

# Supplementary Material

## Phosphate burial in aquatic sediments: rates and mechanisms of vivianite formation from mackinawite

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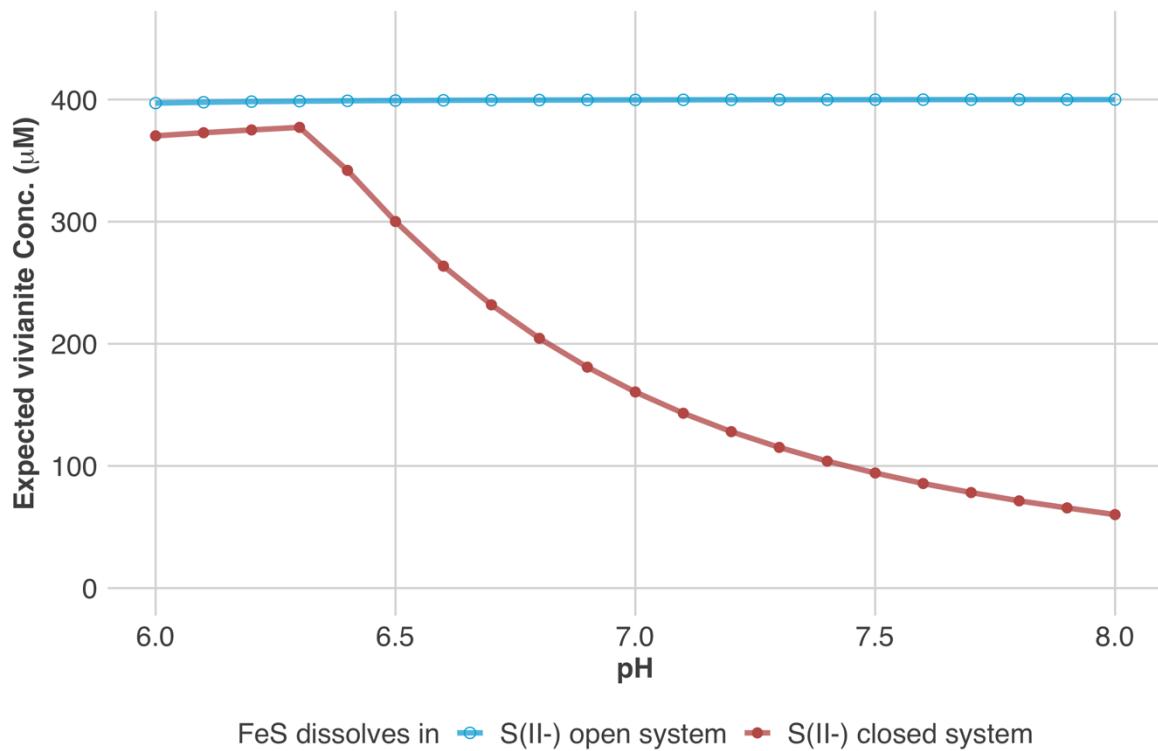
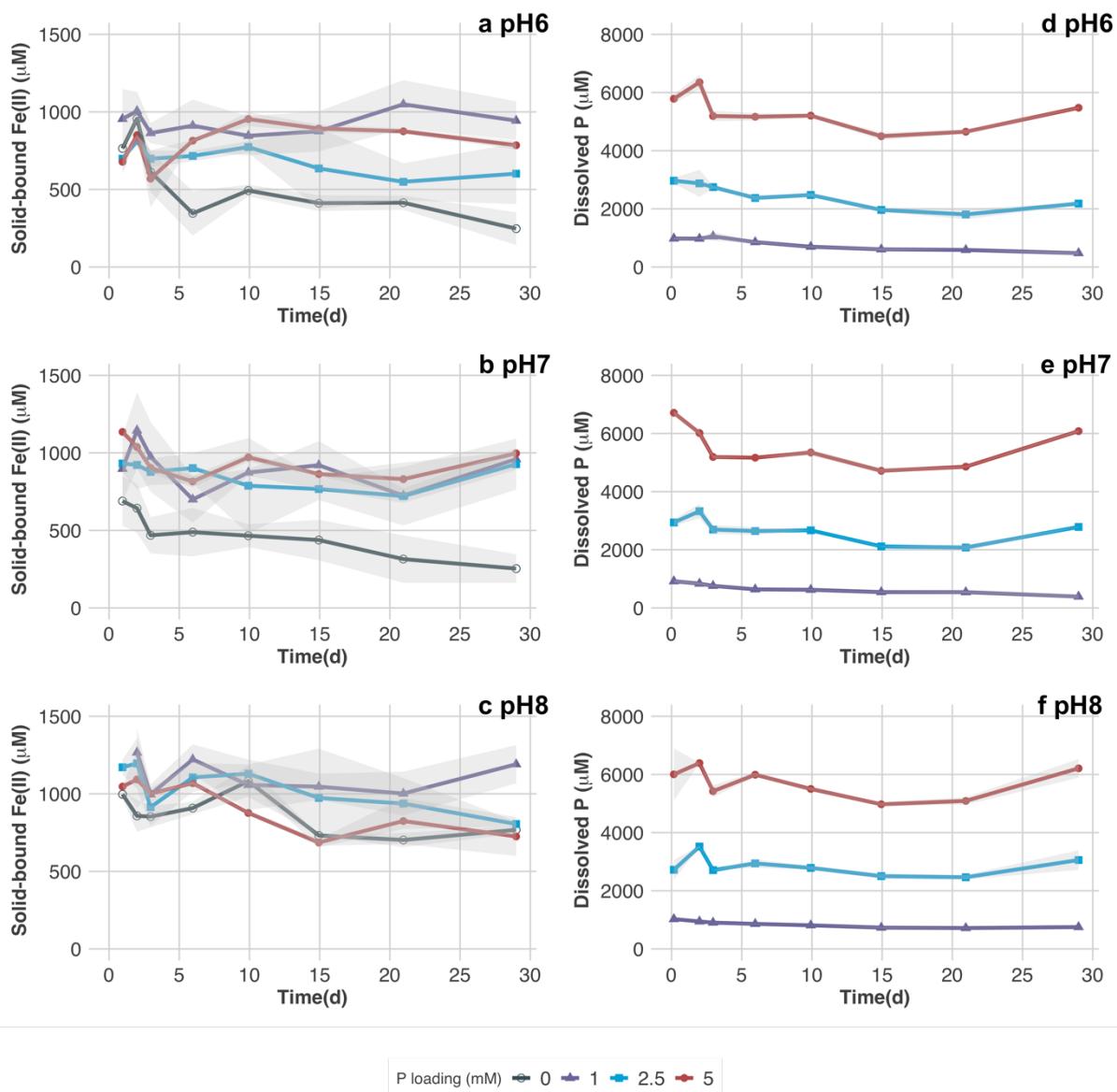


Fig. S1 Calculated results for expected vivianite concentrations when FeS dissolves in open/closed S-II system.

Results were calculated based on the experimental setup: FeS 1.2 mM, P loading 5 mM and ionic strength 0.01M.



*Fig. S2 Time evolution of (a, b and c) solid-bound Fe (II) and (d, e and f) dissolved phosphate concentration at (a, d) pH 6, (b, e) pH 7 and (c, f) pH 8 for different P loading (0, 1, 2.5, and 5mM). The shaded areas represent the minimum/maximum values for duplicates.*

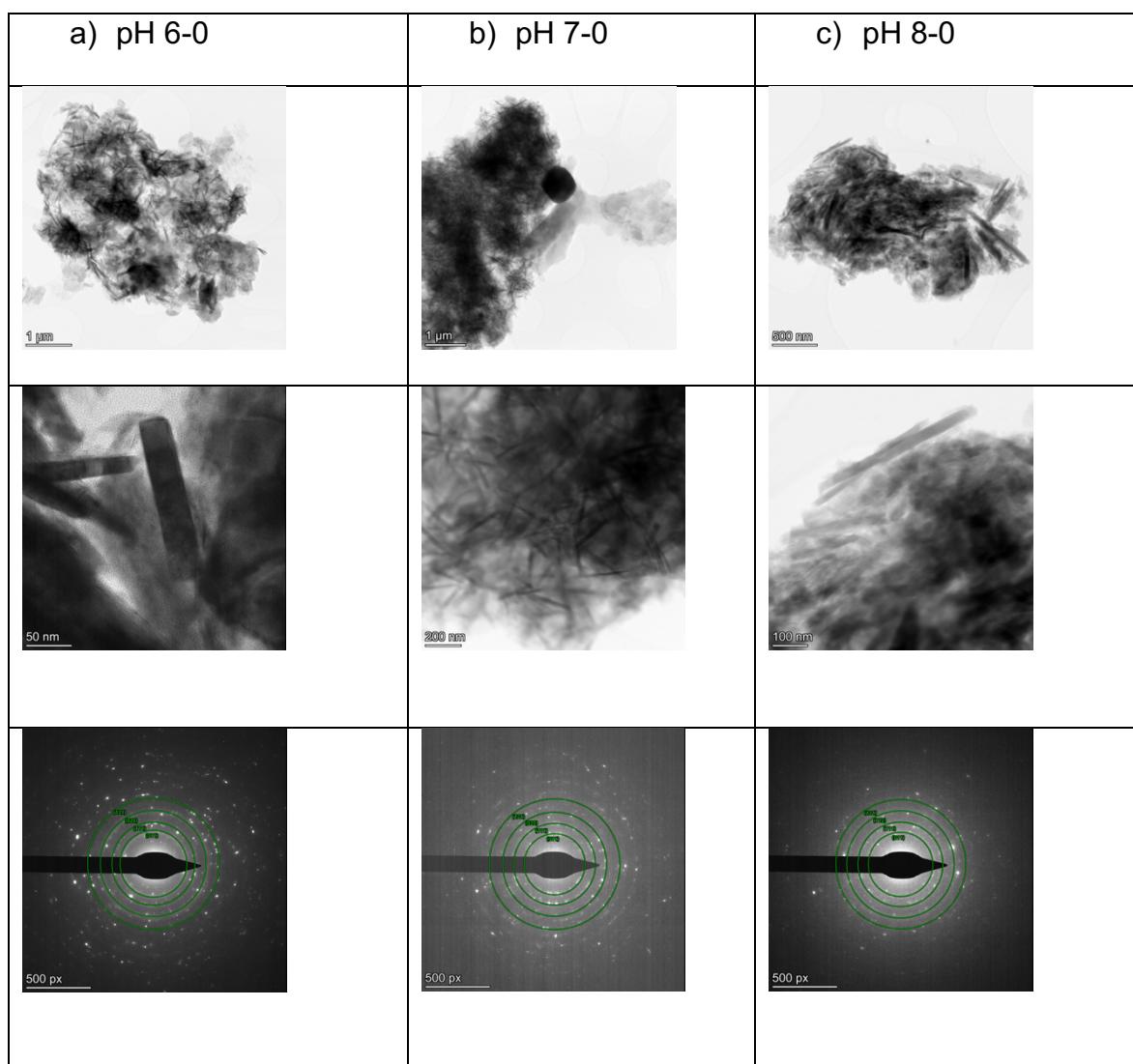


Fig. S3 Transmission electron microscopy (TEM) images and SAED pattern of samples from the control experiments ( $P_{ini} = 0 \text{ mM}$ ) at pH a) pH 6, b) pH 7, c) pH 8.

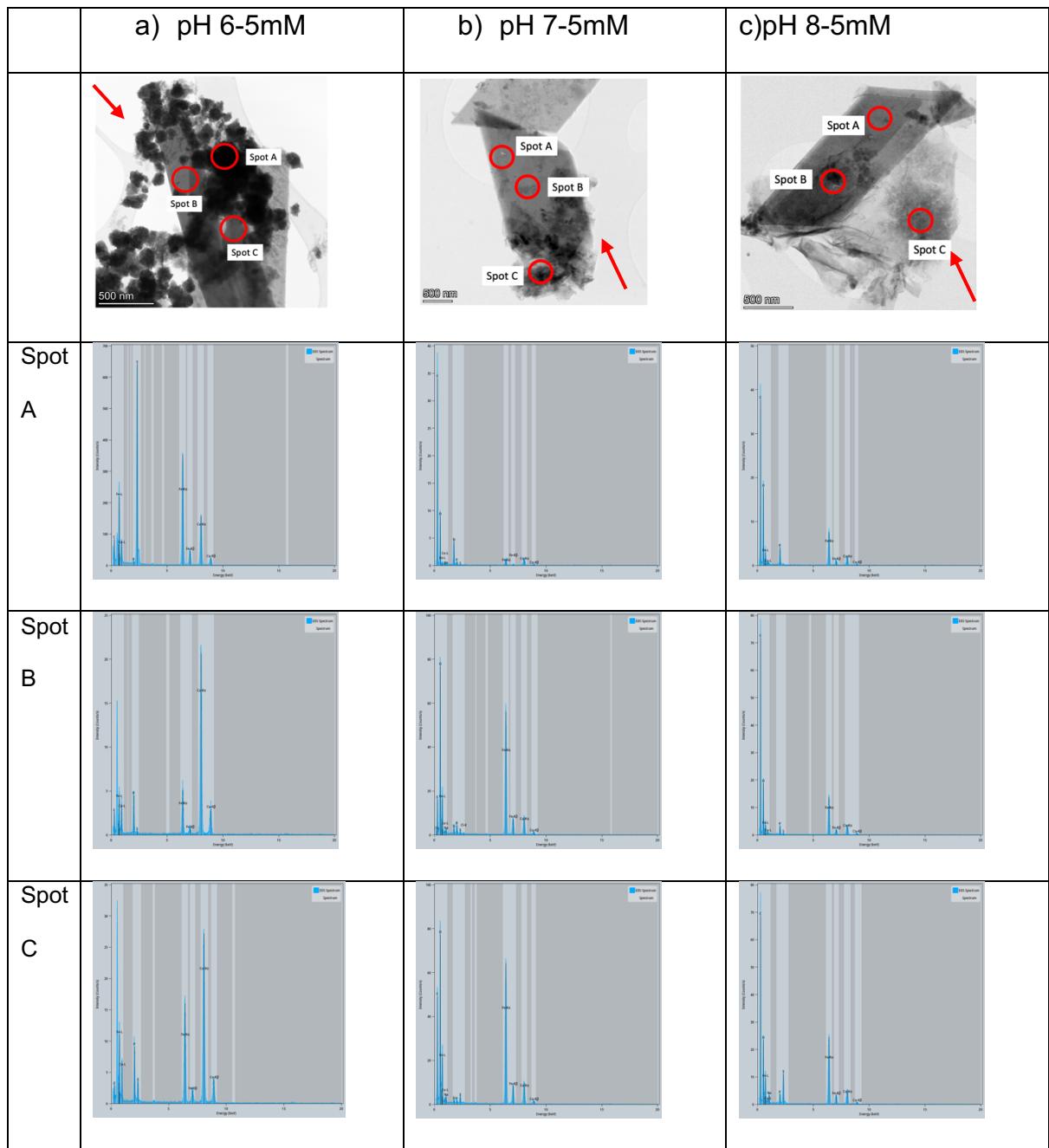


Fig. S4 Spectrum of Energy-dispersive X-ray spectroscopy (TEM-EDS) for corresponding spots of the P-loaded ( $P_{ini} = 5 \text{ mM}$ ) experiments at pH a) pH 6, b) pH 7, c) pH 8. The arrows indicate increasing values of Fe:S and P : Fe ratios obtained from energy-dispersive X-ray spectroscopy (TEM – EDS), as summarized at Table S1.

Table S1: Relative content of P, S and Fe calculated from TEM-EDS spectra.

Treatment	Spot	Peak Area			Relative content (%)			P/Fe ratio	S/Fe ratio
		P	S	Fe	P	S	Fe		
pH 6 - 5mM	A	2625	65261	51604	2.20%	54.62%	43.19%	0.05	1.26
	B	450	62	758	35.43%	4.88%	59.69%	0.59	0.08
	C	964	429	2574	24.30%	10.81%	64.89%	0.37	0.17
pH 7 - 5mM	A	95	0	164	36.68%	0.00%	63.32%	0.58	0
	B	518	202	7925	5.99%	2.34%	91.67%	0.07	0.03
	C	268	509	9540	2.60%	4.93%	92.47%	0.02	0.05
pH 8 - 5mM	A	418	54	1165	25.53%	3.30%	71.17%	0.35	0.05
	B	340	96	2102	13.40%	3.78%	82.82%	0.16	0.05
	C	436	1226	3659	8.19%	23.04%	68.77%	0.11	0.33

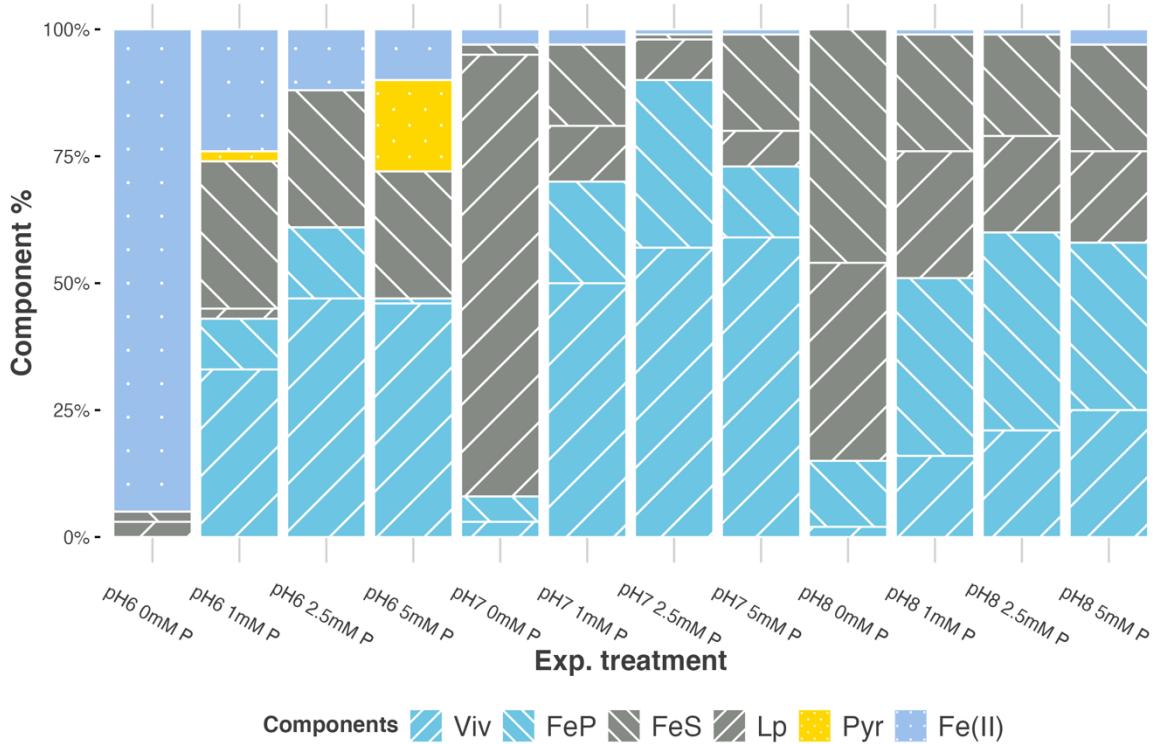


Fig. S5. Results from the LCF analysis of the Fe K-edge XANES spectra of solids collected on day 37 combined with data on dissolved Fe(II). The solid-phase LCF results were scaled by the fraction of solid-phase Fe as estimated from the average fractions of dissolved Fe at days 21 and 29. Viv = vivianite, FeP = amorphous basic Fe(III)-phosphate, FeS = mackinawite, Lp = lepidocrocite, Pyr = pyrite, Fe(II) = dissolved Fe(II). Corresponding results obtained from the EXAFS spectra are shown in Fig. 4.

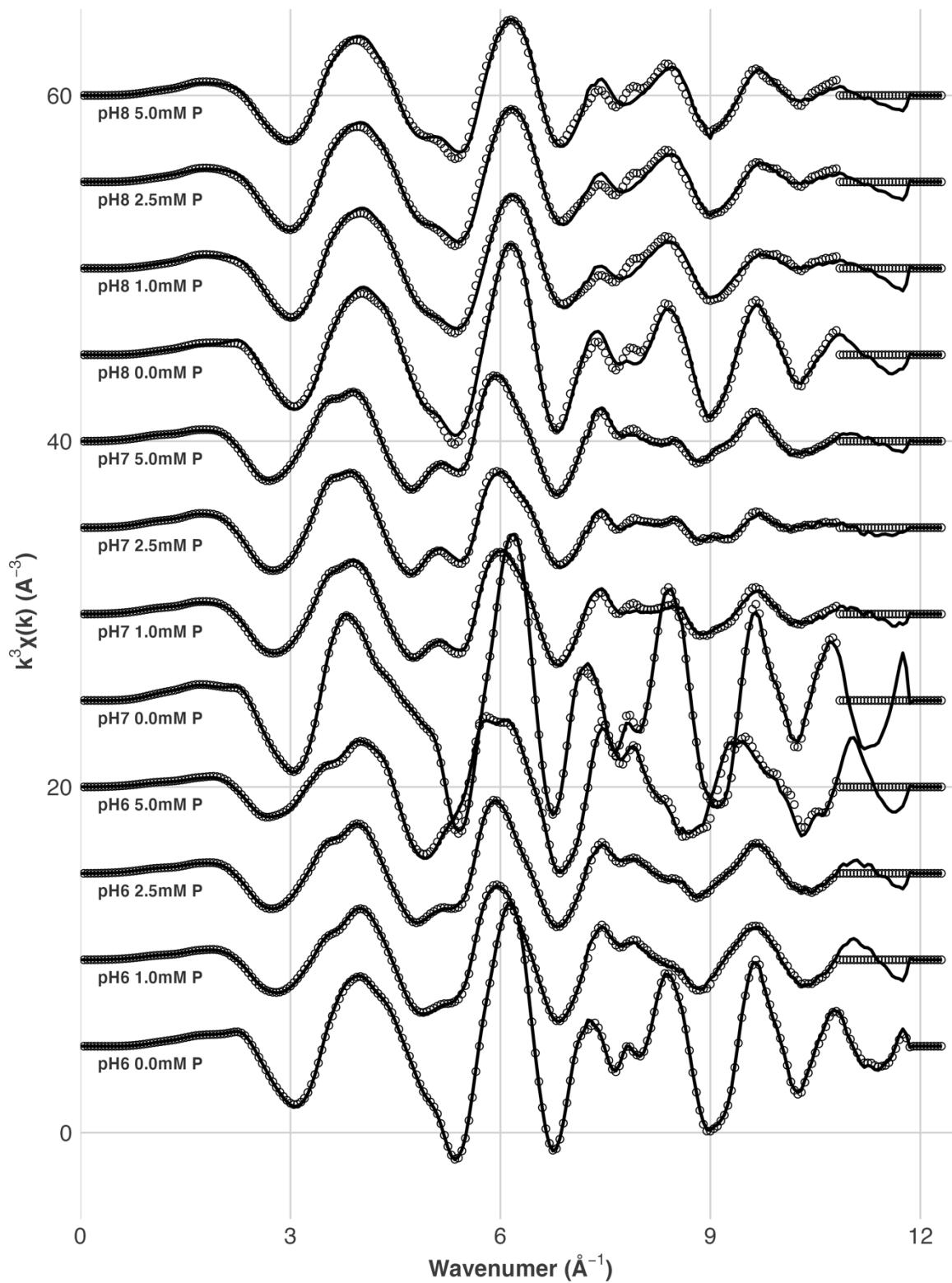
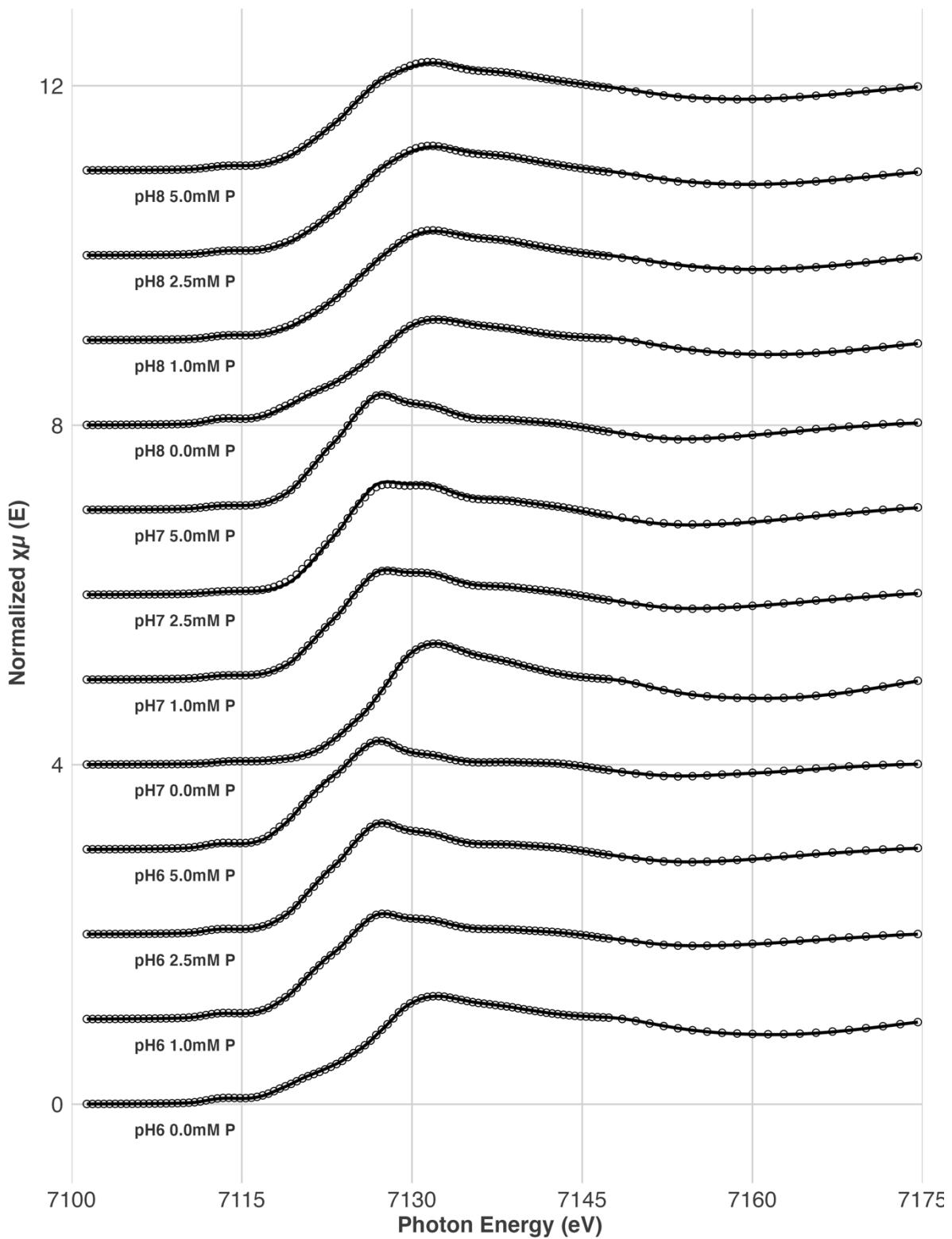
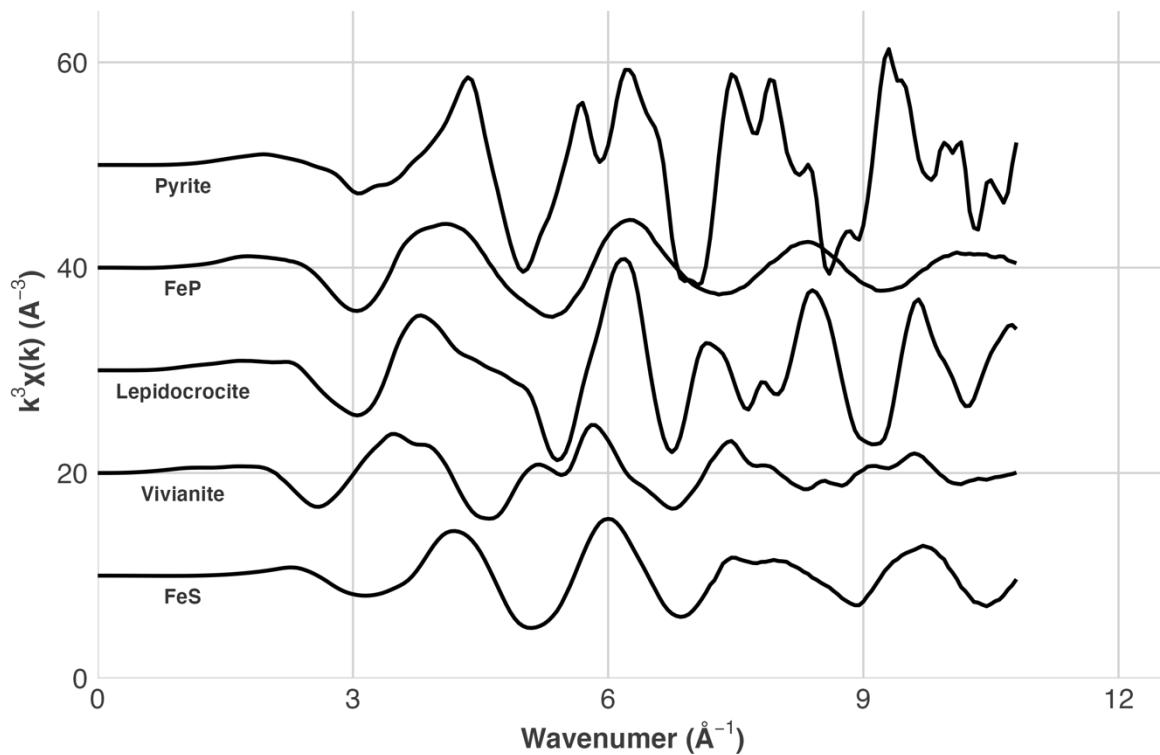


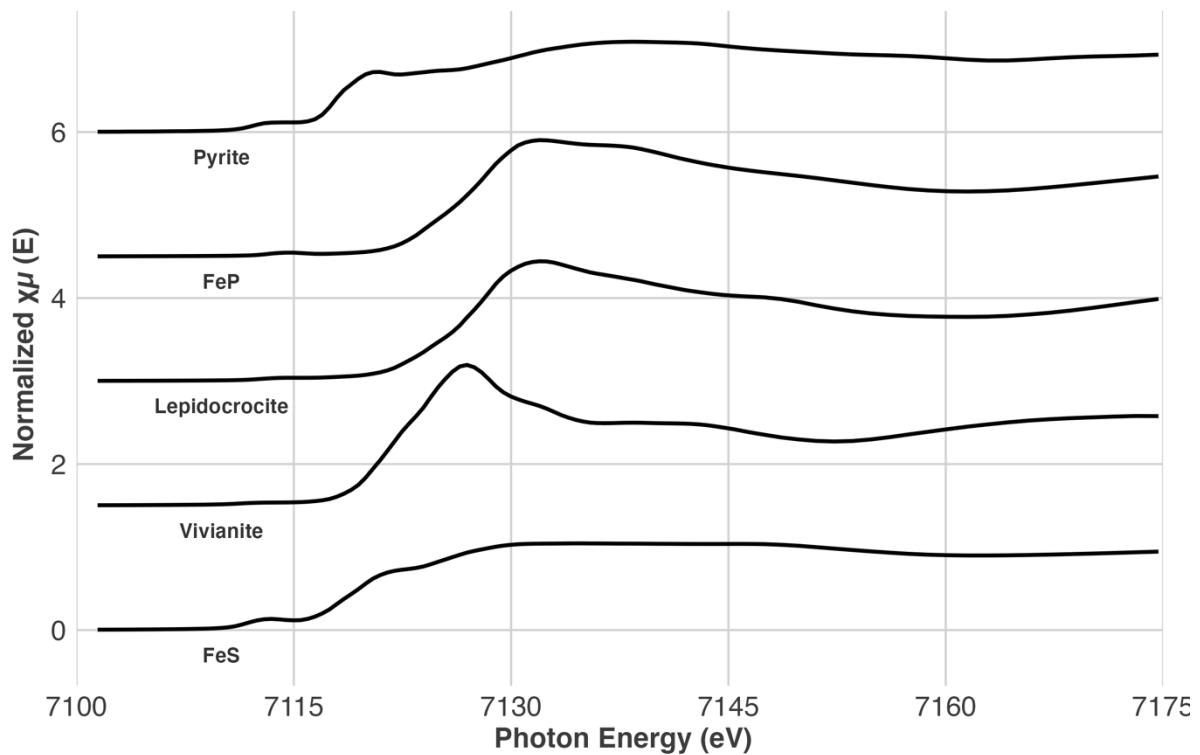
Fig. S6 Results of the Fe K-edge EXAFS spectra of solids collected on day 37 (dot = measurement data, line = fitting results) Corresponding fitting results by LCF are shown in Fig. 4. Reference spectra used for fitting are shown in Fig. S8. Parameters used for the fitting are shown in Table S2.



*Fig. S7 Results of the Fe K-edge XANES spectra of solids collected on day 37 (dot = measurement data, line = fitting results) Corresponding fitting results by LCF are shown in Fig. S5. Reference spectra used for fitting are shown in Fig. S9. Parameters used for the fitting are shown in Table S2.*



*Fig. S8 Reference spectra of minerals used for the EXAFS LCF fitting. The corresponding LCF fitting results, original measurement data and fitting results are shown in Fig. 4 and Fig. S6, respectively. Parameters used for the fitting are shown in Table S2.*



*Fig. S9 Reference spectra of minerals used for the XANES LCF fitting. The corresponding LCF fitting results, original measurement data and fitting results are shown in Fig. S5 and Fig. S7, respectively. Parameters used for the fitting are shown in Table S2.*

Table S2 Summary of the LCF results from the combinational LCF analysis in Athena. ( $Mk = FeS$ ,  $Pyr = pyrite$ ,  $Lp$  = lepidocrocite,  $FeP$  = amorphous basic Fe(III)-phosphate,  $Viv = vivianite$ ).

EXAFS		<b>pH</b>	<b>P<sub>ini</sub></b>	<b>Mk</b>	<b>Pyr</b>	<b>Lp</b>	<b>FeP</b>	<b>Viv</b>	<b>Sum</b>	<b>rfactor</b>
<b>pH</b>	<b>P<sub>ini</sub></b>			<b>Mk</b>	<b>Pyr</b>	<b>Lp</b>	<b>FeP</b>	<b>Viv</b>	<b>Sum</b>	<b>rfactor</b>
6	0	0.46	0.00	0.54	0.04	0.02	1.05	7.09×10 <sup>-4</sup>		
	1	0.41	0.03	0.02	0.13	0.43	1.02	2.79×10 <sup>-3</sup>		
	2.5	0.33	0.00	0.00	0.17	0.51	1.02	1.36×10 <sup>-3</sup>		
	5	0.32	0.19	0.00	0.00	0.49	1.01	1.21×10 <sup>-2</sup>		
	7	0.00	0.01	0.80	0.13	0.04	0.99	1.83×10 <sup>-3</sup>		
7	1	0.10	0.02	0.08	0.27	0.50	0.96	9.08×10 <sup>-3</sup>		
	2.5	0.00	0.01	0.02	0.40	0.56	0.98	6.64×10 <sup>-3</sup>		
	5	0.14	0.02	0.05	0.18	0.58	0.98	4.60×10 <sup>-3</sup>		
	8	0.32	0.05	0.33	0.20	0.04	0.94	1.45×10 <sup>-2</sup>		
8	1	0.08	0.04	0.10	0.52	0.13	0.86	1.71×10 <sup>-2</sup>		
	2.5	0.07	0.04	0.12	0.48	0.18	0.89	1.77×10 <sup>-2</sup>		
	5	0.08	0.05	0.16	0.39	0.23	0.91	2.39×10 <sup>-2</sup>		
XANES		<b>pH</b>	<b>P<sub>ini</sub></b>	<b>Mk</b>	<b>Pyr</b>	<b>Lp</b>	<b>FeP</b>	<b>Viv</b>	<b>Sum</b>	<b>rfactor</b>
<b>pH</b>	<b>P<sub>ini</sub></b>			<b>Mk</b>	<b>Pyr</b>	<b>Lp</b>	<b>FeP</b>	<b>Viv</b>	<b>Sum</b>	<b>rfactor</b>
6	0	0.39	0.03	0.55	0.03	0.00	1.00	2.69×10 <sup>-5</sup>		
	1	0.38	0.03	0.02	0.13	0.44	1.00	4.08×10 <sup>-5</sup>		
	2.5	0.31	0.00	0.01	0.15	0.53	1.00	4.11×10 <sup>-5</sup>		
	5	0.28	0.20	0.00	0.01	0.51	1.00	9.52×10 <sup>-5</sup>		
	7	0.02	0.00	0.90	0.05	0.03	1.00	2.18×10 <sup>-5</sup>		
7	1	0.17	0.00	0.12	0.20	0.51	1.00	6.27×10 <sup>-5</sup>		
	2.5	0.01	0.00	0.08	0.33	0.58	1.00	5.12×10 <sup>-5</sup>		
	5	0.19	0.00	0.08	0.14	0.60	1.00	5.02×10 <sup>-5</sup>		
	8	0.45	0.00	0.39	0.13	0.02	1.00	7.65×10 <sup>-5</sup>		
8	1	0.23	0.00	0.25	0.36	0.16	1.00	1.46×10 <sup>-4</sup>		
	2.5	0.21	0.00	0.20	0.38	0.21	1.00	1.39×10 <sup>-4</sup>		
	5	0.22	0.00	0.18	0.34	0.26	1.00	1.30×10 <sup>-4</sup>		

Table S3: Hyperfine parameters derived from fits to 80 K Mössbauer spectra.

	pH 6	pH7	pH8
<b>viv<sub>a</sub>: vivianite Fe<sup>2+</sup>II</b>		<b>vivianite Fe<sup>2+</sup> average</b>	
CS (mm/s)	1.32 (2)	1.32 (1)	1.32 (2)
QS (mm/s)	3.19 (5)	2.99 (2)	2.90 (2)
FWHM (mm/s)	0.49 (5)	0.94 (6)	0.85 (7)
Area (%)	19 (3)	21 (3)	19 (3)
<hr/>			
<b>viv<sub>b</sub>: vivianite Fe<sup>2+</sup>I</b>			
CS (mm/s)	1.28 (2)		
QS (mm/s)	2.58 (6)		
FWHM (mm/s)	0.44 (6)		
Area (%)	10 (3)		
<hr/>			
<b>FeS<sub>a</sub>: mackinawite FeS</b>			
CS (mm/s)	0.49 (1)		
FWHM (mm/s)	0.95 (3)		
Area (%)	43 (3)		
<hr/>			
<b>FeS<sub>b</sub>: mackinawite Fe<sub>x</sub>S</b>			
CS (mm/s)	0.48 (5)	0.42 (4)	0.42 (5)
E (mm/s)	0.09 (9)	0.00 (3)	0.00 (4)
B (T)	27 (1)	-	-
B <sub>1</sub> (T)		14 (1)	14 (2)
σ <sub>B1</sub> (T)		7 (1)	8 (2)
p <sub>1</sub> (%)		48 (6)	39 (11)
B <sub>2</sub> (T)		27 (1)	27 (1)

$\sigma_{B2}$ (T)	5 (1)	5 (1)
$p_2$ (%)	52 (6)	61 (11)
FWHM (mm/s)	0.7*	-
Area (%)	11 (3)	79 (3)

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**Grg<sub>a</sub>: greigite tetrahedral site**

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CS (mm/s)	0.37*
$\varepsilon$ (mm/s)	0*
B (T)	31.7*
FWHM (mm/s)	0.60 (8)
Area (%)	6 (4)

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**Grg<sub>b</sub>: greigite octahedral site**

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CS (mm/s)	0.70*
$\varepsilon$ (mm/s)	-0.06*
B (T)	32.9*
FWHM (mm/s)	0.60 (8)
Area (%)	11 (3)

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\*fixed to literature value

Table S4 Final check of  $\text{Fe(II)}_{\text{aq}}$  at 37 d, and  $\text{Fe(III)}$  check before solid characterization for oxidation extent.

<b>pH</b>	<b>P<sub>ini</sub> (mM)</b>	<b>Fe(II)<sub>aq</sub> (<math>\mu\text{M}</math>)</b>	<b>Fe(III)%</b>
<b>6</b>	0	1212	12.9%
	1	316	5.8%
	2.5	147	5.8%
	5	118	0.6%
<b>7</b>	0	25	5.8%
	1	37	7.9%
	2.5	14	2.0%
	5	13	-7.4%
<b>8</b>	0	0	2.5%
	1	7	5.8%
	2.5	12	-2.0%
	5	39	5.8%

*Table S5 Comparison of expected vivianite conversion extent based on  $P_{sb}$  concentrations and EXAFS fitting. The expected vivianite concentration is calculated by the stoichiometry of vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ ) based on  $P_{sb}$  concentrations, and the conversion extent is then calculated by the total Fe concentration (1200  $\mu\text{M}$ ).*

<b>pH</b>	<b><math>P_{ini}</math> (mM)</b>	<b><math>P_{sb}</math></b>	<b>final</b>	<b>Expected</b>	<b>Expected vivianite conversion</b>	<b>Vivianite conversion EXAFS</b>
			<b>Conc. (<math>\mu\text{M}</math>)</b>	<b>vivianite (<math>\mu\text{M}</math>)</b>		
<b>6</b>	1	372	186		47%	56%
	2.5	317	158.5		40%	68%
	5	491	245.5		61%	49%
<b>7</b>	1	383	191.5		48%	77%
	2.5	477	238.5		60%	96%
	5	610	305		76%	76%
<b>8</b>	1	287	143.5		36%	65%
	2.5	324	162		41%	66%
	5	337	223.5		56%	62%