Electronic supplementary information

Formation and transformation of schwertmannite through direct Fe^{3+} hydrolysis under various geochemical conditions

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Supplementary data includes 1 table and 6 figures.

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Table S1. Experimental conditions on formation and transformation of schwertmannite through direct Fe^{3+} hydrolysis

Sample	Fe^{3+} (mM)	SO_4^{2-} (mM)	pH	Temperature	Co-existing ions (mM)	Dialysis time
(a) Schwertmannite formation though Fe^{3+} hydrolysis-dialysis pathway						
Hydrolysis temperature	19.98	10.56	-	25, 40, 50, 60, 70, 80 °C	-	7d
Dialysis time	19.98	10.56	-	25, 60 °C	-	1, 3, 7, 15 d
Coexistence of K^+ or NH_4^+	19.98	10.56	-	60 °C	K^+, NH_4^+ (21.12 mM)	7d
(b) Mineral evolution during Fe^{3+} hydrolysis by adding NaOH						
OH^-/Fe^{3+} = 1	400	600	2.5	25 °C	-	-
Fhy + SO_4^{2-}	48.55	72.825	2.5	25 °C	-	-
(c) Fe^{3+} hydrolysis rate on the formation and long-term aging of schwertmannite						
33.33 μM/min	48.55	24.275	3.0	Formed:25 °C Aging: 60 °C	-	-
6.67 μM/min	48.55	24.275	3.0	Formed:25 °C Aging: 60 °C	-	-
3.33 μM/min	48.55	24.275	3.0	Formed:25 °C Aging: 60 °C	-	-
(d) Schwertmannite transformation under various geochemical conditions						
pH effects	48.55	24.275	2.0, 2.5, 3.0, 3.5	Aging: 80 °C	-	-
Fe/S molar ratios	48.55	32.37, 24.275, 19.42, 9.71, 6.07, 4.855	3.0	Aging: 60 °C	-	-

Aging temperature	48.55	24.275	3.0	25, 60, 80 °C	-	-
Co-existing Fe^{2+}	48.55	24.275	3.0	Aging: 60 °C	Fe^{2+} (4.855 mM)	-
Co-existing Cl^-	48.55	24.274	3.0	Aging: 60 °C	Cl^- (24.275, 242.75 mM)	-
Co-existing K^+ or NH_4^+	48.55	24.275, 247.25	2.0	Aging: 80 °C	K^+, NH_4^+ (48.55, 485.5 mM)	-

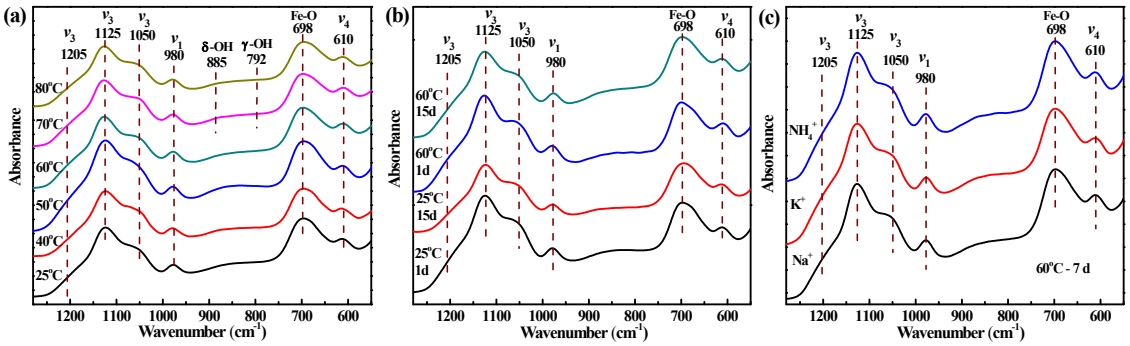


Fig. S1. FTIR spectra of the products obtained from Fe^{3+} hydrolysis-dialysis at different Fe^{3+} hydrolysis temperatures followed by dialysis for 7 d (a), from Fe^{3+} hydrolysis at 25 °C or 60 °C followed by dialysis for 1 d or 15 d (b), and from Fe^{3+} hydrolysis at 60 °C in the presence of K^+ or NH_4^+ followed by dialysis for 7 d (c).

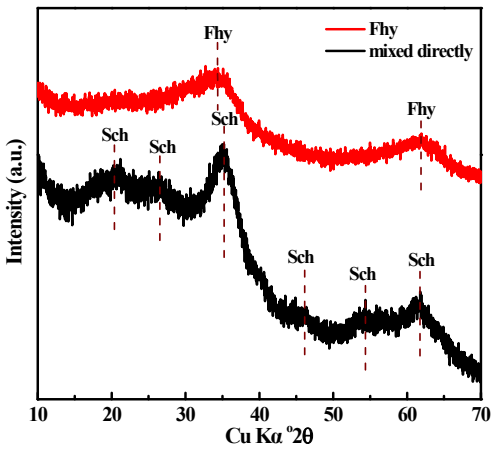


Fig. S2. XRD patterns of the product of "mixed directly" formed through Fe^{3+} hydrolysis

by adding OH^- and of ferrihydrite reference (Sch = schwertmannite, Fhy = Ferrihydrite).

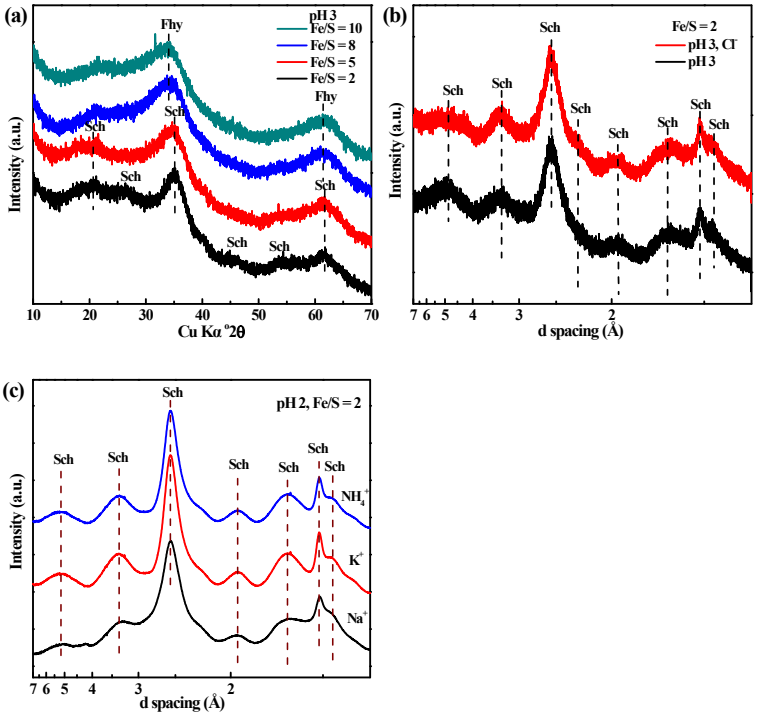
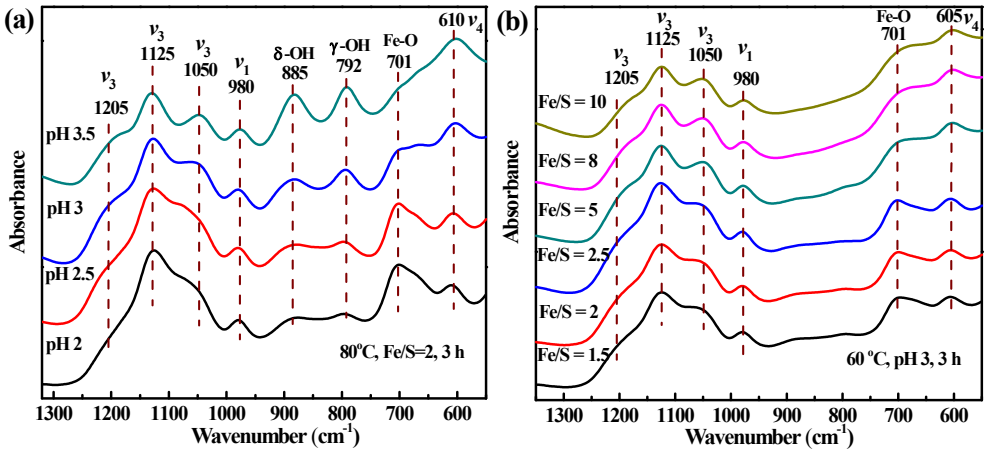


Fig. S3. XRD patterns of the products obtained from Fe^{3+} hydrolysis by adding OH^- over Fe/S molar ratios of 2 – 10 (a), in the presence of Cl^- (b) and K^+ or NH_4^+ (c) (Sch = schwertmannite, Fhy = Ferrihydrite).



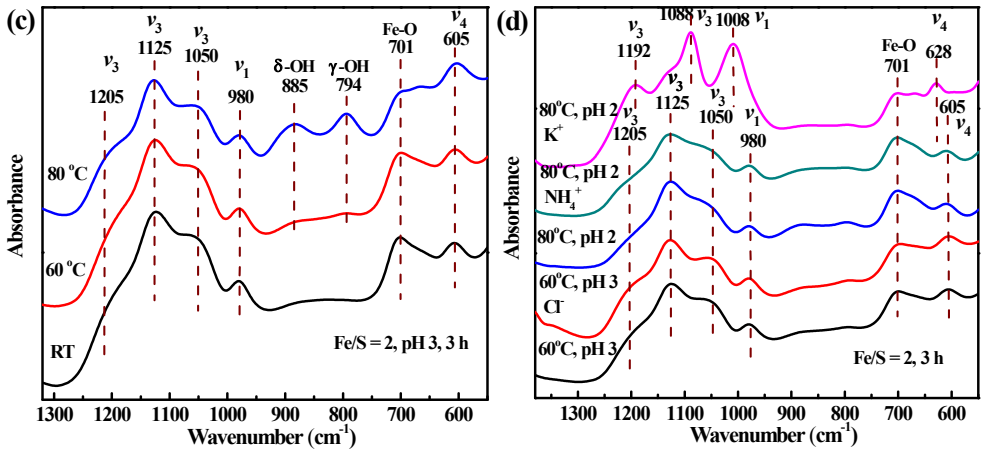


Fig. S4. FTIR spectra of the schwertmannite suspension, obtained from Fe^{3+} hydrolysis by adding OH^-, aged for 3 h at different pHs (a), different Fe/S molar ratios (b), different aging temperatures (c) and in the presence of Cl^-, K^+ or NH_4^+ (d).

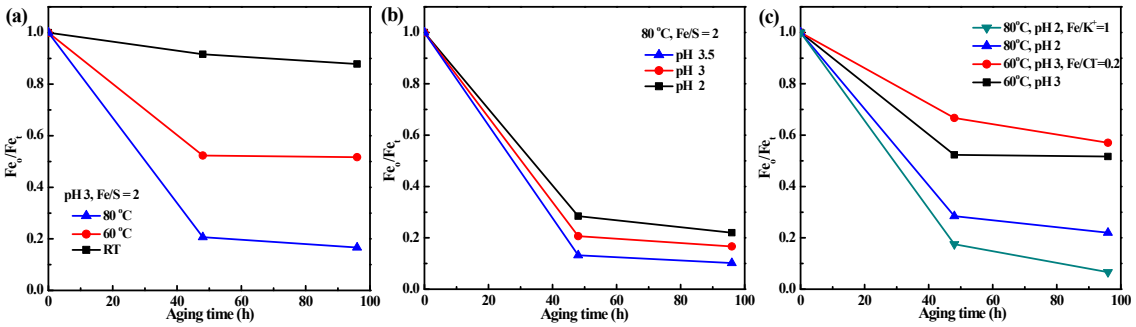


Fig. S5. The transformation rate described as Fe_o/Fe_t of schwertmannite during aging at different temperatures (a), at different pHs (b) and in the presence of Cl^- or K^+ (c) (Fe_o: weak crystalline iron, dissolved by 0.2 M acidic ammonium oxalate; Fe_t: total iron, dissolved by 4 M HCl).

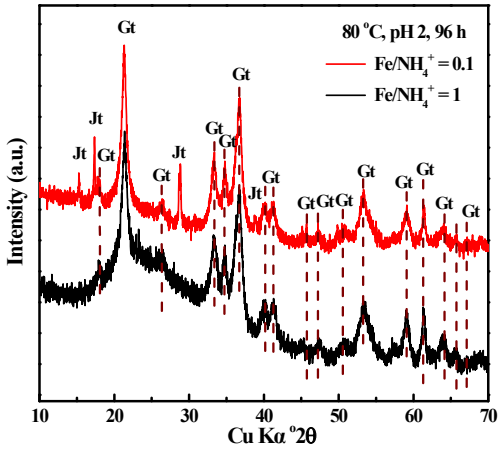


Fig. S6. XRD patterns of the products aged for 96 h in the presence of NH_4^+ (Fe/NH_4^+ = 0.1 or 1) at 80 °C and pH 2 (Gt = goethite, Jt = jarosite).