Journal of Geophysical Research - Planets

Supporting Information for

Transformation of Precursor Iron(III) Minerals in Diagenetic Fluids: Investigating the Origin of Gray Hematite at Vera Rubin Ridge

A. L. Knight[1], K. Mitra[1]†, and J. G. Catalano[1,2]

[1]Department of Earth and Planetary Sciences, Washington University, Saint Louis, Missouri 63130, USA.

[2]McDonnell Center for the Space Sciences, Washington University, Saint Louis, Missouri 63130, USA.

Corresponding author: Abigail L. Knight (alknight@wustl.edu).

†Present Address: Department of Geosciences, Stony Brook University, Stony Brook, New York 11794, USA.

Contents of this file:

Text S1.

Precursor iron(III) mineral syntheses

Nanoparticles of akaganeite were synthesized by partially neutralizing 100 mL of a 1 mol L^{-1} solution of $FeCl_3 \cdot 6H_2O$ with 75 mL of 1 mol L^{-1} NaOH and letting it stand for 50 hours at room temperature (Schwertmann and Cornell, 2000). An additional 20 mL of 10 mol L^{-1} NaOH were then added, and the solution was heated at 70 ºC for eight days. The resulting supernatant was then centrifuged and the solid product washed via dialysis (Schwertmann and Cornell, 2000). Multiple batches of 2-line ferrihydrite were produced by dissolving 40 g of $Fe(NO_3)_3 \cdot 9H_2O$ in 0.5 L of distilled water, adding 1 mol L^{-1} NaOH until the pH reached 7 to 8, and stirring the solution rapidly (Schwertmann and Cornell, 2000). The solution was then centrifuged, the supernatant decanted, the solid resuspended in ultrapure water several times to remove remaining dissolved species before drying it in a desiccator. Acicular needles of goethite were synthesized by adding 50 mL 1 mol L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ to 90 mL of 5 mol L^{-1} NaOH continuously for 2 minutes while rapidly stirring. The resulting solution was then diluted to 1 L with ultrapure water, bringing the pH to 12 to 13, and heated at 70 ºC for 60 hours. After heating, the suspension was removed, the excess supernatant decanted, and the suspension filtered multiple times via vacuum filtration (Schwertmann and Cornell, 2000).

Multiple batches of ~60 nm red hematite particles were prepared by adding 300 mL of 1 mol L^{-1} NaOH continuously to 500 mL of 0.2 mol L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ for 5 minutes and then adding 50 mL of 1 mol L^{-1} $NaHCO_3$ to the solution continuously for 1.5 minutes, bringing the pH to about 8 (Schwertmann and Cornell, 2000). The solution was then heated at 98 ºC for 5 days, removed from heat and cooled to room temperature, and washed multiple times via vacuum filtration. In addition to the crystalline red hematite particles, a smaller (~10 nm) variety of red hematite was synthesized as well by adding 60 mL of 1 mol L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ dropwise into 750 mL of boiling ultrapure water, removing from heat, and centrifuging the product (Madden and Hochella, 2005; Mulvaney et al., 1988). Schwertmannite was prepared by adding 10.8 g $FeCl_3 \cdot 6H_2O$ and 3 g of Na_2SO_4 to 2 L of ultrapure water that had been heated to 60 ºC (Schwertmann and Cornell, 2000). Immediately after combining the reactants, the solution was heated at 60 ºC again for 12 minutes, cooled, and dialyzed for 30 days. Potassium jarosite was prepared by combining 10.8 g $FeCl_3 \cdot 6H_2O$ and 13.9 g K_2SO_4 in 100 mL of ultrapure water. While stirring this solution, 100 mL of 0.4 mol L^{-1} KOH was added over 1 minute, and then the solution was heated at 95 ºC in a covered beaker on a hot plate for 3 hours. After heating, the solution was cooled and washed via vacuum filtration (Baron and Palmer, 1996).

Table S1. Initial mineral batches, relevant experiments, and crystallite sizes.

Mineral	Batch	Experiments	Crystallite Size (nm)
akageneite	1	akageneite (all)	15 ± 1
ferrihydrite	1	ferrihydrite (single-mineral)	-[a]
ferrihydrite	2	ferrihydrite (seeded with hematite)	-
goethite	1	goethite (98 °C)	46 ± 1
goethite	2	goethite (200 °C)	49 ± 1
goethite	3	goethite (seeded with hematite)	31.1 ± 0.6
hematite	1	hematite (~60 nm)	56 ± 1
hematite	2	ferrihydrite (seeded with hematite) goethite (seeded with hematite)	58 ± 1
hematite	3	hematite (~10 nm)	12.3 ± 0.4
schwertmannite	1	schwertmannite (all)	-
jarosite	1	jarosite (all)	89 ± 4

[a]Particle size was too small to accurately determine via XRD.

Table S2. Final fluid compositions (pH values and dissolved iron concentrations) of experiments on the transformation of akageneite, ferrihydrite (seeded and unseeded), goethite (seeded and unseeded), hematite (~10 nm and ~60 nm), and schwertmannite in simulated diagenetic fluids.

Mineral	Temperature (°C)	Salt	Initial pH	Final pH	Fe (mmol/kg)
akaganeite	98	1 mol L^{-1} $MgCl_2$	3	1.21	36 ± 2
			7	1.24	21 ± 2
		1 mol L^{-1} $MgSO_4$	3	1.85	1.41 ± 0.05
			7	2.19	9.2 ± 0.1
	200	1 mol L^{-1} $MgCl_2$	3	0.67	49 ± 2
			7	0.72	40 ± 2
		1 mol L^{-1} $MgSO_4$	3	1.41	0.39 ± 0.02
			7	1.44	0.26 ± 0.02
ferrihydrite	98	1 mol L^{-1} $MgCl_2$	3	1.07	1.37 ± 0.05
			7	1.76	0.063 ± 0.001
		1 mol L^{-1} $MgSO_4$	3	1.93	0.61 ± 0.03
			7	2.60	0.036 ± 0.001
	200	1 mol L^{-1} $MgCl_2$	3	1.55	0.53 ± 0.06
			7	1.71	0.23 ± 0.04
		1 mol L^{-1} $MgSO_4$	3	2.20	0.42 ± 0.05
			7	2.73	0.015 ± 0.002
goethite	98	1 mol L^{-1} $MgCl_2$	3	3.54	-
			7	5.16	-
		1 mol L^{-1} $MgSO_4$	3	3.35	-
			7	5.70	-
	200	1 mol L^{-1} $MgCl_2$	3	2.48	-
			7	8.23	-
		1 mol L^{-1} $MgSO_4$	3	2.78	-
			7	9.13	-
hematite (~10 nm)	98	1 mol L^{-1} $MgCl_2$	3	1.78	0.44 ± 0.02
			7	2.99	0.0191 ± 0.0009
		1 mol L^{-1} $MgSO_4$	3	2.71	0.0195 ± 0.001
			7	4.43	-
	200	1 mol L^{-1} $MgCl_2$	3	1.72	0.061 ± 0.001
			7	2.83	-
		1 mol L^{-1} $MgSO_4$	3	2.50	0.0179 ± 0.0009
			7	3.11	-

hematite (~60 nm)	98	1 mol L^{-1} $MgCl_2$	3	4.71	-
			7	6.09	-
		1 mol L^{-1} $MgSO_4$	3	3.67	-
			7	6.42	-
	200	1 mol L^{-1} $MgCl_2$	3	4.02	-
			7	5.40	-
		1 mol L^{-1} $MgSO_4$	3	3.07	-
			7	2.83	-
schwertmannite	98	1 mol L^{-1} $MgCl_2$	3	0.87	65.7 ± 0.6
			7	0.88	24.9 ± 0.08
		1 mol L^{-1} $MgSO_4$	3	1.26	9.94 ± 0.03
			7	1.42	6.07 ± 0.03
	200	1 mol L^{-1} $MgCl_2$	3	0.59	12.1 ± 0.1
			7	0.64	11.36 ± 0.06
		1 mol L^{-1} $MgSO_4$	3	1.22	4.95 ± 0.02
			7	1.45	2.57 ± 0.04
ferrihydrite seeded with hematite	98	1 mol L^{-1} $MgCl_2$	3	1.17	12.2 ± 0.2
			7	2.25	0.046 ± 0.001
		1 mol L^{-1} $MgSO_4$	3	1.96	1.49 ± 0.05
			7	2.86	0.0133 ± 0.0010
	200	1 mol L^{-1} $MgCl_2$	3	1.18	7.9 ± 0.1
			7	2.13	-
		1 mol L^{-1} $MgSO_4$	3	1.77	0.90 ± 0.03
			7	2.56	0.102 ± 0.002
goethite seeded with hematite	98	1 mol L^{-1} $MgCl_2$	3	3.57	-
			7	9.01	-
		1 mol L^{-1} $MgSO_4$	3	3.43	-
			7	9.12	-
	200	1 mol L^{-1} $MgCl_2$	3	2.22	-
			7	7.34	-
		1 mol L^{-1} $MgSO_4$	3	3.04	-
			7	8.32	-

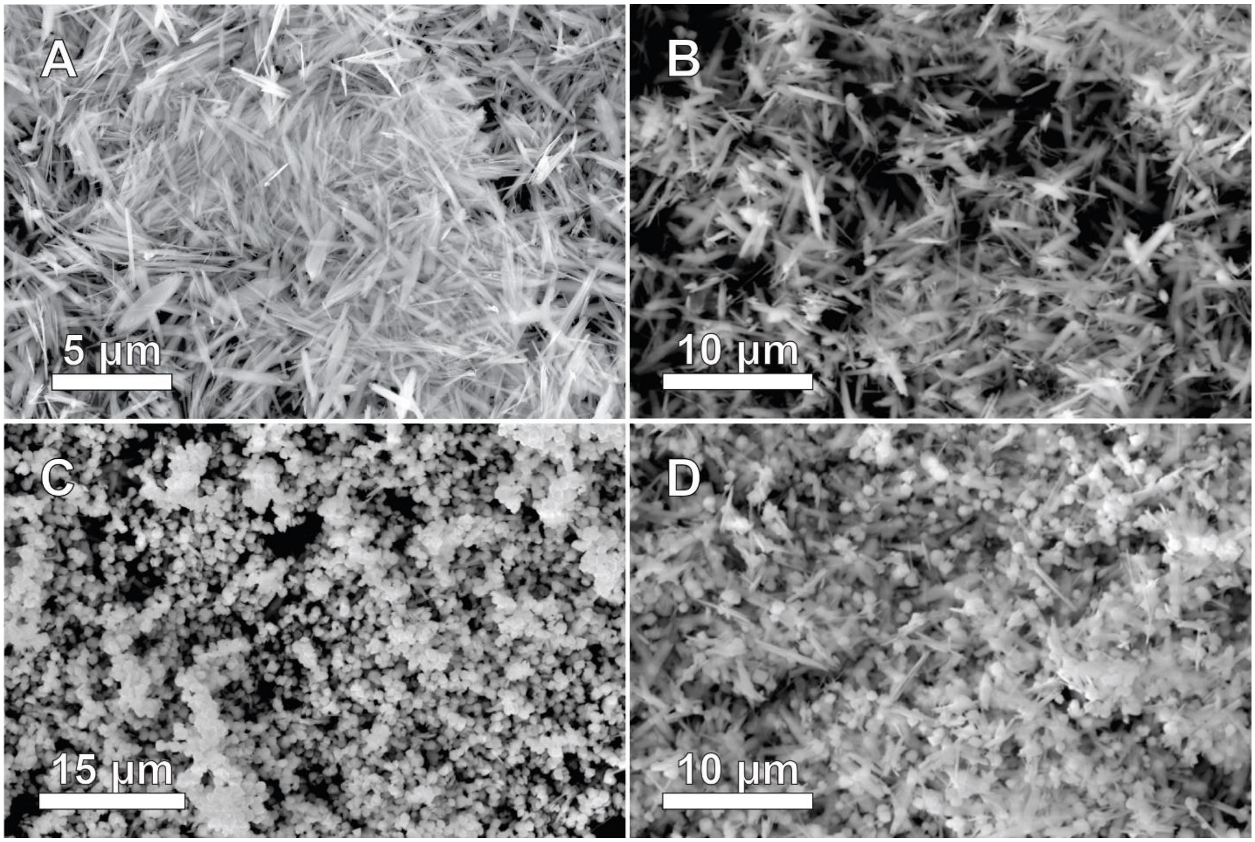

Figure S1. SEM images of (a) goethite batch 1 and the transformation products of goethite batch 2 subjected to (b) pH 7, 1 mol L^{-1} $MgCl_2$, 200 ºC fluids, (c) pH 3, 1 mol L^{-1} $MgSO_4$, 200 ºC fluids, and (d) pH 7, 1 mol L^{-1} $MgSO_4$, 200 ºC fluids.

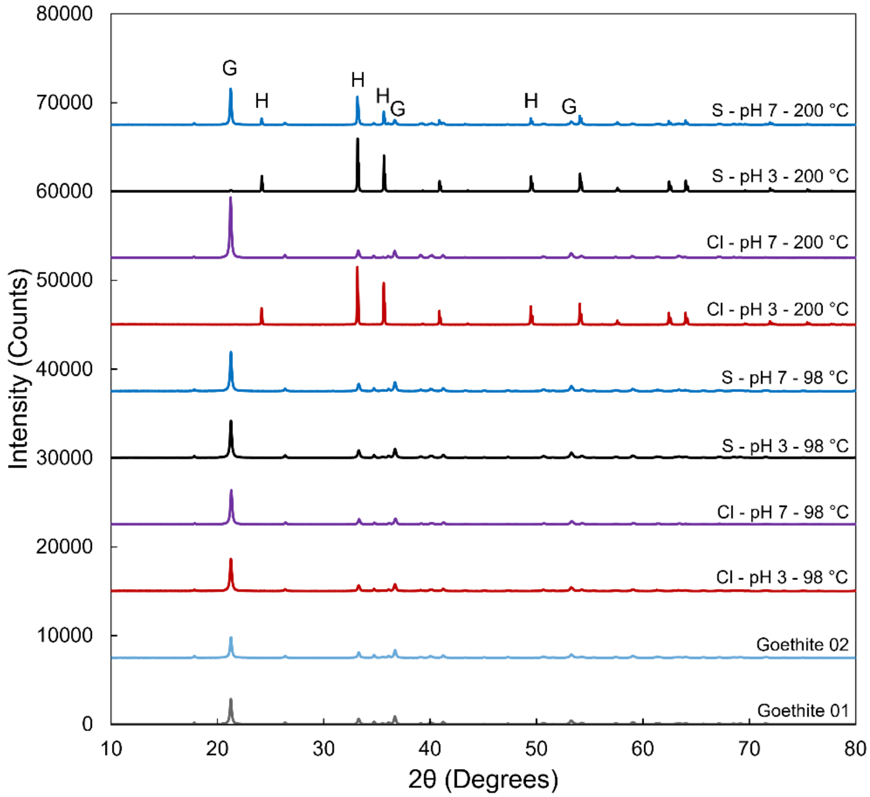

Figure S2. XRD patterns of synthesized goethite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic goethite ("G") and hematite ("H") peaks are labeled. Patterns offset in intervals of 7500 and horizontally stretched by a factor of 2 for clarity.

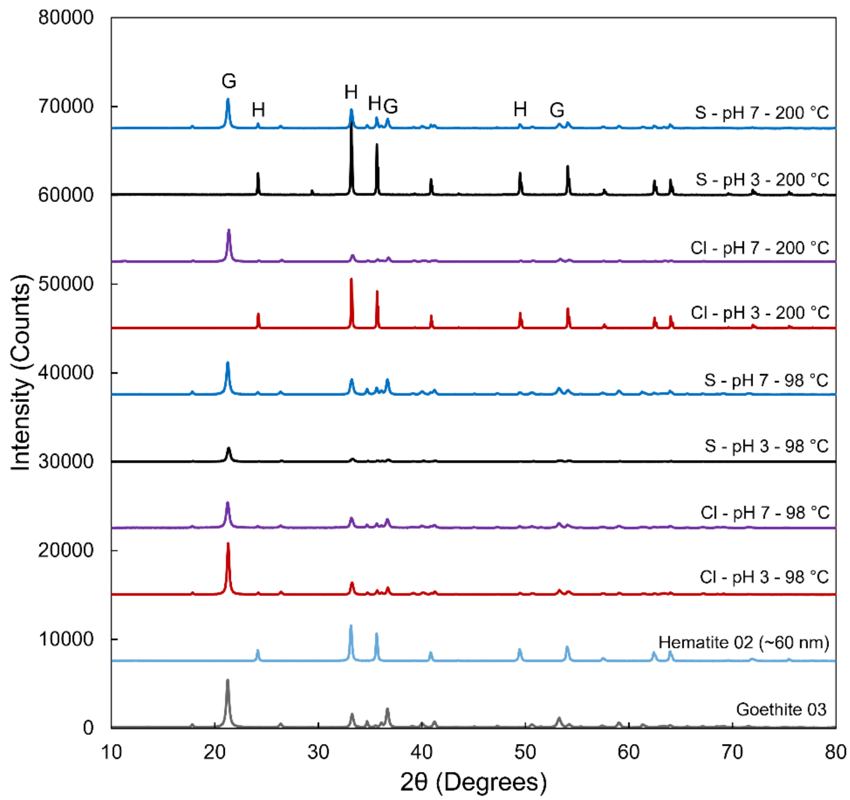

Figure S3. XRD patterns of synthesized goethite seeded with hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic goethite ("G") and hematite ("H") peaks are labeled. Spectra offset in intervals of 7500 for clarity.

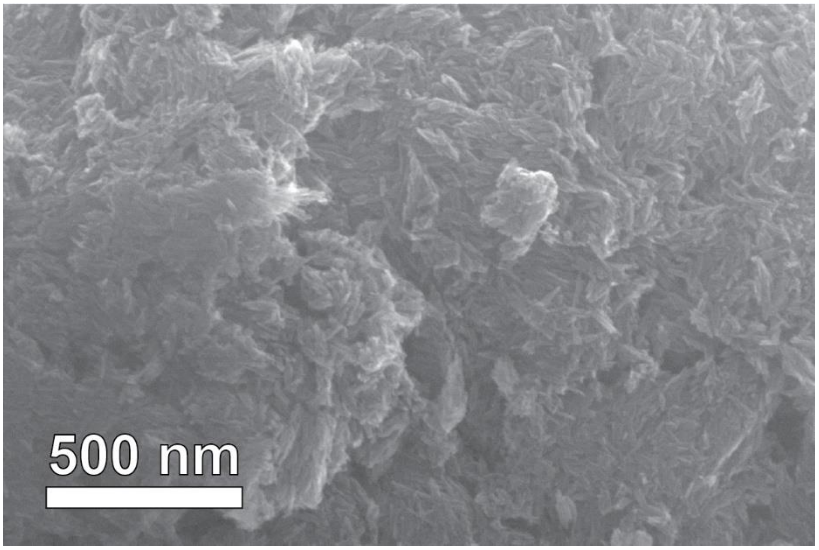

Figure S4. SEM image of synthesized akaganeite.

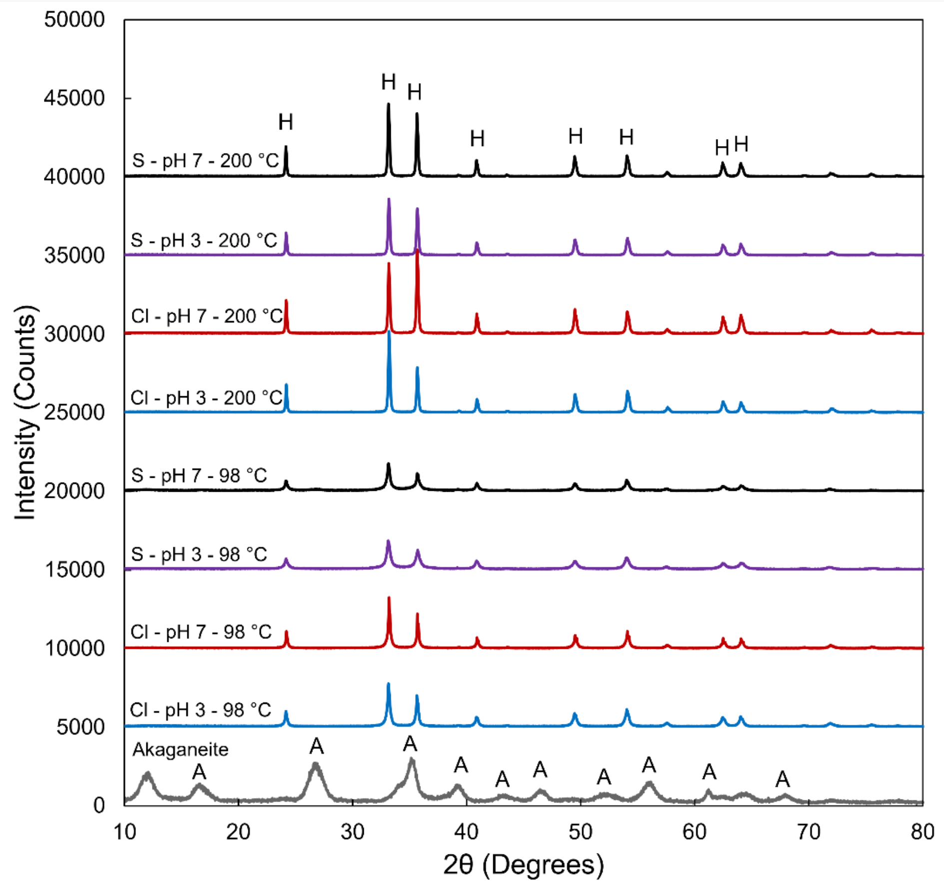

Figure S5. XRD patterns of synthesized akaganeite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic akaganeite ("A") and hematite ("H") peaks are labeled. Patterns offset in intervals of 5000 and akaganeite pattern vertically stretched by a factor of 5 for clarity.

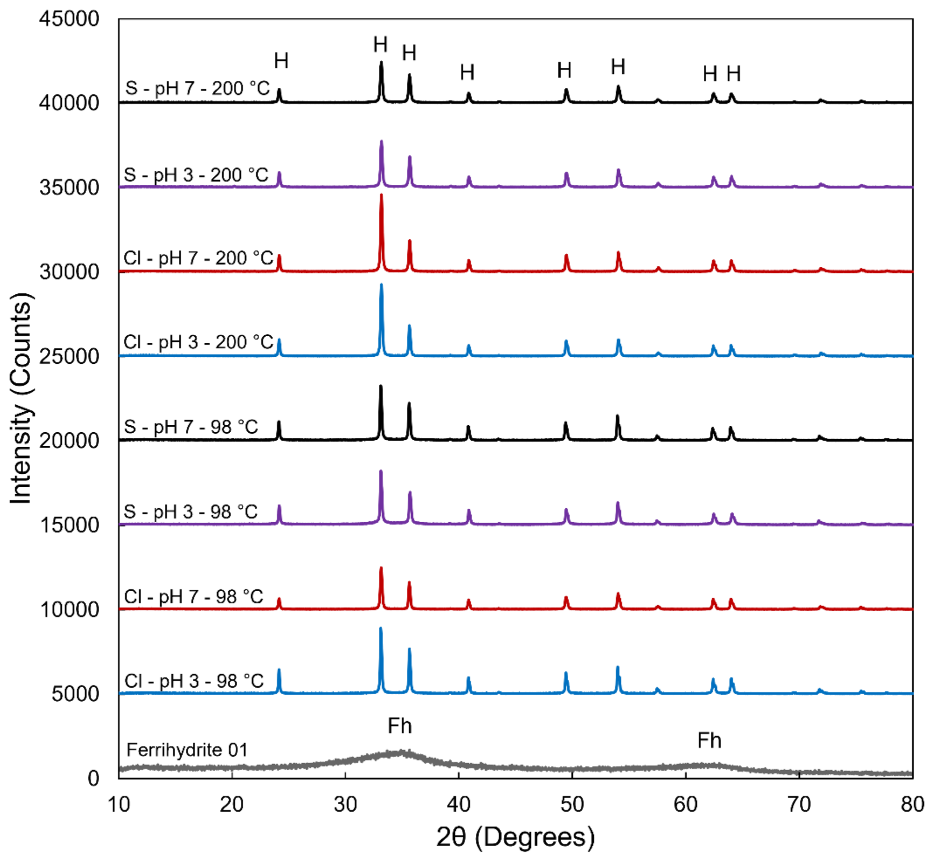

Figure S6. XRD patterns of synthesized ferrihydrite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic ferrihydrite ("Fh") and hematite ("H") peaks are labeled. Patterns offset in intervals of 5000 and ferrihydrite pattern vertically stretched by a factor of 5 for clarity.

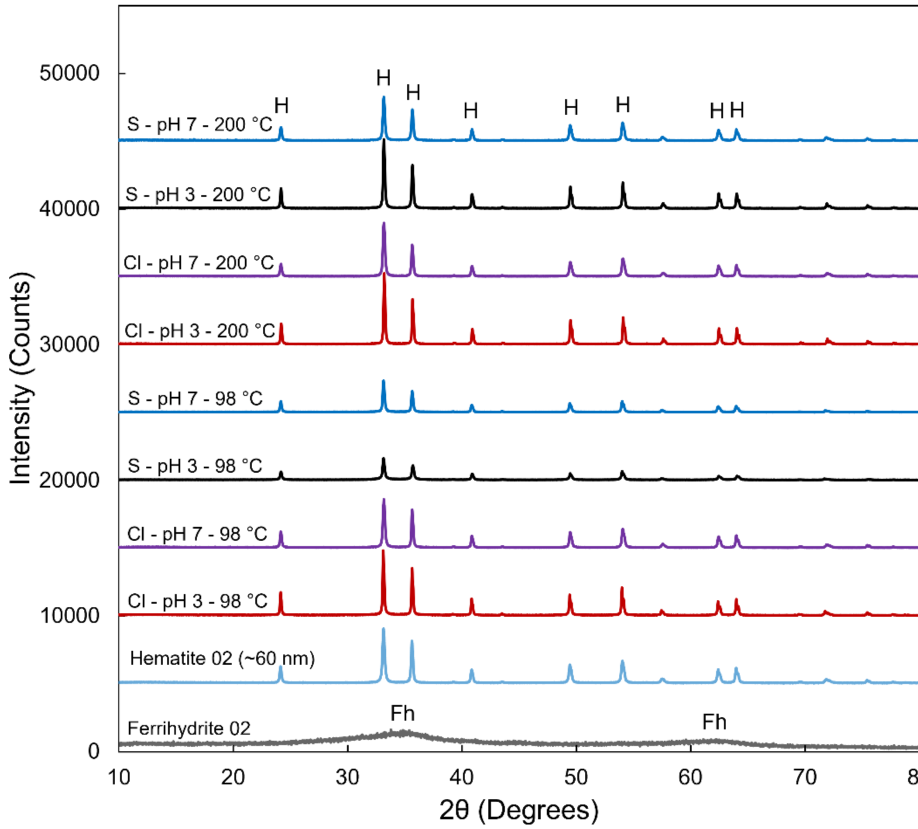

Figure S7. XRD patterns of synthesized ferrihydrite seeded with hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic ferrihydrite ("Fh") and hematite ("H") peaks are labeled. Patterns offset in intervals of 5000 and ferrihydrite pattern vertically stretched by a factor of 5 for clarity.

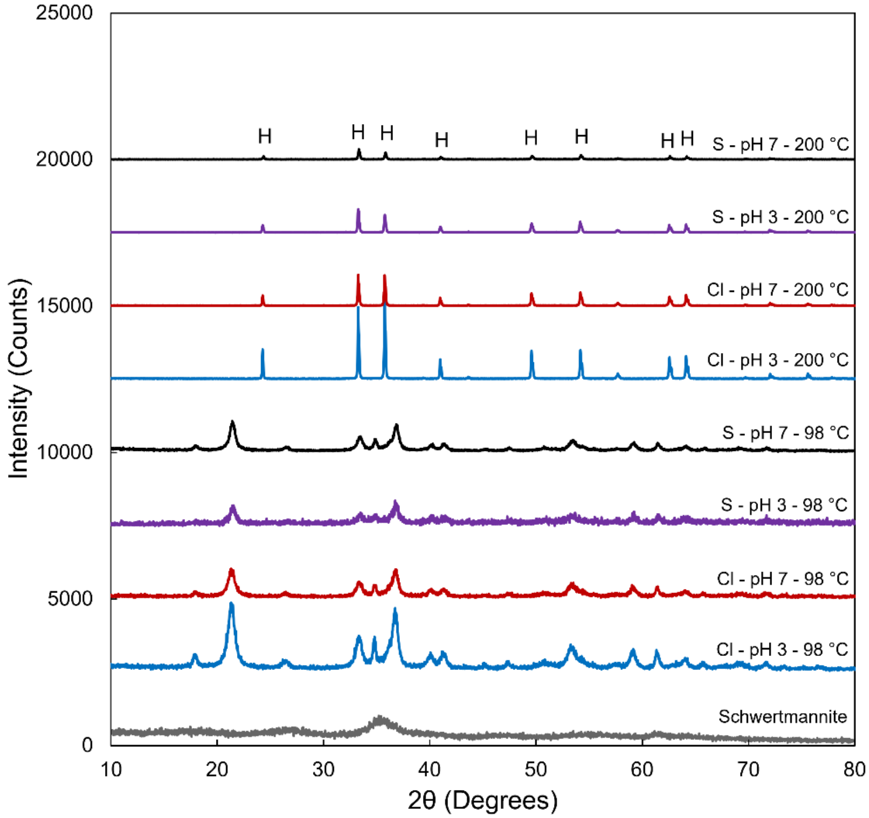

Figure S8. XRD patterns of synthesized schwertmannite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic hematite (“H”) peaks are labeled. Patterns offset in intervals of 2500 and vertically stretched as indicated for clarity.

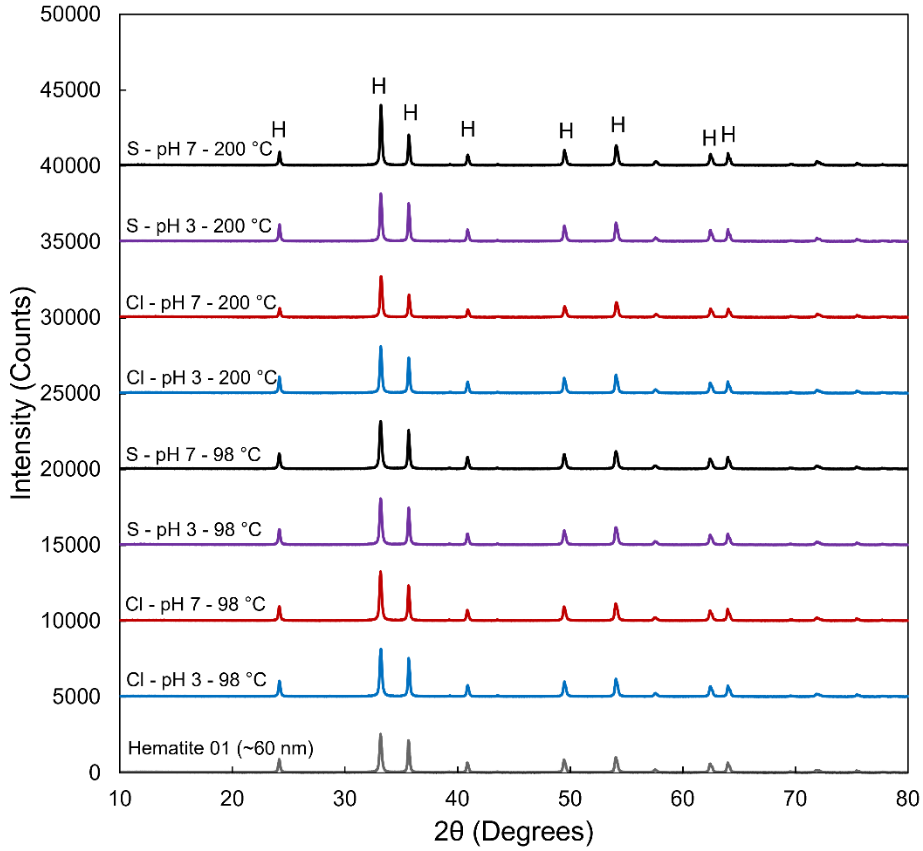

Figure S9. XRD patterns of synthesized ~60 nm red hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic hematite (“H”) peaks are labeled. Patterns offset in intervals of 5000 for clarity.

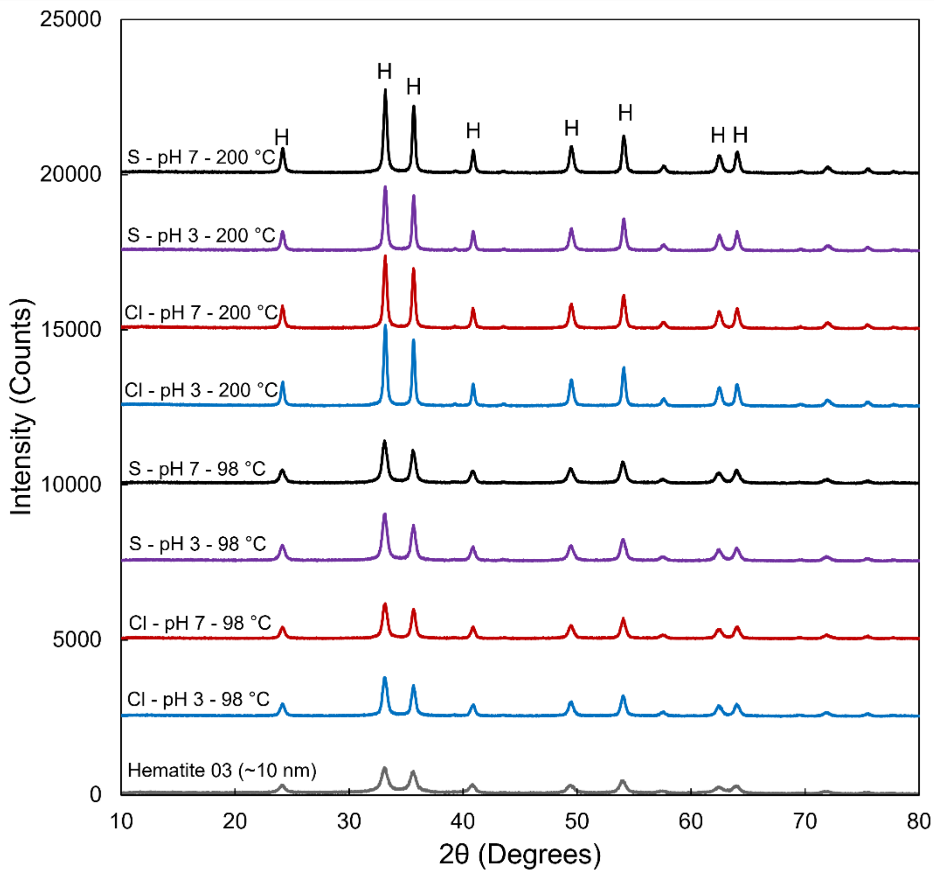

Figure S10. XRD patterns of synthesized ~10 nm red hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Characteristic hematite ("H") peaks are labeled. Patterns offset in intervals of 2500 for clarity.

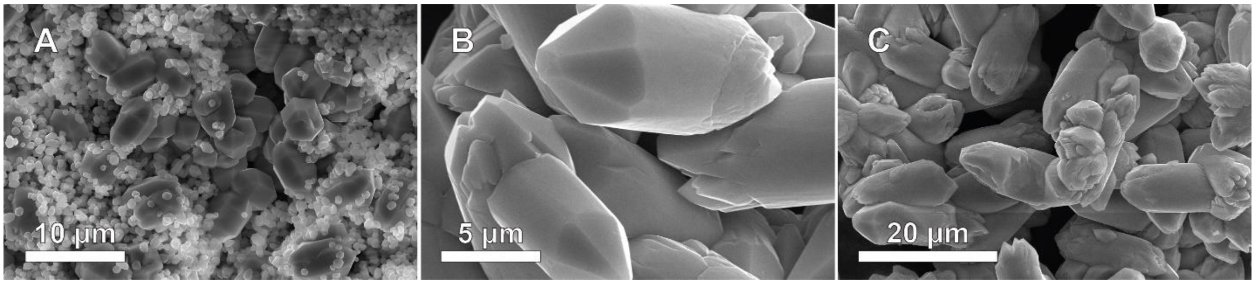

Figure S11. SEM images of the transformation products of jarosite subjected to (a) pH 3, 0.1 mol L^{-1} $MgCl_2$, 200 ºC fluids, (b) pH 3, 1 mol L^{-1} $MgCl_2$, 200 ºC fluids, and (c) pH 7, 1 mol L^{-1} $MgCl_2$, 200 ºC fluids.

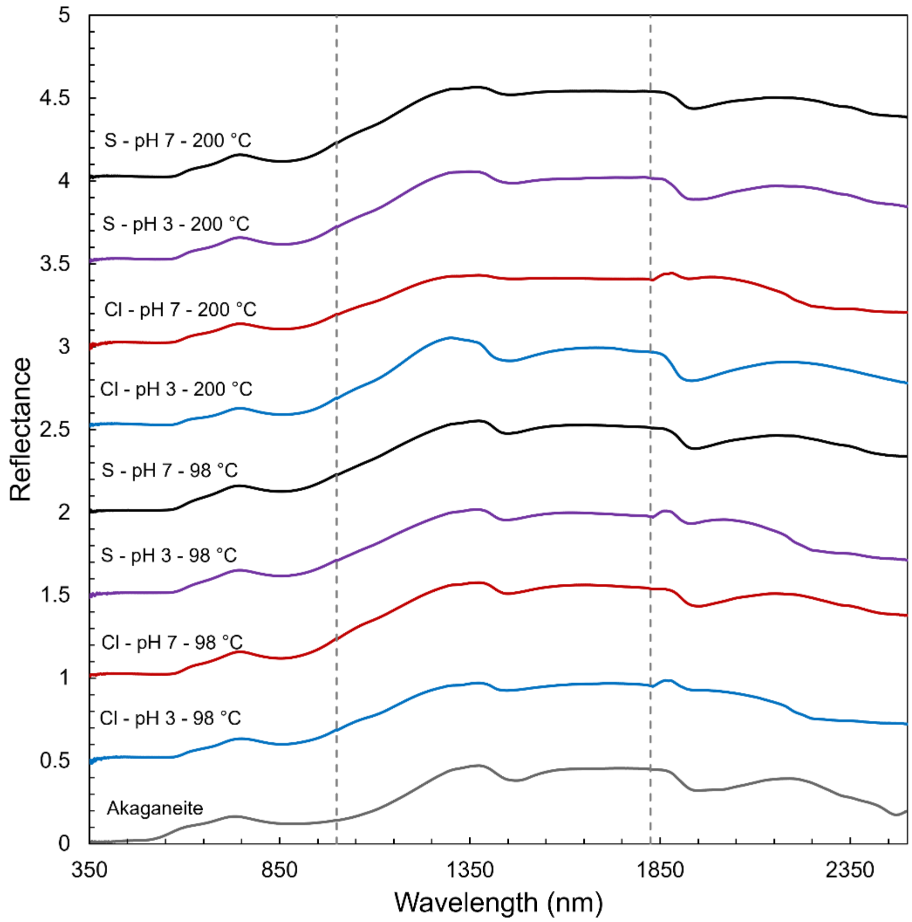

Figure S12. VNIR reflectance spectra of synthesized akaganeite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

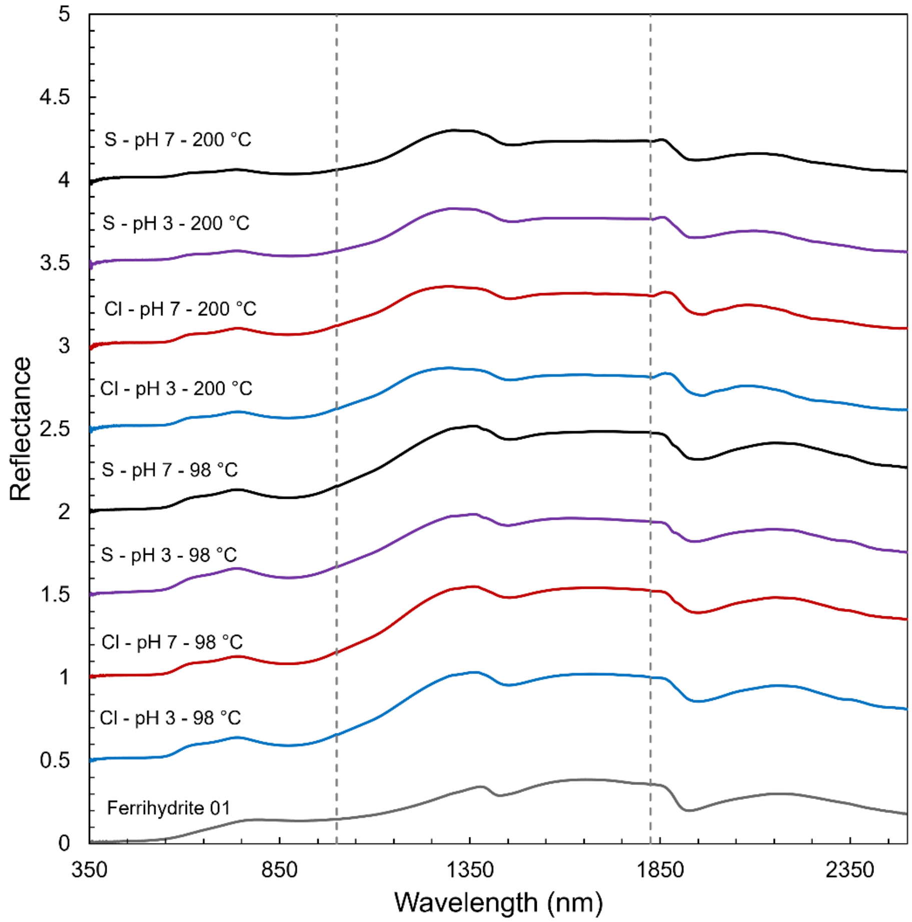

Figure S13. VNIR reflectance spectra of synthesized ferrihydrite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

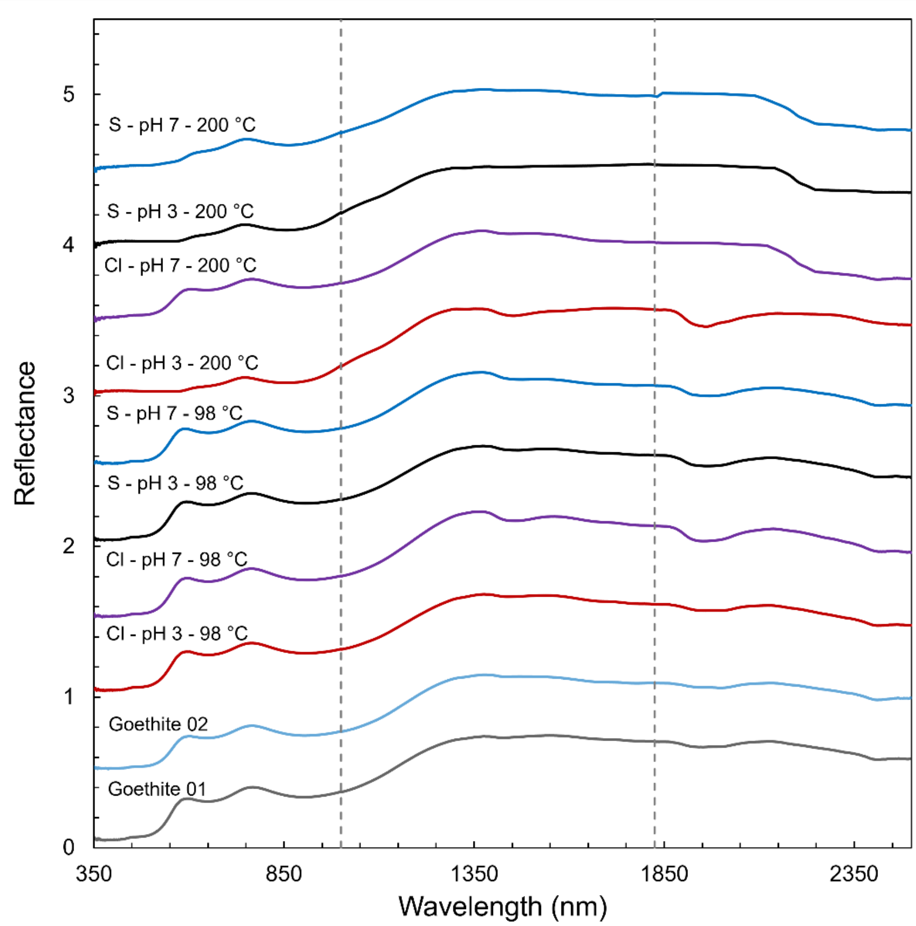

Figure S14. VNIR reflectance spectra of synthesized goethite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

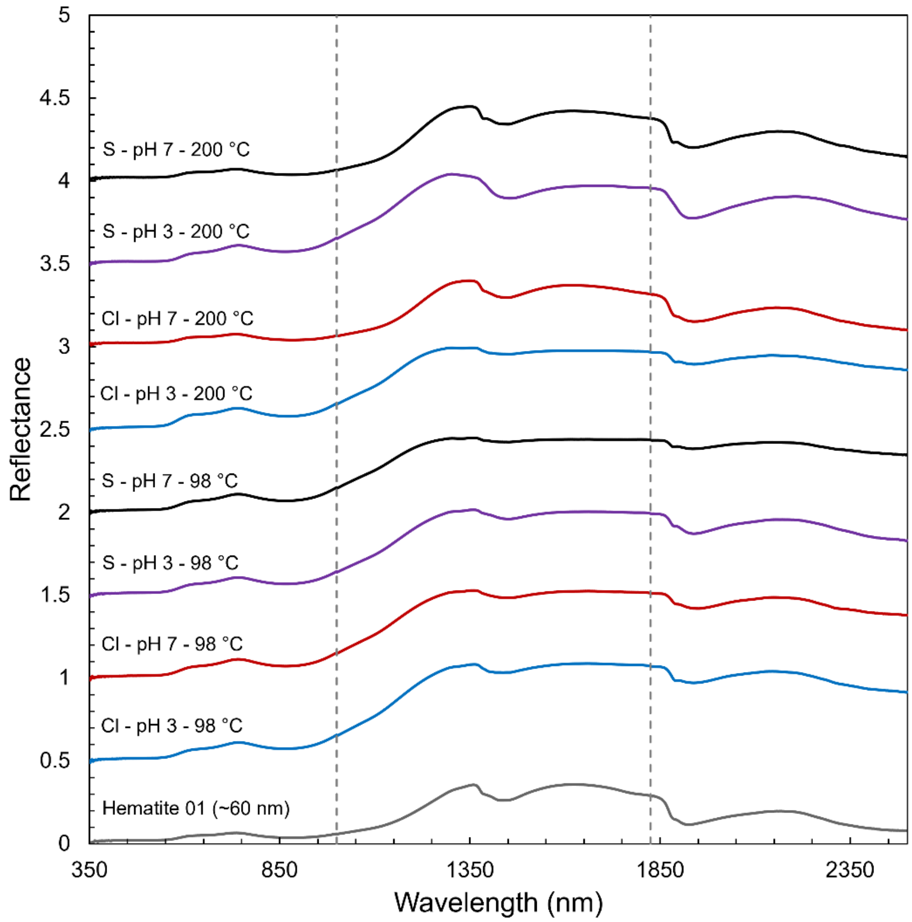

Figure S15. VNIR reflectance spectra of synthesized ~60 nm red hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

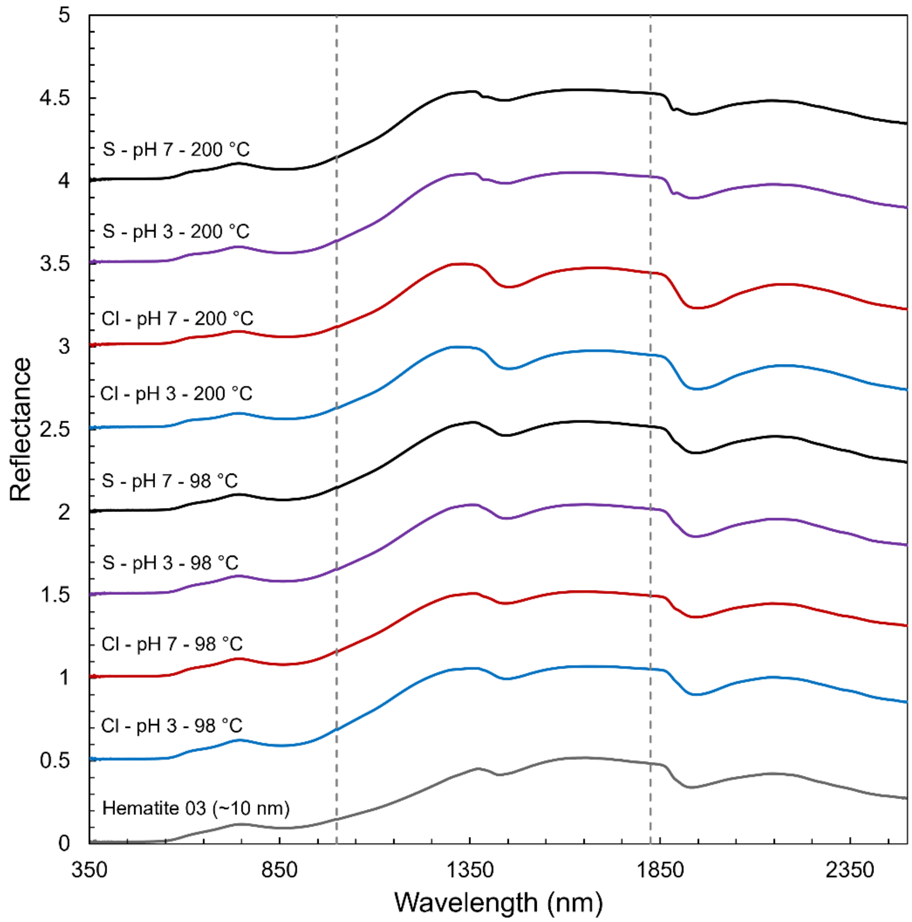

Figure S16. VNIR reflectance spectra of synthesized ~10 nm red hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

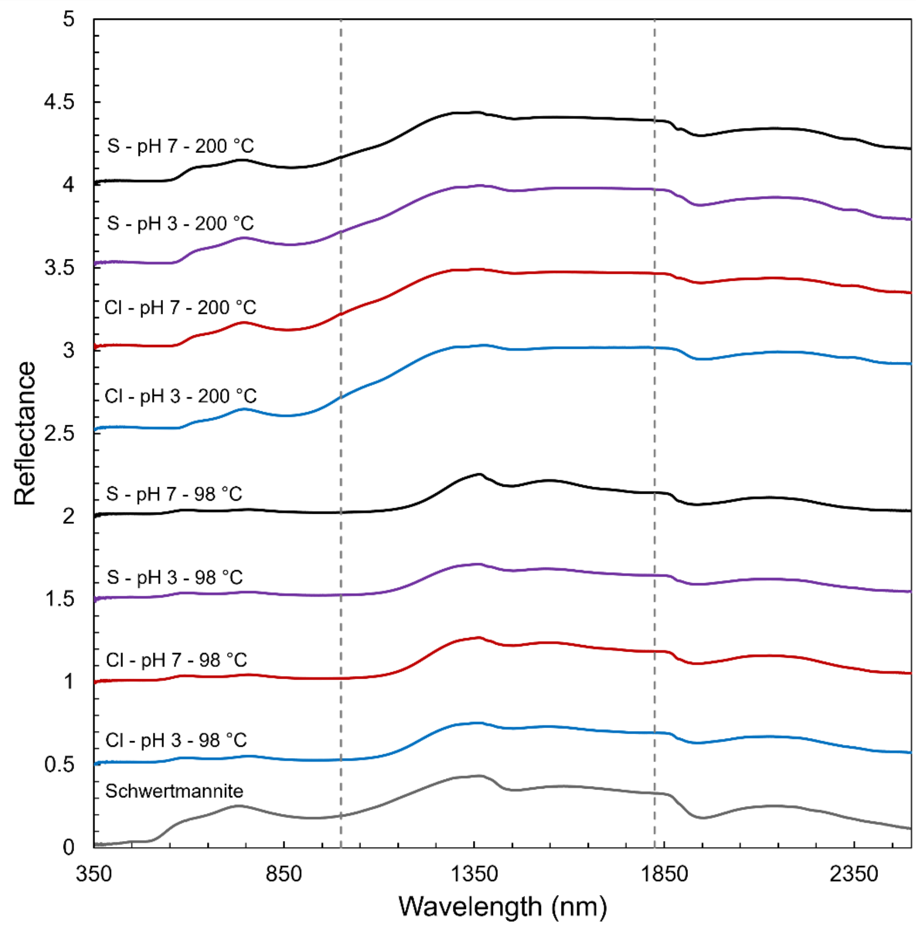

Figure S17. VNIR reflectance spectra of synthesized schwertmannite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

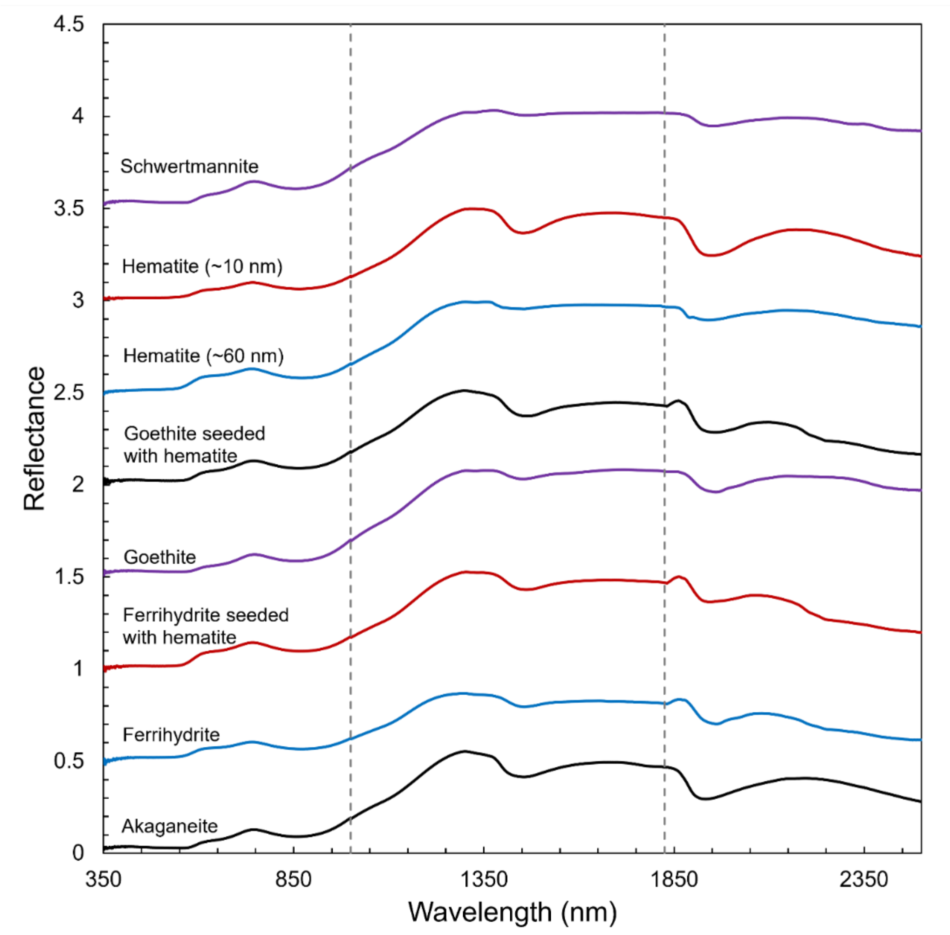

Figure S18. VNIR reflectance spectra of the red hematite transformation products of synthesized minerals subjected to pH 3, 1 mol L^{-1} $MgCl_2$ 200 ºC fluid conditions for 20 days. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

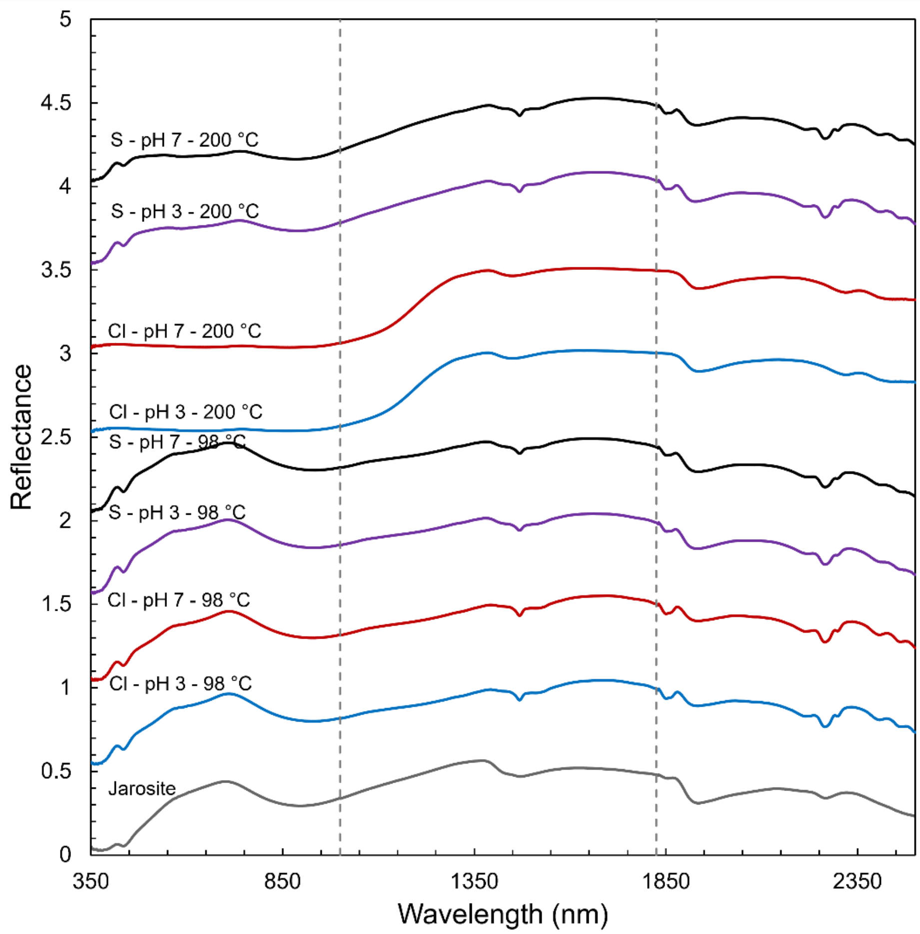

Figure S19. VNIR reflectance spectra of synthesized jarosite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

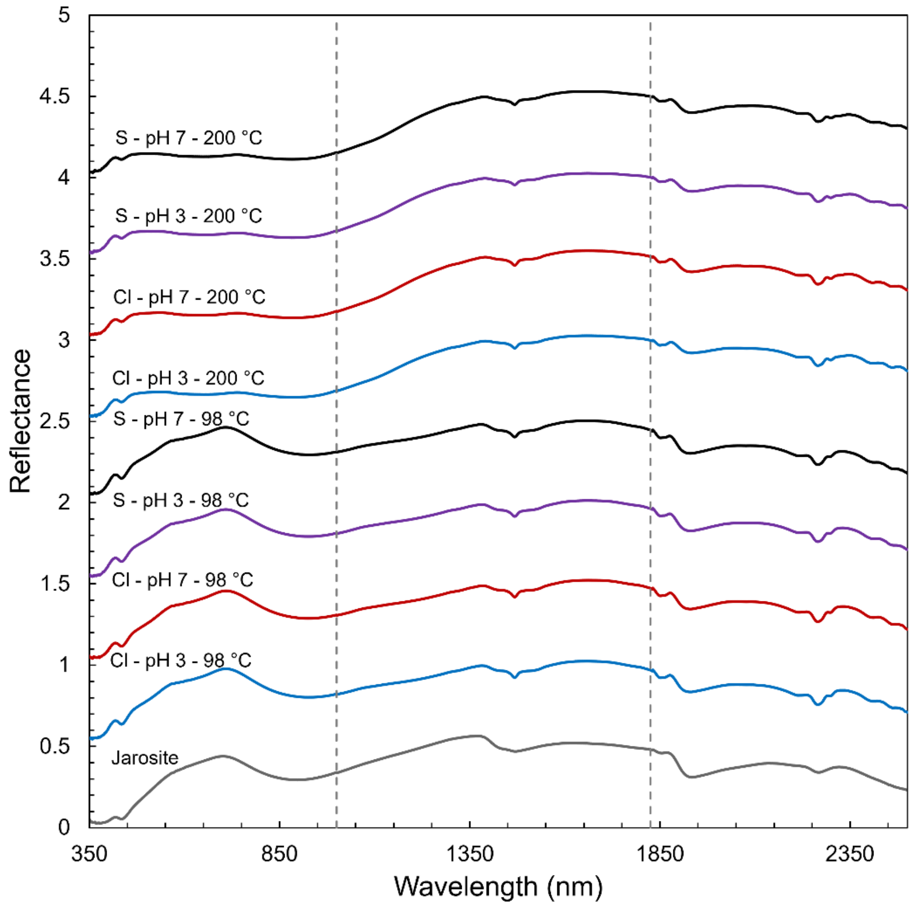

Figure S20. VNIR reflectance spectra of synthesized jarosite and its transformation products in various fluid conditions. Cl and S indicate 0.1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

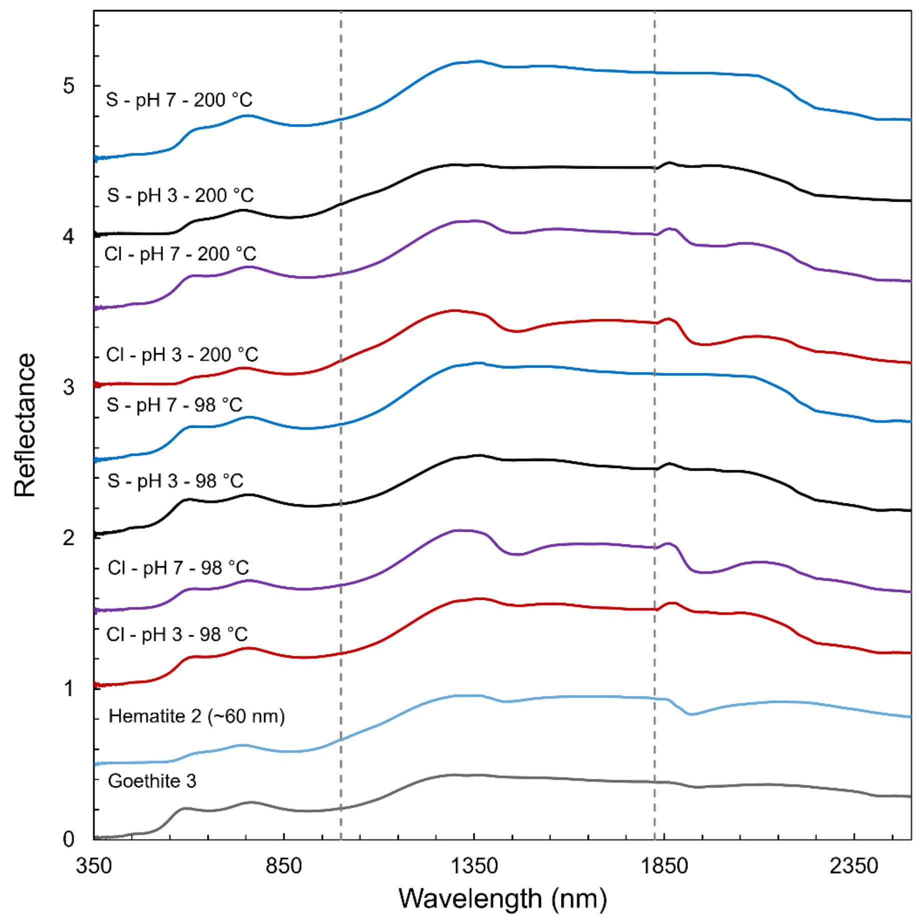

Figure S21. VNIR reflectance spectra of synthesized goethite seeded with red hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

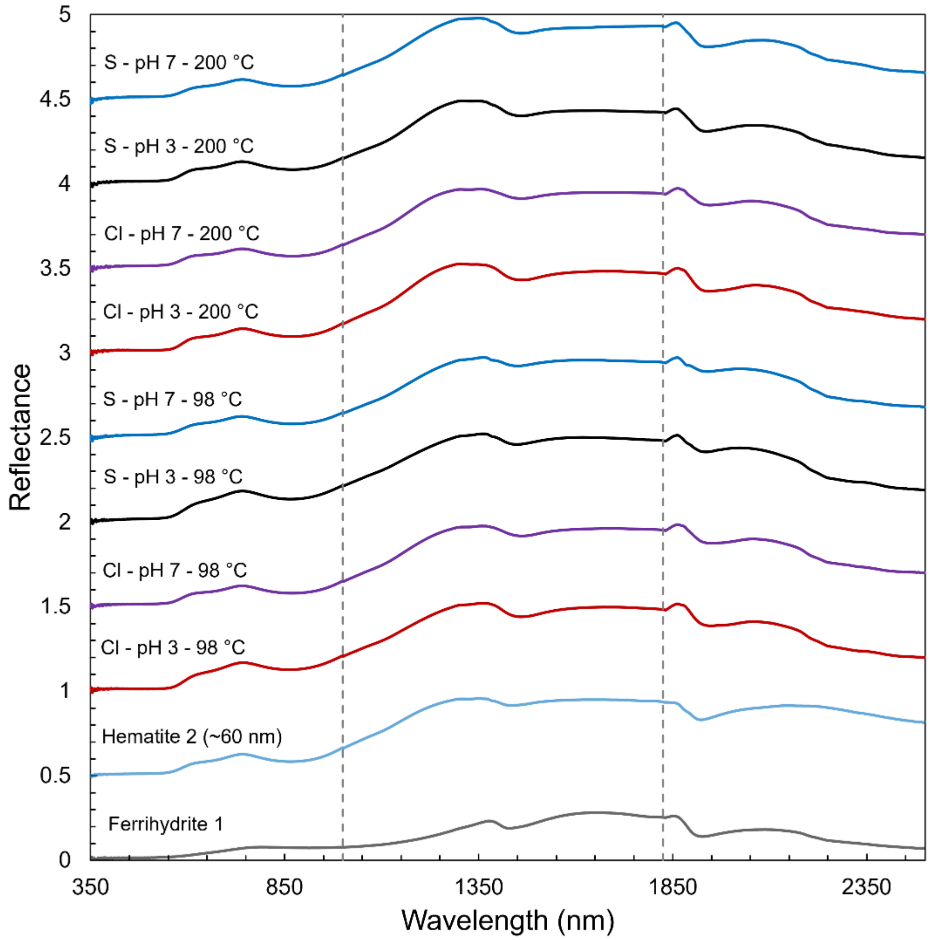

Figure S22. VNIR reflectance spectra of synthesized ferrihydrite seeded with red hematite and its transformation products in various fluid conditions. Cl and S indicate 1 mol L^{-1} background salts of $MgCl_2$ and $MgSO_4$, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 ºC or 200 ºC) are provided for each sample. Spectra offset in intervals of 0.5 for clarity. Detector boundaries marked with dashed lines.

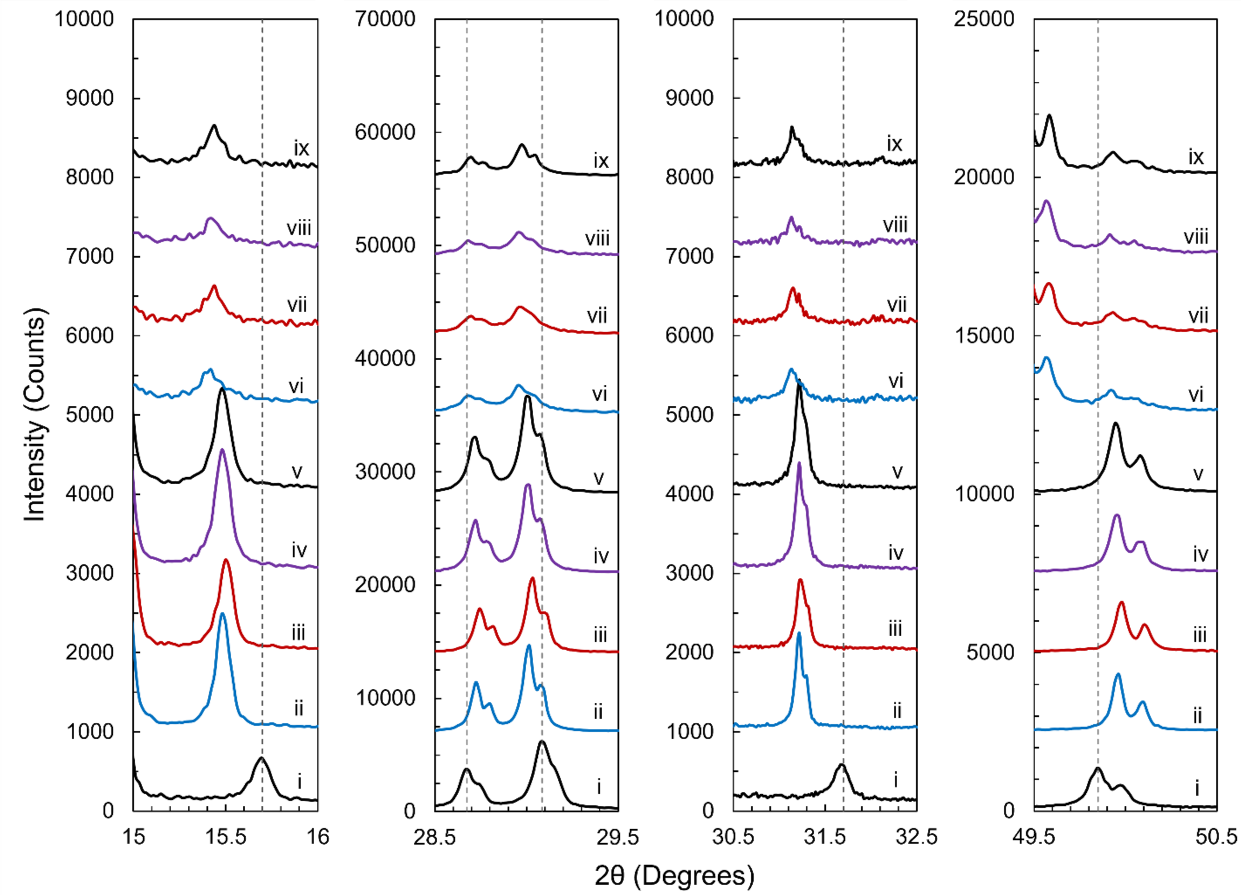

Figure S23. Diagnostic XRD lines of (i) synthesized jarosite and its transformation products in various fluid conditions: (ii) $MgCl_2$, pH 3, 98 ºC; (iii) $MgCl_2$, pH 7, 98 ºC; (iv) $MgSO_4$, pH 3, 98 ºC; (v) $MgSO_4$, pH 7, 98 ºC; (vi) $MgCl_2$, pH 3, 200 ºC; (vii) $MgCl_2$, pH 7, 200 ºC; (viii) $MgSO_4$, pH 3, 200 ºC; (ix) $MgSO_4$, pH 7, 200 ºC. All background salts are 0.1 mol L^{-1}. Patterns offset in intervals of (from left to right) 1000, 7000, 1000, and 2500 and patterns from experiments on jarosite in 200 ºC fluids with 0.1 mol L^{-1} salt vertically exaggerated by a factor of 2 for clarity.

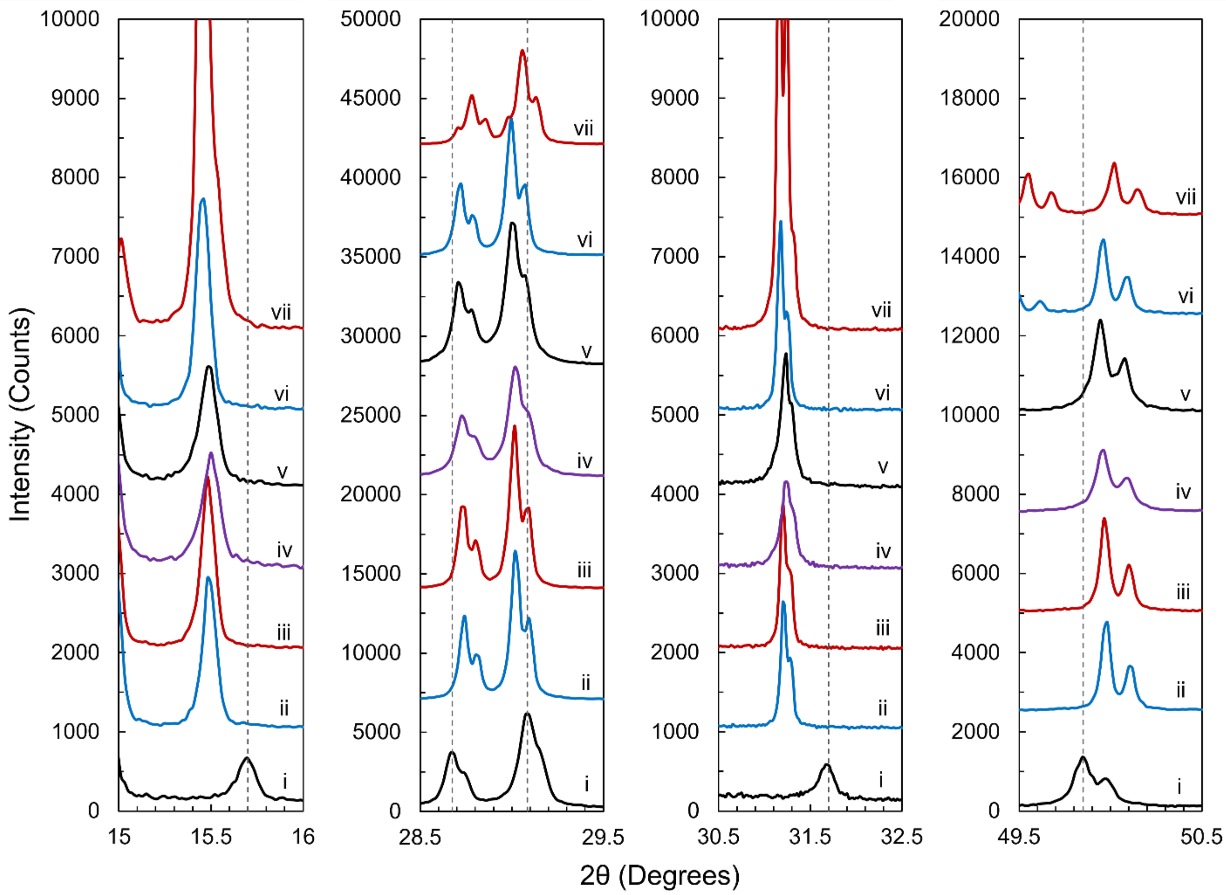

Figure S24. Diagnostic XRD lines of (i) synthesized jarosite and its transformation products in various fluid conditions: (ii) $MgCl_2$, pH 3, 98 ºC; (iii) $MgCl_2$, pH 7, 98 ºC; (iv) $MgSO_4$, pH 3, 98 ºC; (v) $MgSO_4$, pH 7, 98 ºC; (vi) $MgSO_4$, pH 3, 200 ºC; (vii) $MgSO_4$, pH 7, 200 ºC. All background salts are 1 mol L^{-1}. Patterns offset in intervals of (from left to right) 1000, 7000, 1000, and 2500 for clarity.