

Interfacial Precipitation of Phosphate on Hematite and Goethite

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Table S1. Main surface speciation of goethite and hematite in equilibrium with $\text{NH}_4\text{H}_2\text{PO}_4$ reaction solutions at pH 2.0 and 4.5 and saturation indices (SI) with respect to different iron phosphate phases of various $\text{NH}_4\text{H}_2\text{PO}_4$ reaction solutions after equilibration with goethite and hematite. ^a

$\text{NH}_4\text{H}_2\text{PO}_4$ solution	IS	FeHPO_4^+	$\text{FeH}_2\text{PO}_4^+$	$\text{FeH}_2\text{PO}_4^{+2}$	FeHPO_4	Fe^{+3}	$\text{Fe}(\text{OH})_2^+$	FeOH^{+2}
50 mM, pH 2.0, goethite	0.065	−2.74	−3.60	−3.31	−7.77	−5.89	−6.23	−5.95
50 mM, pH 4.5, goethite	0.050	−7.18	−6.73	−10.12	−8.53	−13.0	−8.60	−10.70
50 mM, pH 2.0, hematite	0.063	−3.73	−4.50	−4.19	−8.78	−6.75	−7.32	−6.92
50 mM, pH 4.5, hematite	0.050	−8.37	−7.76	−11.30	−9.56	−14.2	−9.80	−11.9

to be continued

H_2PO_4^-	HPO_4^{2-}	H_3PO_4	SI		
			strengite	tenticite	cacoxenite
−1.69	−6.76	−1.67	3.5	23.9	34.4
−1.39	−4.08	−3.74	1.4	19.8	28.2
−1.72	−6.90	−1.58	2.4	20.5	29.9
−1.39	−4.08	−3.74	0.2	16.2	23.4

^alog activity

$\text{NH}_4\text{H}_2\text{PO}_4$ solution	IS	FeHPO_4^+	$\text{FeH}_2\text{PO}_4^+$	$\text{FeH}_2\text{PO}_4^{+2}$	FeHPO_4	Fe^{+3}	$\text{Fe}(\text{OH})_2^+$	FeOH^{+2}	Al^{+3}
50 mM +10 mM AlCl_3 pH 4.5, hematite	0.1	-7.67	-7.27	-10.3	-9.43	-13.1	-9.44	-11.2	-3.0
50 mM + 10 mM AlCl_3 pH 4.5, goethite	0.1	-6.47	-6.25	-9.05	-8.41	-11.9	-8.24	-9.97	-3.0
to be continued									
AlOH^{+2}	$\text{Al}(\text{OH})_2^+$	$\text{Al}(\text{OH})_3$	H_2PO_4^-	HPO_4^{-2}	H_3PO_4	<i>SI</i>			
						strengite	tinticite	cacoxenite	wavellite
-3.87	-4.83	-7.39	-1.41	-4.47	-3.40	0.6	16.9	24.4	8.5
-3.87	-4.83	-7.39	-1.41	-4.47	-3.40	1.8	20.5	29.2	8.5

^alog activity

NH ₄ H ₂ PO ₄ solution	IS	FeHPO ₄ ⁺	FeH ₂ PO ₄ ⁺	FeH ₂ PO ₄ ⁺²	FeHPO ₄	Fe ⁺³	Fe(OH) ₂ ⁺	FeOH ⁺²
50 mM + 1 μM citrate pH 4.5	0.05	-8.47	-7.83	-11.5	-9.58	-14.4	-9.85	-11.99
50 mM + 10 μM citrate pH 4.5	0.05	-8.50	-7.85	-11.5	-9.59	-14.4	-9.87	-12.02
50 mM + 50 μM citrate pH 4.5	0.05	-8.62	-7.94	-11.7	-9.61	-14.6	-9.92	-12.14
to be continued								

H_2PO_4^-	HPO_4^{2-}	H_3PO_4	$\text{Fe}(\text{citrate})$	$\text{H}(\text{citrate})^{-2}$	$\text{H}_2(\text{citrate})^-$	$\text{H}_3(\text{citrate})$	<i>SI</i>		
							strengite	tinticite	cacoxenite
-1.39	-4.04	-3.79	-9.81	-6.71	-6.50	-7.92	0.18	16.10	23.28
-1.39	-4.02	-3.80	-8.83	-5.70	-5.51	-6.94	0.17	16.07	23.24
-1.39	-3.96	-3.86	-8.23	-4.98	-4.84	-6.34	0.11	15.95	23.06

^alog activity

Table S4. Main surface speciation of goethite in equilibrium with $\text{NH}_4\text{H}_2\text{PO}_4$ reaction solutions in the presence of citrate and saturation indices (*SI*) with respect to different iron phosphate phases of $\text{NH}_4\text{H}_2\text{PO}_4$ reaction solutions after equilibration with goethite.^a

$\text{NH}_4\text{H}_2\text{PO}_4$ solution	<i>IS</i>	FeHPO_4^+	$\text{FeH}_2\text{PO}_4^+$	$\text{FeH}_2\text{PO}_4^{+2}$	FeHPO_4	Fe^{+3}	$\text{Fe}(\text{OH})_2^+$	FeOH^{+2}
50 mM + 1 μM citrate pH 4.5	0.05	-7.27	-6.80	-10.3	-8.55	-13.2	-8.65	-10.79
50 mM + 10 μM citrate pH 4.5	0.05	-7.30	-6.82	-10.3	-8.56	-13.2	-8.67	-10.79
50 mM + 50 μM citrate pH 4.5	0.05	-7.42	-6.91	-10.5	-8.59	-13.4	-8.72	-10.94

to be continued

H_2PO_4^-	HPO_4^{2-}	H_3PO_4	$\text{Fe}(\text{citrate})$	$\text{H}(\text{citrate})^{-2}$	$\text{H}_2(\text{citrate})^-$	$\text{H}_3(\text{citrate})$	<i>SI</i>		
							strengite	tinticite	cacoxenite
-1.39	-4.04	-3.79	-8.61	-6.71	-6.50	-7.92	1.38	19.70	28.08
-1.39	-4.02	-3.80	-7.63	-5.71	-5.51	-6.94	1.37	19.67	28.04
-1.39	-3.96	-3.86	-7.03	-4.98	-4.84	-6.34	1.31	19.55	27.86

^alog activity

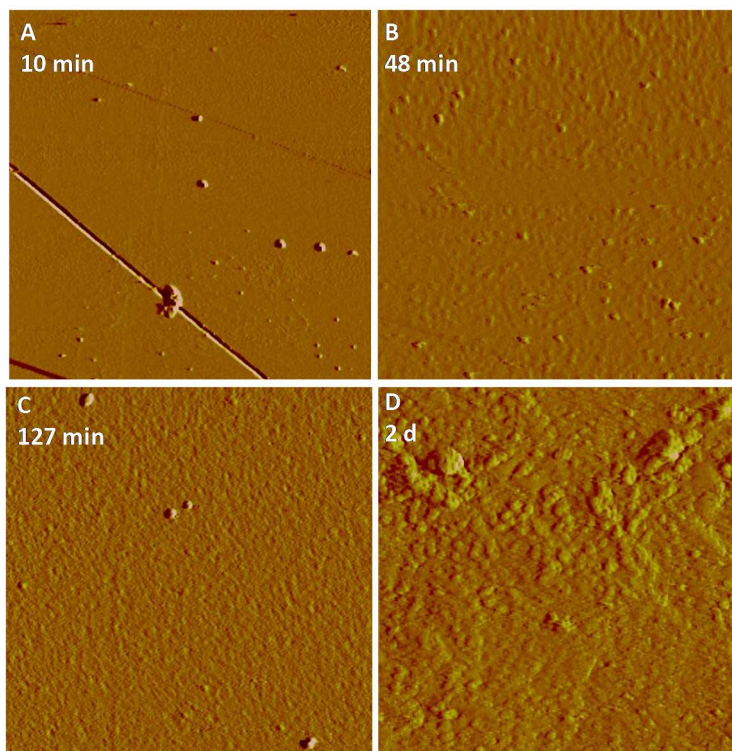


Figure S1. AFM time sequence (deflection images) showing in situ nucleation kinetics of Fe-P phases on a dissolving hematite surface in 50.0 mM $\text{NH}_4\text{H}_2\text{PO}_4$ (pH 2.0) at (A) $t = 10$ min, (B) 48 min, (C) 127 min, and (D) 2 d, respectively. After 127 min reaction, the scan area was almost fully covered with the nucleating fine particles, which passivated the reacting surfaces. AFM images, $5\ \mu\text{m} \times 5\ \mu\text{m}$.



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