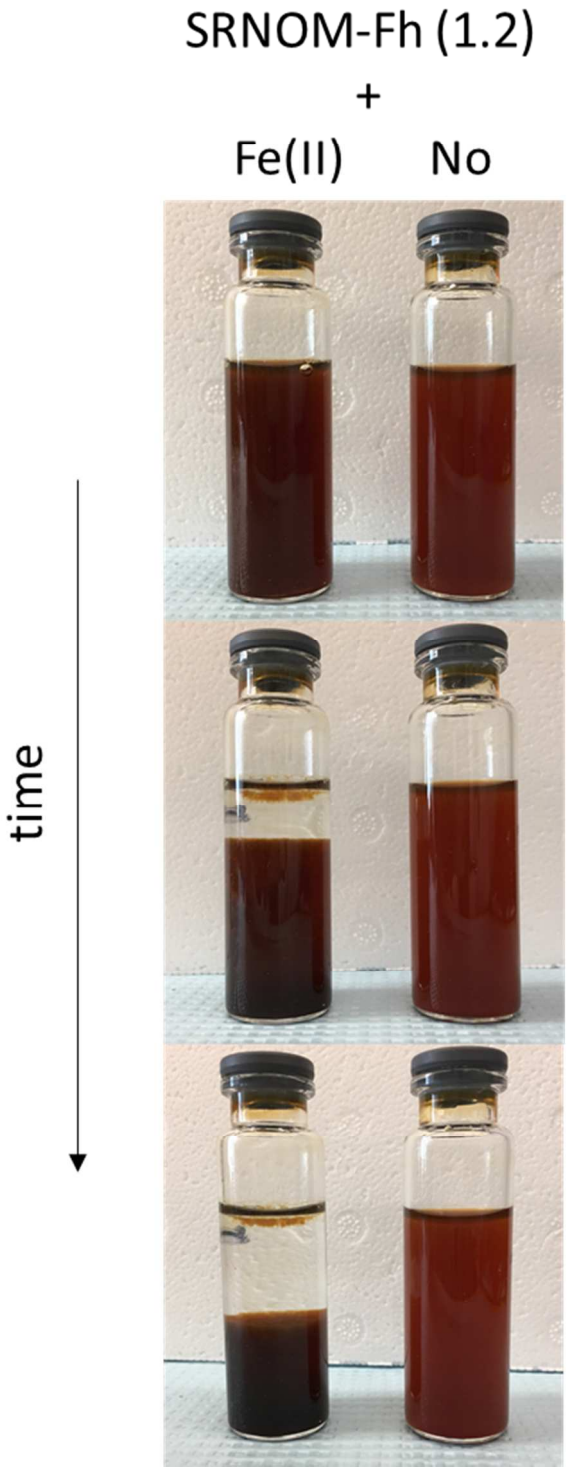


Figure S12. Acid dissolution with 0.2 M HCl to (a) SRNOM-Fh (C/Fe = 1.2) treated with Fe(II) in PIPES buffer (pH 7.0) over time; (b) SRNOM-Fh (C/Fe = 1.2) aged in PIPES buffer (pH 7.0) over time.



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159 Figure S13. The sedimentation of SRNOM-Fh (C/Fe = 1.2) in PIPES buffer (pH 7.0) with or
160 without 2 mM Fe(II) over 30 minutes.

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References

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