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

Hong Ying, Xionghan Feng, Mengqiang Zhu, Bruno Lanson, Fan Liu, Xiaoming Wang

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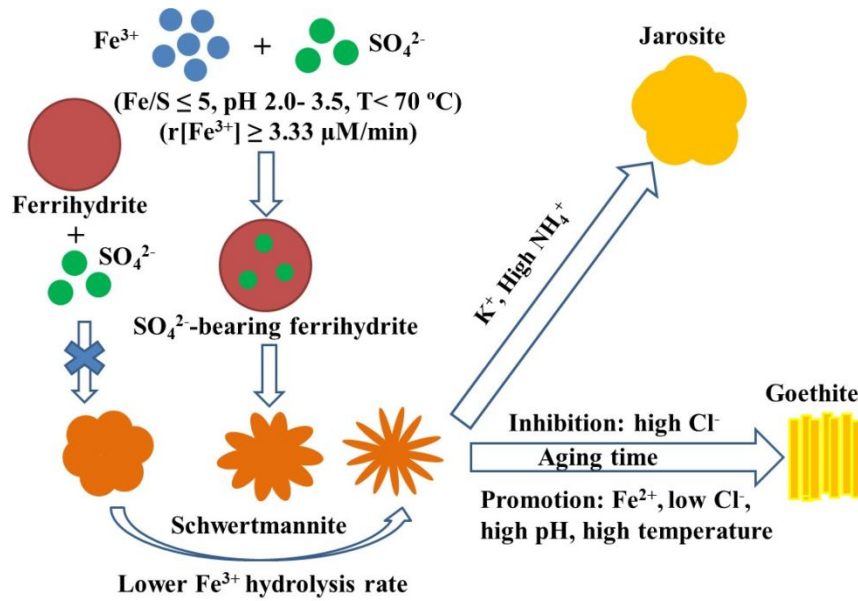
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TOC figure

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

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4 1 **Formation and transformation of schwertmannite through direct Fe³⁺ hydrolysis**
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6 2 **under various geochemical conditions**
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11 4 Hong Ying^a, Xionghan Feng^a, Mengqiang Zhu^b, Bruno Lanson^c, Fan Liu^a, Xiaoming
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14 5 Wang^{a,*}
15

16
17 6 ^a Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze
18
19 7 River), Ministry of Agriculture and Rural Affairs, College of Resources and
20
21
22 8 Environment, Huazhong Agricultural University, Wuhan 430070, China
23

24
25 9 ^b Department of Ecosystem Science and Management, University of Wyoming,
26
27 10 Laramie, WY, 82071
28

29
30 11 ^c Univ. Grenoble Alpes, Univ. Savoie-Mont Blanc, CNRS, IRD, IFSTTAR, ISTERre,
31
32 12 F-38000 Grenoble, France
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37 14 **Manuscript includes 1 table and 11 figures.**
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44 17 *Corresponding author:

45 18 Xiaoming Wang, Tel: +86 27 87280271; Fax: +86 27 87288618; E-mail:
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47 19 wangxm338@mail.hzau.edu.cn
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56 Electronic supplementary information (ESI) is available free of charge via the internet at
57 <http://pubs.rsc.org>, including (1) specific experimental conditions of the formation and transformation of
58 schwertmannite; (2) FTIR spectra of schwertmannite obtained from Fe³⁺ hydrolysis-dialysis pathway and
59 of the aging products of schwertmannite formed through Fe³⁺ hydrolysis by adding NaOH; (3) XRD
60 patterns of schwertmannite with the coexistence of K⁺ or NH₄⁺ and the final aging products of
schwertmannite in the presence of NH₄⁺; and (4) schwertmannite transformation rate indicated by Fe_o/Fe_t
obtained from acidic dissolution experiments.

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4 20 **Formation and transformation of schwertmannite through direct Fe³⁺ hydrolysis**
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6 21 **under various geochemical conditions**
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8

9 22 **Abstract**

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11 23 Schwertmannite formation and transformation, key processes that influence the
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14 24 speciation, mobility, and environmental fate of associated trace elements in acid mine
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17 25 drainage (AMD), are primarily studied through Fe²⁺ oxidation. Direct Fe³⁺ hydrolysis is
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20 26 another important schwertmannite formation pathway, but the effects of geochemical
21
22 27 conditions on the mineralogical properties of schwertmannite formed via such pathway
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24
25 28 are poorly known. Here, the formation of schwertmannite through direct Fe³⁺ hydrolysis
26
27 29 enforced by heating or adding NaOH and subsequent transformation were
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29
30 30 systematically examined under various geochemical conditions. Pure schwertmannite is
31
32 31 obtained through Fe³⁺ hydrolysis at 25 - 60 °C for 12 mins and subsequent dialysis for
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34
35 32 1- 15 days, while minor goethite appear at higher hydrolysis temperatures. Shorter
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37
38 33 dialysis time and the presence of K⁺ or NH₄⁺ both slightly increase schwertmannite
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40
41 34 crystallinity. During Fe³⁺ hydrolysis by adding NaOH, sulfate-bearing ferrihydrite
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43
44 43 initially forms and then quickly transforms to schwertmannite. In contrast, pre-formed
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46
47 46 ferrihydrite does not transform to schwertmannite under the same solution conditions,
48
49
50 48 despite sulfate adsorption. Schwertmannite crystallinity slightly increases with
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52
53 51 decreasing Fe³⁺ hydrolysis rate, and its morphology of “network” structure becomes
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56 53 larger and less dense. As to schwertmannite transformation, high temperature, high pH,
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59 56 and the presence of Fe²⁺ favor its transformation to goethite, while a low Fe³⁺
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62 60 hydrolysis rate and high concentration of Cl⁻ hinder the transformation. In contrast, the

[Type here]

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4 42 presence of K^+ or high NH_4^+ concentration favors schwertmannite transformation to
5
6 43 jarosite with the former more readily. These new insights into schwertmannite
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9 44 formation and transformation are essential for predicting the environmental fates of
10
11
12 45 associated trace elements in AMD environments.

13
14 **Keyword:** schwertmannite; Fe^{3+} hydrolysis; formation; transformation; AMD

15 16 17 **1. Introduction**

18
19 48 Acid mine drainage (AMD, $pH < 5$) is mainly generated from mining activities of
20
21
22 49 coal and metal sulfide minerals and subsequent waste oxidative weathering, threatening
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24
25 50 the surrounding environmental quality and ecosystem equilibrium due to its low pH
26
27 51 conditions and high concentrations of various metallic contaminants.¹⁻³ AMD is usually
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29
30 52 enriched in ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, sulfate (SO_4^{2-}), and many other cations
31
32
33 53 and anions, resulting in the formation of secondary iron (Fe) minerals with various ions
34
35 54 adsorbed on their surface and/or accumulated in their structure.⁴⁻⁸ Schwertmannite is
36
37
38 55 one of the most common Fe minerals in AMD, with an optimal formation pH of 2.8 -
39
40
41 56 4.5 and a variable chemical composition described as $Fe_8O_8(OH)_{8-2x}(SO_4)_x \cdot nH_2O$ ($1 \leq x$
42
43 57 ≤ 1.75).^{3, 9-12} Due to its high specific surface area and tunnel structure, schwertmannite
44
45
46 58 is considered as an important sink for trace elements such as As, Se, and Cr, and its
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48
49 59 formation and transformation thus affect and control the speciation, migration, and
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52 60 environmental fate of these elements in AMD environments.¹³⁻¹⁹

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54 61 Schwertmannite formation commonly occurs through two pathways depending on
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56 62 the iron sources, *i.e.*, oxidation of Fe^{2+} via biotic and abiotic processes and direct Fe^{3+}
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59 63 hydrolysis.^{11, 15, 20-22} In AMD systems, it was reported that schwertmannite is mainly

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[Type here]

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4 64 formed from biotic oxidation of Fe^{2+} , ^{7, 9, 23, 24} hence the schwertmannite formation is
5
6 65 primarily studied in laboratory through Fe^{2+} oxidation mediated by microbes or strong
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9 66 chemical oxidants, and subsequent Fe^{3+} hydrolysis-precipitation.^{3, 21, 23, 25, 26} However, in
10
11 67 AMD affected areas, whether schwertmannite forms through Fe^{2+} oxidation or direct
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14 68 Fe^{3+} hydrolysis depends on the specific solution pH and redox potential of the waters.^{27,}
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17 69 ²⁸ Additionally, AMD often contains a mixture of Fe^{2+} and Fe^{3+} ,²⁹ and the regeneration
18
19
20 70 of Fe^{3+} is a key process to promote the oxidation of sulfide minerals and the formation
21
22 71 of secondary iron oxides.^{29, 30} Therefore, direct Fe^{3+} hydrolysis can be an important
23
24 72 schwertmannite formation pathway, especially when AMD solution contacts surface
25
26
27 73 water or infiltrates soils. However, the formation of schwertmannite through direct Fe^{3+}
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29
30 74 hydrolysis under various geochemical conditions has not been systematically
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32 75 investigated.

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35 76 Results of a limited number of studies about the formation of schwertmannite
36
37 77 through Fe^{3+} hydrolysis are summarized as follows. The common synthesis of
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39
40 78 schwertmannite implies Fe^{3+} hydrolysis at 60 °C and subsequent dialysis for 30 d
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43 79 (hereafter referred to as Fe^{3+} hydrolysis-dialysis),³ but the influence of Fe^{3+} hydrolysis
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45
46 80 temperature, dialysis time, and coexistence of ions on the formation of schwertmannite
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48 81 is lacking. In addition to Fe^{3+} hydrolysis-dialysis, Loan et al.³¹ examined the formation
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51 82 of schwertmannite by directly mixing acidified $\text{Fe}_2(\text{SO}_4)_3$ solutions with NaOH at 85
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54 83 °C, indicating that low degree of Fe^{3+} supersaturation results in the formation of
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57 84 schwertmannite that possibly nucleates on two-line ferrihydrite aggregates. Studies also
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59
60 85 showed that schwertmannite formation from direct Fe^{3+} hydrolysis can occur at room

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4 86 temperature (RT),³²⁻³⁴ with ferrihydrite-like molecular clusters as intermediate
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6 87 product.³⁴ The presence of As(V) can inhibit schwertmannite formation.³⁵ Overall, it
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8
9 88 remains elusive regarding how Fe³⁺ hydrolysis rate, sulfate concentration, pH, and types
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11 89 of coexisting ions affect schwertmannite formation from Fe³⁺ hydrolysis by adding a
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14 90 base.

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17 91 Schwertmannite can transform to various Fe-bearing minerals in response to
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19 92 changes in solution conditions. The transformation of schwertmannite is affected by
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21
22 93 many factors, such as temperature, pH, and types and concentrations of coexisting ions,
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25 94 as well as the formation conditions of pre-formed schwertmannite.³⁶⁻⁴³ Under AMD
26
27 95 conditions, schwertmannite gradually transforms to jarosite or goethite through a
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29
30 96 dissolution-recrystallization process.^{36, 37, 42} Schwertmannite can also transform to
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32 97 mackinawite or siderite under reducing conditions^{44, 45} and to a mixture of lepidocrocite
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34
35 98 and goethite in the presence of Fe²⁺ at pH 6 and anoxic conditions.²² The
36
37 99 schwertmannite used to study its transformation is mostly synthesized through Fe²⁺
38
39
40 100 oxidation. However, the physicochemical properties of schwertmannite formed via Fe²⁺
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43 101 oxidation and Fe³⁺ hydrolysis exhibit significant differences, such as crystal-growth
44
45 102 time, morphologies, electro-kinetic properties, etc.⁴⁶ Such differences may lead to
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47
48 103 different behaviors on the transformation of schwertmannite synthesized using the two
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50
51 104 pathways, which, however, remains unknown.

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53 105 The objectives of this study are, therefore, to reveal the formation and
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56 106 transformation processes and properties of schwertmannite formed through direct Fe³⁺
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59 107 hydrolysis under various geochemical conditions. The effects of hydrolysis temperature,
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4 108 pH, Fe/S ratio (*i.e.*, sulfate concentration), and Fe³⁺ hydrolysis rate on schwertmannite
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6 109 formation and transformation were investigated. The effects of coexisting ions,
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9 110 including Fe²⁺, Cl⁻, K⁺, and NH₄⁺, were also considered because they might
10
11 111 significantly affect the mineralogical properties of schwertmannite and commonly occur
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14 112 in AMD environments.⁴⁷⁻⁴⁹ The concentrations of dissolved Fe³⁺ and SO₄²⁻ during
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16 113 schwertmannite transformation were determined, and the intermediate and final
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19 114 products were characterized by conventional and synchrotron-based X-ray diffraction
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21
22 115 (SXRD), Fourier transform infrared spectroscopy (FTIR), high-resolution scanning
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24
25 116 electron microscopy (SEM), and acidic dissolution experiments.

117 2. Materials and methods

118 2.1 Fe³⁺ hydrolysis pathways and the geochemical conditions used for 119 schwertmannite formation and transformation

120 Schwertmannite formation through direct Fe³⁺ hydrolysis includes two pathways:
121 Fe³⁺ hydrolysis at a certain temperature and subsequent dialysis for some days (*i.e.*, Fe³⁺
122 hydrolysis-dialysis), and Fe³⁺ hydrolysis by adding NaOH. For the Fe³⁺
123 hydrolysis-dialysis pathway, influence of hydrolysis temperature, dialysis time, and
124 coexistence of K⁺ or NH₄⁺ on schwertmannite formation were examined. As to the
125 pathway with Fe³⁺ hydrolysis by adding NaOH, the effects of Fe³⁺ hydrolysis rate, pH,
126 Fe/S molar ratio, and coexistence of Cl⁻, K⁺, or NH₄⁺ on schwertmannite formation were
127 investigated. The effects of these factors, as well as aging temperature and the presence
128 of Fe²⁺ were determined on schwertmannite transformation.

129 2.2 Effects of hydrolysis temperature, dialysis time, and coexistence of K⁺ or NH₄⁺

[Type here]

130 **on schwertmannite formation through Fe³⁺ hydrolysis-dialysis**

131 Synthesis of schwertmannite via Fe³⁺ hydrolysis-dialysis was conducted at 60 °C.³
132 Briefly, 5.4 g FeCl₃·6H₂O and 1.5 g Na₂SO₄ were added into 1 L of deionized water
133 preheated to 60 °C, and the obtained suspension was then stirred at 60 °C for an
134 additional 12 mins. The suspension was subsequently cooled to RT and dialyzed for 7 d
135 with a final conductivity < 20 μS·cm⁻¹. Finally, the suspension was centrifuged,
136 freeze-dried, ground, and stored at 4 °C before being characterized by XRD, SEM, and
137 FTIR. To investigate the hydrolysis temperature effect, similar experiments were
138 performed at 25 °C, 40 °C, 50 °C, 70 °C, and 80 °C. In addition, the influence of dialysis
139 time (1, 3, 7, 10, and 15 d with hydrolysis temperatures of 25 °C and 60 °C) and of the
140 additional presence of K⁺ or NH₄⁺ (hydrolysis temperature of 60 °C and dialysis time of
141 7 d) on schwertmannite formation were also investigated. The initial molar ratio of Fe/S
142 (Fe/S = 2) was the same in all experiments. All reaction conditions for the formation
143 and transformation of schwertmannite were summarized in [Table S1](#).

144 The S and Fe contents in the final dried products were measured by dissolving 10
145 mg solids in 10 mL of 0.2 M acidic ammonium oxalate solution [(NH₄)₂C₂O₄, pH 3].⁵⁰
146 The concentrations of Fe and SO₄²⁻ in the solution were determined using the modified
147 1, 10-phenanthroline colorimetric method⁵¹ and ion chromatography (Dionex
148 ICS-1100), respectively.

149 **2.3 Formation and transformation of schwertmannite through Fe³⁺ hydrolysis by** 150 **adding NaOH in simulated AMD environments**

151 AMD is acidic (usually pH 2 - 3.5) and enriched in ferrous (Fe²⁺) and ferric (Fe³⁺)

ions with total Fe and SO_4^{2-} concentrations, respectively, ranging from 500 - 4500 $\text{mg}\cdot\text{L}^{-1}$ and from 2000 - 6000 $\text{mg}\cdot\text{L}^{-1}$.⁷ Thus, to simulate AMD environments, the pH and dissolved Fe^{3+} and SO_4^{2-} concentrations used in this study were largely varied in these ranges.

2.3.1 Initial phase evolution during Fe^{3+} hydrolysis

To determine the initial phase evolution during Fe^{3+} hydrolysis, 2 mL of 0.8 M NaOH was rapidly mixed with an equal volume of 0.4 M $\text{Fe}_2(\text{SO}_4)_3$ in a 10 mL tube ($\text{OH}^-/\text{Fe}^{3+} = 1$, $\text{Fe}/\text{S} = 0.67$, $\sim\text{pH } 2.5$). The mixed solution was hydrolyzed at 25 °C for different durations (3.2, 8.7, 45, 50, 59, 70, and 140 min) in different tubes. The obtained suspensions were washed with deionized water, air dried, ground, stored at 4 °C, and then analyzed by SXRD and pair distribution functions (PDF) at beamline 11-ID-B at the Advanced Photon Source (APS).

To further clarify the effects of SO_4^{2-} distribution on the transformation of ferrihydrite to schwertmannite, pre-formed ferrihydrite suspension was aged in the presence of SO_4^{2-} under the same solution conditions. Specifically, SO_4^{2-} solution was added to 50 mL of freshly synthesized ferrihydrite suspension, with pH 2.5, Fe/S molar ratio of 0.67 and a final volume of 200 mL. After that, the ferrihydrite suspension was aged for the same durations (3.2, 8.7, 45, 50, 59, 70, and 140 min) under stirring.

2.3.2 Effects of Fe^{3+} hydrolysis rate on the formation and long-term aging of schwertmannite

126 mL of 0.2 M NaOH was added dropwise to a 74 mL mixed solution containing $\text{Fe}(\text{NO}_3)_3$ and Na_2SO_4 at addition rates of 0.5, 0.1, and 0.05 mL/min, respectively,

[Type here]

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4 174 corresponding Fe^{3+} hydrolysis rates of 33.33, 6.67, and 3.33 $\mu\text{M}/\text{min}$. The direct mix of
5
6 175 NaOH , $\text{Fe}(\text{NO}_3)_3$ and Na_2SO_4 solutions was recognized as control system (named as
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8
9 176 mixed directly), approximately representing an infinite Fe^{3+} hydrolysis rate. Solution pH
10
11 177 was then adjusted to 3 for all experiments with a Fe/S molar ratio of 2 [$c(\text{Fe}^{3+}) = 48.55$
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13
14 178 mM , $c(\text{SO}_4^{2-}) = 24.275 \text{ mM}$]. In addition, to determine the effects of Fe^{2+} on
15
16
17 179 schwertmannite transformation, a Fe^{2+} solution [$c(\text{Fe}^{3+})/c(\text{Fe}^{2+}) = 10$] was added to the
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20 180 fresh schwertmannite suspension formed from the condition of a NaOH addition rate of
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22 181 0.1 mL/min. Subsequently, all samples were sealed and aged at 60 °C for 96 h, during
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24
25 182 which, the solution pH were maintained at pH 3 by adding 0.1 M NaOH or HNO_3 at
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27
28 183 regular time intervals. The containers were open to air during pH adjustment and
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30
31 184 sampling, allowing entrance of atmospheric O_2 to the reaction systems. At pre-set time
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34 185 intervals, a 15 mL suspension was sampled and passed through a 0.22 μm membrane
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37 186 filter mounted on a vacuum apparatus. The dissolved SO_4^{2-} and Fe concentrations in the
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40 187 filtrates were measured as described above, whereas the wet solids on the membrane
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43 188 were rinsed with 30 mL deionized water, air dried, ground, and analyzed by XRD,
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45
46 189 FTIR, SEM, and acidic dissolution.

190 **2.3.3 Effects of pH, Fe/S molar ratio, and temperature on the long-term aging of** 191 **schwertmannite**

192 Solutions containing $\text{Fe}(\text{NO}_3)_3$ and Na_2SO_4 with Fe/S molar ratios of 1.5, 2.0, 2.5,
193 5.0, 8.0 or 10.0 [$c(\text{Fe}^{3+}) = 48.55 \text{ mM}$] were directly mixed with different amounts of 0.2
194 M NaOH solution, leading to final pH values of pH 2.0, 2.5, 3.0 and 3.5 with total
195 suspension volume of 200 mL. The suspensions with different pHs (Fe/S molar ratio =

[Type here]

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4 196 2.0) were aged at 80 °C for 96 h, while the suspensions with different Fe/S molar ratios
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6 197 (pH = 3.0) were aged at 60 °C for 96 h. Subsequent experimental details are the same as
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9 198 in Section 2.3.2.

11 199 **2.3.4 Effects of co-existing Cl⁻, K⁺, or NH₄⁺ on the long-term aging of** 12 13 14 200 **schwertmannite**

17 201 Solutions containing Fe(NO₃)₃, Na₂SO₄, and NaCl [c(Fe³⁺) = 48.55 mM, Fe/S = 2,
18
19 202 Fe/Cl = 2, 0.2] were directly mixed with 0.2 M NaOH solution to obtain
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21 203 schwertmannite suspensions with a total volume of 200 mL. The schwertmannite
22
23 204 suspensions were then aged at 60 °C and pH 3 for 96 h. In addition, solutions containing
24
25 205 Fe(NO₃)₃, K₂SO₄ or (NH₄)₂SO₄ [c(Fe³⁺) = 48.55 mM, Fe/S = 2 and 0.2, Fe/K⁺ or
26
27 206 NH₄⁺=1 and 0.1] were directly mixed with 0.2 M NaOH solution to obtain
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31 207 schwertmannite suspensions. The suspensions were subsequently aged at 80 °C and pH
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33 208 2 for 96 h. Subsequent experimental details are the same as in Section 2.3.2.

37 209 **2.3.5 Acidic dissolution experiments**

40 210 To explore the transformation rate of schwertmannite under different conditions,
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42 211 10 mg of dried intermediate samples were dissolved in 10 mL of 0.2 M acidic
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44 212 ammonium oxalate solution (pH 3, Fe_o) or 4 M HCl solution (Fe_t) at RT for 2 h under
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46 213 stirring. Resulting solution was then immediately filtered through a 0.22 μm membrane.
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49 214 The Fe concentration in the solution was measured using a modified 1,
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51 215 10-phenanthroline colorimetric method.⁵¹ The ratio of Fe_o/Fe_t indicates the
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54 216 transformation rate of schwertmannite.

58 217 **2.4 Solid characterizations**

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[Type here]

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4 218 Conventional XRD patterns for phase identification were recorded from 10 to 70°
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6 219 at a scan speed of 1°·min⁻¹ on a Bruker D8 Advance X-ray diffractometer equipped with
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9 220 a LynxEye detector using Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm). To identify
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11 221 mineral phases with poor crystallinity, synchrotron-based XRD data of part samples
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13
14 222 were collected at beamline BL14B1 ($\lambda = 0.6895$ Å, scanning from 0.5 to 30° and
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16
17 223 exposure time of 30 s) at the Shanghai Synchrotron Radiation Facility (SSRF)⁵² or at
18
19 224 beamline 11-ID-B at the Advanced Photon Source (APS), Argonne National Laboratory
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21
22 225 (X-ray energy of 58.86 keV, $\lambda = 0.2112$ Å).⁵⁰

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24
25 226 The morphology and particle size of the samples were observed by SEM (SU8000)
26
27 227 at an accelerating voltage of 10 or 20 kV. Specifically, a small amount of sample was
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30 228 pasted on conductive glue, and then plated using a sputtering apparatus. In addition,
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32 229 FTIR of the samples was recorded on a Bruker VERTEX 70 spectrophotometer. The
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35 230 samples were mixed gently with KBr (~1% sample weight) in an agate mortar and
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38 231 pelletized. Each sample was collected 128 scans with a resolution of 4 cm⁻¹ over the
39
40 232 4000–400 cm⁻¹ against the air background.

41 42 43 233 **3. Results and discussion**

44 45 234 **3.1 Formation of schwertmannite through Fe³⁺ hydrolysis-dialysis**

46
47
48 235 XRD patterns of the products obtained from different Fe³⁺ hydrolysis temperatures
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50 236 are shown in Figure 1a. With increasing hydrolysis temperature from 25 - 60 °C, pure
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52
53 237 schwertmannite is obtained, and its crystallinity gradually increases evidenced by the
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56 238 enhanced peak intensity at 2.55 Å (Fig. 1a). As shown in Table 1, a higher hydrolysis
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58 239 temperature (25 - 60 °C) leads to a higher SO₄²⁻ content and a lower Fe/S ratio,
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4 240 suggesting that schwertmannite crystallinity might be related to the sulfate content,³ *i.e.*,
5
6 241 a higher sulfate content leads to an increased crystallinity. At 25 °C, schwertmannite is
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9 242 flower-shaped and composed of small thin plates (Fig. 2a). With increasing hydrolysis
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11 243 temperature, the thin plates transform to long strips, connecting to a “sea-urchin”-like
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14 244 structure (Fig. 2a-d). When the hydrolysis temperature increases to 70 °C and above,
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16 245 minor goethite impurities form, evidenced by its characteristic peaks at 4.18 Å and 1.72
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18
19 246 Å (Fig. 1a), while the crystallinity of schwertmannite slightly decreases (Fig. 1a). In
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21
22 247 addition, SO₄²⁻ content decreases and Fe/S ratio increases (Table 1), and the long strips
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25 248 of schwertmannite become more clustered (Fig. 2e-f).

26
27 249 The FTIR spectra of these samples are similar and consistent with typical
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29
30 250 schwertmannite IR fingerprint.^{50, 53} These spectra consist of a broad triply degenerate
31
32 251 asymmetric stretching (ν_3) band at ~1125 cm⁻¹ with two shoulder bands at ~1050 and
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34
35 252 ~1205 cm⁻¹, a ν_1 fundamental of the symmetric sulfate stretching at 980 cm⁻¹, a ν_4
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37
38 253 bending band at ~610 cm⁻¹, and a Fe-O stretching band at ~698 cm⁻¹ (Fig. S1a).
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40 254 Additional weak IR vibration bands at 885 cm⁻¹ and 792 cm⁻¹ are shown for the
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43 255 samples hydrolyzed at 70 °C and 80 °C, indicating the formation of minor goethite (Fig.
44
45 256 S1a), consistent with XRD results (Fig. 1a).

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47
48 257 With increasing dialysis time, diffraction peak intensities of schwertmannite
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50
51 258 slightly decrease, especially for the peak at 2.55 Å (Fig. 1b), consistent with the
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53 259 decrease of SO₄²⁻ content and of sulfate IR band intensities (Table 1 and Fig. S1b). In
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56 260 addition, schwertmannite particles aggregate more closely (Figs. 2g-i), leading to a
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58
59 261 "hedgehog" morphology.⁵⁴ Furthermore, compared to the Na⁺ system, the presence of

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4 262 K^+ or NH_4^+ (Fig. 1c) slightly increases the crystallinity of schwertmannite but decreases
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6 263 the SO_4^{2-} content in schwertmannite (Table 1).
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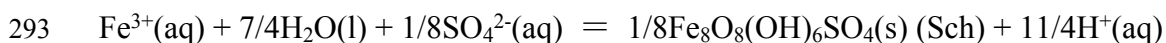
9 264 **3.2 Mineral evolution during Fe^{3+} hydrolysis by adding NaOH**

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11 265 During Fe^{3+} hydrolysis in the presence of SO_4^{2-} , XRD patterns of the intermediate
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14 266 products indicate that ferrihydrite is the initial product and schwertmannite is observed
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17 267 later but within 45 min (Fig. 3a). The corresponding PDF data [G(r)s] of intermediate
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20 268 products show that the PDF data of initial sample (~3.2 min) is similar to that of a
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22 269 ferrihydrite reference. With increasing aging time, the intensity of Fe-Fe peak at 5.42 Å
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24 270 increases, and the Fe-Fe peaks at 7.40 Å and 11.06 Å and Fe-O peak at 6.08 Å gradually
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26
27 271 appear and increase, indicative of schwertmannite formation (Fig. 3b). In contrast, the
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30 272 pre-formed two-line ferrihydrite aged in the same sulfate concentration and solution pH
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32 273 does not transform to schwertmannite (Fig. 3c).
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35 274 Sulfate-bearing ferrihydrite thus appears as an intermediate phase during the
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38 275 formation of schwertmannite (Fig. 3), similar with the observation in Zhu et al.³⁴.
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40 276 Transformation from ferrihydrite to schwertmannite is most likely because of a higher
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43 277 thermodynamic stability than ferrihydrite.^{31, 54} However, the contrast between the
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46 278 transformation from intermediate ferrihydrite-like mineral (Fig. 3a) and from
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48 279 pre-formed ferrihydrite (Fig. 3c) suggests that sulfate is closely associated with
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51 280 ferrihydrite in a way that differs from simple surface adsorption.⁵⁵ This is not
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54 281 unexpected because sulfate and ferrihydrite co-precipitate during Fe^{3+} hydrolysis in the
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57 282 presence of sulfate. The sulfate may be incorporated into the structural defects of
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59 283 ferrihydrite. Such structure may have some similarity to that of schwertmannite^{3, 50} and
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4 284 thus the formed ferrihydrite readily transforms to schwertmannite. In addition, the
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6 285 ferrihydrite formed in the presence of sulfate may have smaller particle size and more
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9 286 structural defects than ferrihydrite synthesized in the absence of sulfate, which further
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11 287 enhances its transformation to schwertmannite.⁵⁶

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14 288 Schwertmannite can form at 25 °C through both Fe³⁺ hydrolysis-dialysis (Fig. 1)
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16 289 and Fe³⁺ hydrolysis by adding NaOH (Fig. 3, 4a and S2). However, a theoretical
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19 290 calculation indicates that schwertmannite formation through direct Fe³⁺ hydrolysis is not
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22 291 thermodynamically spontaneous under ambient condition (~ 25 °C), due to the reaction
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25 292 free energy ΔG°_{298} of 6.275 kJ·mol⁻¹ as the following equation.⁷



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30 294 This apparent discrepancy could be explained by the migration of protons (H⁺)
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32 295 through the dialysis membrane into distilled water during dialysis process. As a result,
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35 296 the solution pH in the dialysis bag, initially very low and unfavorable to Fe³⁺ hydrolysis,
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37 297 gradually increases and then induces schwertmannite formation. On the other hand, the
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40 298 schwertmannite readily forms from Fe³⁺ hydrolysis in the presence of sulfate by adding
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43 299 NaOH at 25 °C (Fig. 3 and 4), consistent with previous reports.³²⁻³⁴ Consequently, direct
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46 300 Fe³⁺ hydrolysis should be considered as an important pathway of schwertmannite
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48 301 formation in watershed or soils surrounded by AMD with a relative high pH.

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50 302 **3.3 Effects of geochemical conditions on schwertmannite formation through Fe³⁺**
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53 303 **hydrolysis by adding NaOH**

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55 304 **3.3.1 Effect of Fe³⁺ hydrolysis rate**

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58 305 XRD patterns indicate that pure schwertmannite forms at different Fe³⁺ hydrolysis
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4 306 rates (above 3.33 $\mu\text{M Fe/min}$), with a lower hydrolysis rate leading to an improved
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6 307 crystallinity, compared to the mixed directly system (Fig. 4a). In addition,
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8 308 schwertmannite morphology varies substantially with Fe^{3+} hydrolysis rate, exhibiting
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10 309 longer strips and resulting in larger and looser aggregates at a lower Fe^{3+} hydrolysis
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12 310 rate, similar to the sea urchin-like aggregates that form from Fe^{2+} oxidation.⁴⁶ However,
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14 311 the morphology obtained from mixed directly system is block agglomerate (Fig. 4b).
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16 312 These schwertmannite samples, obtained from different Fe^{3+} hydrolysis rates, should
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18 313 have distinct surface reactivity and geochemical behaviors, which need to be further
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20 314 studied.

27 315 **3.3.2 Effects of pH, Fe/S molar ratio and co-existing ions**

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29 316 Schwertmannite can form through Fe^{3+} hydrolysis over the pH range of 2.0 – 3.5
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31 317 (Fig 4a, 9a and S2) that is slightly wider compared to that of Fe^{2+} oxidation (*i.e.*, pH 2.4
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33 318 - 3.2⁴⁶). In addition, schwertmannite can be obtained only at low initial Fe/S molar ratio
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35 319 ($\text{Fe/S} \leq 5$) (Fig. 3 and 9b), *i.e.*, high sulfate concentration, while ferrihydrite forms when
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37 320 the Fe/S molar ratios exceed 8 to 10, suggesting that sulfate must be present in excess,
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39 321 relative to the ideal mineral composition, to allow for schwertmannite formation.

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41 322 XRD patterns indicate that the presence of Cl^- does not affect schwertmannite
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43 323 formation (Fig. 9d), suggesting that although Cl^- can promote akaganéite
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45 324 ($\text{FeO}(\text{OH})_{1-x}\text{Cl}_x$) formation under acidic conditions,³⁴ the presence of numerous sulfate
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47 325 probably inhibits the formation of akaganéite, similar to the reports in Fe^{2+}
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49 326 bio-oxidation system.^{48, 57} Pure schwertmannite could thus be synthesized through FeCl_3
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51 327 hydrolysis-dialysis if sufficient sulfate is present.³ Additionally, the presence of K^+ or
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4 328 NH_4^+ slightly increases schwertmannite crystallinity (Fig. S2), similar to the Fe^{3+}
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6 329 hydrolysis-dialysis pathway (Fig. 1c), probably because K^+ or NH_4^+ ions enter the
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9 330 schwertmannite tunnel structure during Fe^{3+} hydrolysis, thus enhancing schwertmannite
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11 331 crystal growth.

332 **3.4 Effects of geochemical conditions on the transformation of schwertmannite** 333 **formed through Fe^{3+} hydrolysis by adding NaOH**

334 **3.4.1 Effect of Fe^{3+} hydrolysis rate**

335 During the transformation of schwertmannite formed at different Fe^{3+} hydrolysis
336 rates, minor goethite form only in the mixed directly sample after a 3 h aging (Fig. 5a).
337 With increasing aging time to 24 h, goethite is present in all samples, with more
338 goethite occurring at higher Fe^{3+} hydrolysis rate (Fig. 5b), suggesting that the
339 schwertmannite obtained at a higher Fe^{3+} hydrolysis rate is less stable, possibly due to
340 its lower crystallinity. FTIR spectra of the samples aged for 3 h (Fig. 5c) and 24 h (Fig.
341 5d) show that the characteristic Fe-O stretching band of schwertmannite at $\sim 698\text{ cm}^{-1}$
342 decreases with aging time, whereas the characteristic OH bending vibration bands of
343 goethite at 885 cm^{-1} and 792 cm^{-1} increase with increasing Fe^{3+} hydrolysis rate and
344 aging time, confirming XRD results (Fig. 5a and 5b). Thus, lower Fe^{3+} hydrolysis rate
345 leads to larger crystallite size and higher structural stability of schwertmannite, thus
346 disfavoring its transformation to other phases. This observation was also made for
347 schwertmannite formed from Fe^{2+} oxidation.^{15, 20, 58}

348 **3.4.2 Effect of the presence of Fe^{2+}**

349 After aging for 24 h, XRD patterns indicate that goethite diffraction peaks are

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4 350 stronger if Fe^{2+} is present (Fig. 6a), compared to the Fe^{2+} -free system (Fig. 5b),
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6 351 suggesting that Fe^{2+} significantly accelerates schwertmannite transformation to goethite.
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9 352 In addition, the concentration of dissolved SO_4^{2-} is higher in the presence of Fe^{2+} than
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11 353 that in the Fe^{2+} -free system (Fig. 6b), indicating that Fe^{2+} promotes the release of sulfate
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14 354 during schwertmannite dissolution and transformation. During the aging process, the
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16 355 concentration of dissolved Fe^{2+} decreases with increasing aging time, while that of
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19 356 dissolved SO_4^{2-} increases (Fig. 6b), suggesting that schwertmannite transformation to
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22 357 goethite occurs through a dissolution-recrystallization mechanism by consuming Fe^{2+}
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25 358 and releasing SO_4^{2-} . Enhancement of schwertmannite transformation in the presence of
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27 359 Fe^{2+} possibly results from two aspects. On one hand, aqueous $\text{Fe}(\text{II})$ species can
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30 360 exchange structural $\text{Fe}(\text{III})$, thus enhancing the mineral phase reorganization, as
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33 361 evidenced by stable Fe isotope tracers.⁵⁹⁻⁶¹ On the other hand, electron transfer between
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36 362 adsorbed $\text{Fe}(\text{II})$ and structural $\text{Fe}(\text{III})$ promotes the reductive dissolution of
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39 363 schwertmannite and its subsequent recrystallization.^{60, 62, 63}

364 3.4.3 Effects of pH, temperature, and Fe/S molar ratio

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43 365 At 80 °C and $\text{Fe}/\text{S} = 2$, the concentration of dissolved Fe^{3+} decreases with
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46 366 increasing pH from 2.0 to 3.5 (Fig. 7a), while that of dissolved SO_4^{2-} increases (Fig. 8a),
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49 367 indicating that a higher pH enhances SO_4^{2-} release and thus the transformation from
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52 368 schwertmannite to goethite. This transformation is supported by the XRD patterns (Fig.
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55 369 9a) and the lower Fe_o/Fe_t (ratio of dissolved Fe in oxalate to total Fe) measured at
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58 370 higher pH values (Fig. S4b). Additionally, FTIR spectra indicate that the characteristic
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60 371 Fe-O stretching band of schwertmannite at $\sim 701 \text{ cm}^{-1}$ gradually decreases whereas OH

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4 372 bending vibration bands of goethite at 885 cm^{-1} and 792 cm^{-1} increase with increasing
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6 373 pH (Fig. S3a), further confirming the above analyses. The increased transformation rate
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9 374 of schwertmannite to goethite can be partially ascribed to the easier sulfate release at a
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11 375 higher pH.³⁶

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14 376 For a given pH and Fe/S molar ratio, the concentration of dissolved Fe^{3+}
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16 377 substantially decreases with increasing aging temperature (from 25 to 80 °C) and aging
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18 378 time (Fig. 7c). As to dissolved SO_4^{2-} , it increases slightly at 25 °C and more
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20 379 significantly at higher temperatures with increasing aging time (Fig. 8b), suggesting that
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22 380 SO_4^{2-} release is enhanced at a higher temperature during schwertmannite
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24 381 transformation. Additionally, XRD patterns (Fig. 9c and S3c) and acidic dissolution
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26 382 results (Fig. S4a) indicate that goethite formation is favored at higher aging
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28 383 temperatures and longer aging time, consistent with lower concentration of dissolved
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30 384 Fe^{3+} (Fig. 7c) and higher concentration of dissolved SO_4^{2-} (Fig. 8b). In addition, the
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32 385 mineral phases formed at different Fe/S molar ratios exhibit different stabilities at 60 °C
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34 386 and pH 3 (Fig. 9b and S3b), with lower Fe/S molar ratio resulting in lower
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36 387 concentration of dissolved Fe^{3+} (Fig. 8b). As a consequence, schwertmannite obtained at
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38 388 a lower Fe/S molar ratio ($\text{Fe/S} \leq 5$) transforms more readily to goethite than ferrihydrite
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40 389 which is obtained at higher Fe/S ratios ($\text{Fe/S} > 5$) (Fig. 9b and S3b).

41 390 **3.4.4 Effects of co-existing Cl^- , K^+ , or NH_4^+**

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43 391 Compared to the system without Cl^- , the presence of Cl^- ($\text{Fe/Cl} = 2$) accelerates the
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45 392 release of SO_4^{2-} (Fig. 8c), possibly because Cl^- promotes SO_4^{2-} release by ligand
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47 393 exchange, enhancing goethite formation (Fig. 9d). In contrast, a high concentration of

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4 394 Cl^- ($\text{Fe}/\text{Cl}^- = 0.2$) inhibits SO_4^{2-} release and the transformation of schwertmannite to
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6 395 goethite (Fig. 8c and 9d), possibly because massive Cl^- adsorption on schwertmannite
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9 396 surface impedes SO_4^{2-} release and thus the dissolution-recrystallization process. As
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11 397 reported previously, adsorption of ions on schwertmannite surface could stabilize its
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14 398 structure.^{40, 64}

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17 399 The presence of K^+ promotes hydrolysis and precipitation of dissolved Fe^{3+} (Fig.
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19 400 7d) and inhibits SO_4^{2-} release (Fig. 8d) through the formation of K^+ -bearing jarosite,
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21 401 exhibiting aggregated spherical particle morphology (Fig. 9d and 10d). K^+ -bearing
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23 402 jarosite formation is also confirmed by FTIR spectrum with bands at around 1080 ~
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25 403 1200 cm^{-1} , 1008 cm^{-1} , and 628 cm^{-1} (Fig. S3d), respectively, assigned to the vibrational
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27 404 modes of $\nu_3(\text{SO}_4^{2-})$, $\nu_1(\text{SO}_4^{2-})$, and $\nu_4(\text{SO}_4^{2-})$.⁶⁵ Similarly, a high NH_4^+ concentration
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29 405 ($\text{Fe}/\text{NH}_4^+ = 0.1$) favors jarosite formation with very low concentration of dissolved
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31 406 SO_4^{2-} (Fig. 8d), leading to the coexistence of goethite and NH_4^+ -bearing jarosite (Fig.
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33 407 S5), coincident with the results observed in Fe^{2+} bio-oxidation system.^{66, 67} More
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35 408 lath-like particles and looser aggregates are observed at a higher concentration of NH_4^+
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37 409 (Fig. 10 b). However, the presence of low NH_4^+ ($\text{Fe}/\text{NH}_4^+ = 1$) increases SO_4^{2-} release
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39 410 (Fig. 8d), thus favoring the formation of goethite (Fig. S5). Compared to NH_4^+ , the
40
41 411 presence of K^+ is easier to induce jarosite formation, consistent with a previous study
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43 412 indicating that the ability of K^+ to promote jarosite formation is $\sim 75\times$ greater than that
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45 413 of NH_4^+ ,⁶⁸ probably because that the ionic radius of hydrated K^+ (1.32 Å) fits better in
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47 414 jarosite structure than that of NH_4^+ (1.44 Å).

415 4. Conclusion and implications

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4 416 In the present study, schwertmannite formation through direct Fe^{3+} hydrolysis and
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6 417 its subsequent transformation have been systematically investigated under various
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9 418 geochemical conditions. Schwertmannite can be obtained over a Fe^{3+} hydrolysis
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11 419 temperature range of 25 - 60 °C, a pH range of 2.0 – 3.5, molar ratios of Fe/S lower than
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14 420 5, Fe^{3+} hydrolysis rates higher than 3.33 $\mu\text{M}/\text{min}$, and in the presence of Cl^- , K^+ or NH_4^+
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17 421 (Fig. 11). Such an extended range of conditions suggests that direct Fe^{3+} hydrolysis is an
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19 422 important pathway for schwertmannite formation in natural AMD affected
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21 423 environments, and that the chemical composition, micro-structure, and reactivity of
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23 424 schwertmannite vary with these geochemical conditions. Actually, schwertmannite
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26 425 formed through Fe^{2+} oxidation also includes a process of Fe^{3+} hydrolysis-precipitation,
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29 426 and these new insights into schwertmannite formation through direct Fe^{3+} hydrolysis are
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32 427 also essential to understand the mineralization process during Fe^{2+} oxidation in AMD
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35 428 surroundings.

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38 429 During the schwertmannite formation through direct Fe^{3+} hydrolysis,
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40 430 sulfate-bearing ferrihydrite is an intermediate product and sulfate is likely incorporated
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42 431 into structural defects of ferrihydrite particles, rather than simply adsorbed on their
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45 432 surfaces, to induce schwertmannite formation. Due to the abundance of sulfate in AMD
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48 433 environments, these anions readily co-precipitate with ferrihydrite through Fe^{3+}
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51 434 hydrolysis, allowing for the subsequent transformation to schwertmannite and
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53 435 accounting for the more occurrence of schwertmannite than ferrihydrite in AMD
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56 436 affected areas.

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58 437 Schwertmannite readily transforms to more stable goethite and jarosite. High
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4 438 temperature, high pH, and the presence of Fe²⁺ all enhance the transformation to
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6 439 goethite by promoting the release of structural sulfate, whereas a low Fe³⁺ hydrolysis
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9 440 rate and high concentration of Cl⁻ hinder this transformation. Moreover, the presence of
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11 441 both K⁺ and high concentration of NH₄⁺ favor schwertmannite transformation to K⁺- or
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13 442 NH₄⁺-bearing jarosite (Fig. 11). These new insights into schwertmannite formation and
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16 443 transformation under various geochemical conditions are vital to understand the
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19 444 mineralogical properties of schwertmannite and predict the environmental behavior and
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22 445 fate of trace elements associated with schwertmannite in AMD affected environments.
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43 453 assistance during data collection.
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634 **Figure Captions**

635 **Fig. 1.** XRD patterns of the products obtained from Fe³⁺ hydrolysis-dialysis at different
636 Fe³⁺ hydrolysis temperatures followed by dialysis for 7 d (a), from Fe³⁺ hydrolysis at 25
637 and 60 °C followed by dialysis for 1 d and 15 d (b), and from Fe³⁺ hydrolysis at 60 °C in
638 the presence of K⁺ or NH₄⁺ followed by dialysis for 7 d (c) (Gt = goethite; Sch =
639 schwertmannite).

640 **Fig. 2.** SEM images of schwertmannite obtained from Fe³⁺ hydrolysis-dialysis at
641 different Fe³⁺ hydrolysis temperatures followed by dialysis for 7 d (a-25 °C, b-40 °C,
642 c-50 °C, d-60 °C, e-70 °C, f-80 °C) and from different dialysis time at 25 °C (g-1 d; h-15
643 d) or at 60 °C (i-15 d).

644 **Fig. 3.** Synchrotron-based XRD patterns (a) and pair distribution functions [G(r)s] (b)
645 of the intermediate products at different aging time after the quickly mixed of a 0.8 M
646 NaOH solution with an equal volume of 0.4 M Fe₂(SO₄)₃ and XRD patterns of
647 intermediate products for SO₄²⁻ adsorption on pre-formed ferrihydrite (c) at Fe/S molar
648 ratio of 0.67 and pH 2.5 (Sch = Schwertmannite, Fhy = Ferrihydrite).

649 **Fig. 4.** XRD patterns (a) and SEM images (b) of the initial products obtained from
650 direct Fe³⁺ hydrolysis at different Fe³⁺ hydrolysis rates (mixed directly, 33.33, 6.67, and
651 3.33 μM/min) and pH 3.

652 **Fig. 5.** Synchrotron-based XRD patterns and FTIR spectra of the products obtained
653 from direct Fe³⁺ hydrolysis at different Fe³⁺ hydrolysis rates after aging for 3 h (a and c)
654 and 24 h (b and d) at 60 °C and pH 3 (Gt = goethite; Sch = schwertmannite).

655 **Fig. 6.** XRD patterns of the transformation products of schwertmannite, obtained from

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4 656 Fe^{3+} hydrolysis rate of $6.67 \mu\text{M}/\text{min}$, at pH 3 and $60 \text{ }^\circ\text{C}$ in the presence of Fe^{2+} (a) and
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6 657 the concentrations of dissolved Fe^{2+} and SO_4^{2-} (mM) during the transformation (b)
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9 658 ($\text{Fe}^{3+}/\text{Fe}^{2+} = 10$; Gt = goethite; Sch = schwertmannite).

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11 659 **Fig. 7.** Concentration of dissolved Fe^{3+} (mM) during the transformation of
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14 660 schwertmannite, obtained from the quick Fe^{3+} hydrolysis (mixed directly), over the pH
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17 661 range of 2.0 - 3.5 (a), Fe/S molar ratios of 1.5 - 10 (b), the temperature range of 25 - 80
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19 662 $^\circ\text{C}$ (c) and in the presence of Cl^- , K^+ or NH_4^+ (d).

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22 663 **Fig. 8.** Concentration of dissolved SO_4^{2-} (mM) during the transformation of
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24 664 schwertmannite, obtained from the quick Fe^{3+} hydrolysis (mixed directly, Fe/S = 2), at
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27 665 different pHs (a), different temperatures (b), in the presence of Cl^- (c) and K^+ or NH_4^+
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29 666 (d).

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32 667 **Fig. 9.** XRD patterns of the mineral phases obtained from quick hydrolysis of Fe^{3+} and
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34 668 SO_4^{2-} (mixed directly) aged for 3 h at different pHs (a), different Fe/S molar ratios (b),
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37 669 different aging temperatures (c) and in the presence of Cl^- , K^+ , or NH_4^+ (d) (Gt =
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39 670 goethite; Sch = schwertmannite; Fhy = ferrihydrite; Jt = jarosite).

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43 671 **Fig. 10.** SEM images of mineral phases obtained from the quick hydrolysis of Fe^{3+} and
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45 672 SO_4^{2-} (mixed directly) in the presence of Cl^- at $60 \text{ }^\circ\text{C}$ or in the presence of K^+ or NH_4^+ at
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48 673 $80 \text{ }^\circ\text{C}$ after aging for 96 h (a: $\text{Fe}/\text{NH}_4^+ = 1$; b: $\text{Fe}/\text{NH}_4^+ = 0.1$; c: $\text{Fe}/\text{Cl}^- = 0.2$; d: $\text{Fe}/\text{K}^+ =$
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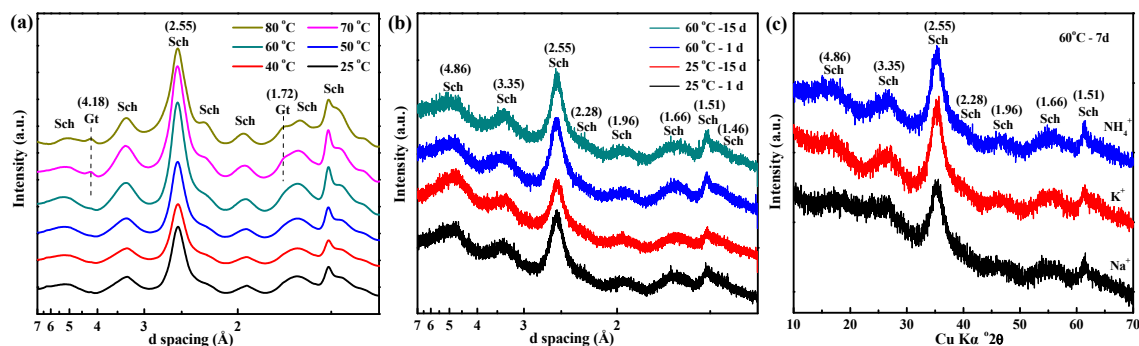
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53 675 **Fig. 11.** Schematic diagram of schwertmannite formation and transformation through
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55
56 676 direct Fe^{3+} hydrolysis under various geochemical conditions.

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678 **Table 1.** The Fe and S contents in the schwertmannite samples formed through Fe^{3+}
 679 hydrolysis-dialysis at different hydrolysis temperatures, dialysis time, and in the
 680 presence of K^+ or NH_4^+ .

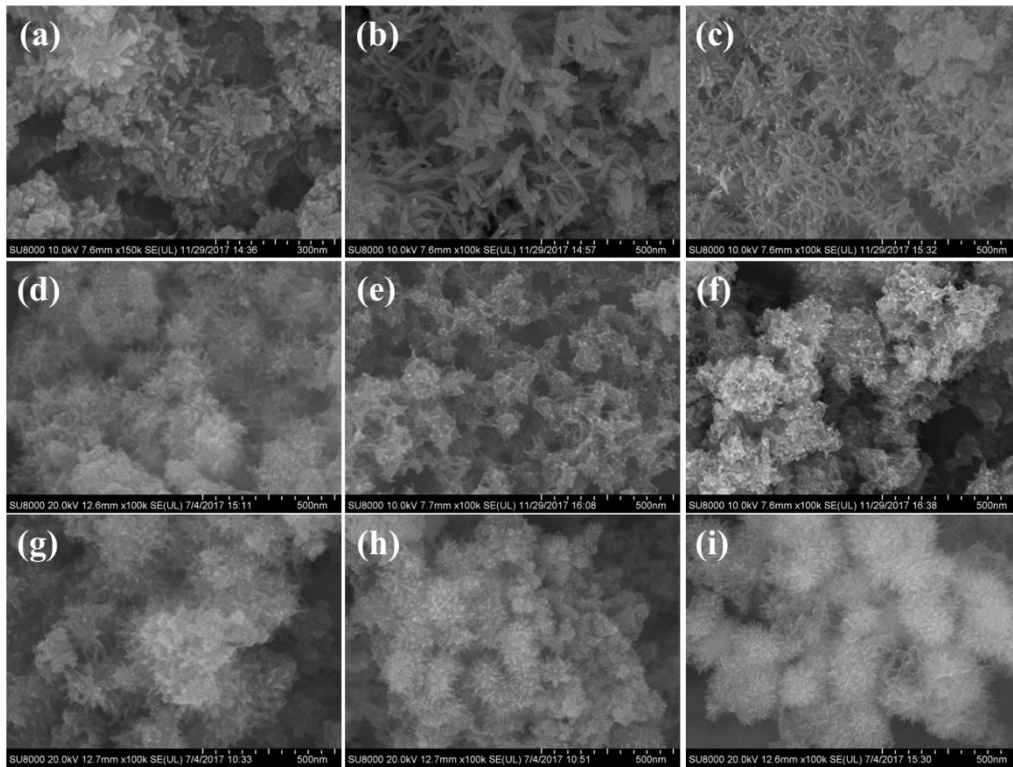
Sample	Fe		SO ₄	molar ratio of Fe/S
	(mmol/g)			
25 °C -7d	10.69	1.71		6.25
40 °C -7d	10.27	1.78		5.77
50 °C -7d	10.65	1.86		5.73
60 °C -7d	10.52	2.03		5.18
70 °C -7d	10.28	1.73		5.94
25 °C -15d	11.55	1.67		6.92
60 °C -15d	11.69	1.79		6.53
60 °C -7d - K^+	9.83	1.66		5.92
60 °C -7d - NH_4^+	11.63	2.13		5.46

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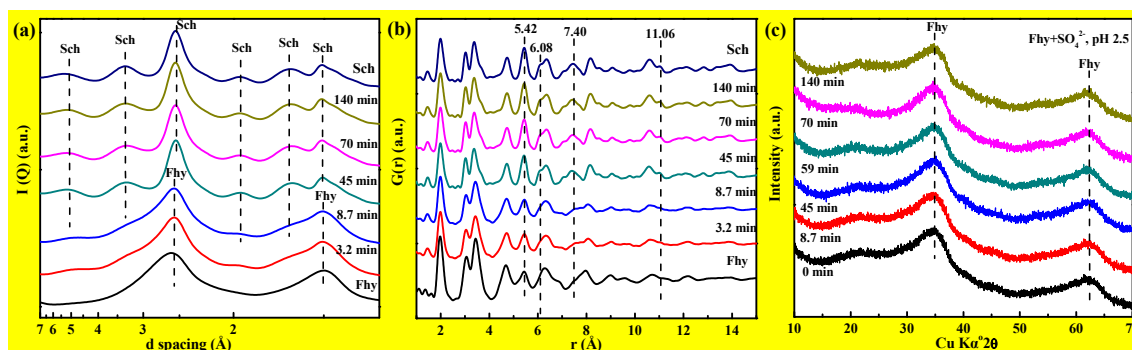
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683 **Fig. 1.** XRD patterns of the products obtained from Fe^{3+} hydrolysis-dialysis at different
 684 Fe^{3+} hydrolysis temperatures followed by dialysis for 7 d (a), from Fe^{3+} hydrolysis at 25
 685 and 60 °C followed by dialysis for 1 d and 15 d (b), and from Fe^{3+} hydrolysis at 60 °C in
 686 the presence of K^+ or NH_4^+ followed by dialysis for 7 d (c) (Gt = goethite; Sch =
 687 schwertmannite).



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689 **Fig. 2.** SEM images of schwertmannite obtained from Fe³⁺ hydrolysis-dialysis at
690 different Fe³⁺ hydrolysis temperatures followed by dialysis for 7 d (a-25 °C, b-40 °C,
691 c-50 °C, d-60 °C, e-70 °C, f-80 °C) and from different dialysis time at 25 °C (g-1 d; h-15
692 d) or at 60 °C (i-15 d).



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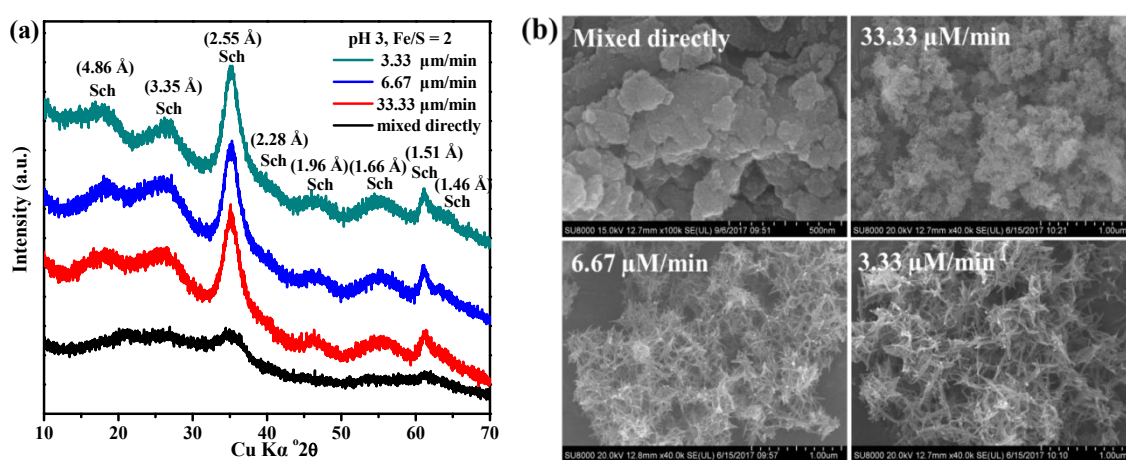
694 **Fig. 3.** Synchrotron-based XRD patterns (a) and pair distribution functions [G(r)s] (b)

695 of the intermediate products at different aging time after the quickly mixed of a 0.8 M

696 NaOH solution with an equal volume of 0.4 M $\text{Fe}_2(\text{SO}_4)_3$ and XRD patterns of697 intermediate products for SO_4^{2-} adsorption on pre-formed ferrihydrite (c) at Fe/S molar

698 ratio of 0.67 and pH 2.5 (Sch = Schwertmannite, Fhy = Ferrihydrite).

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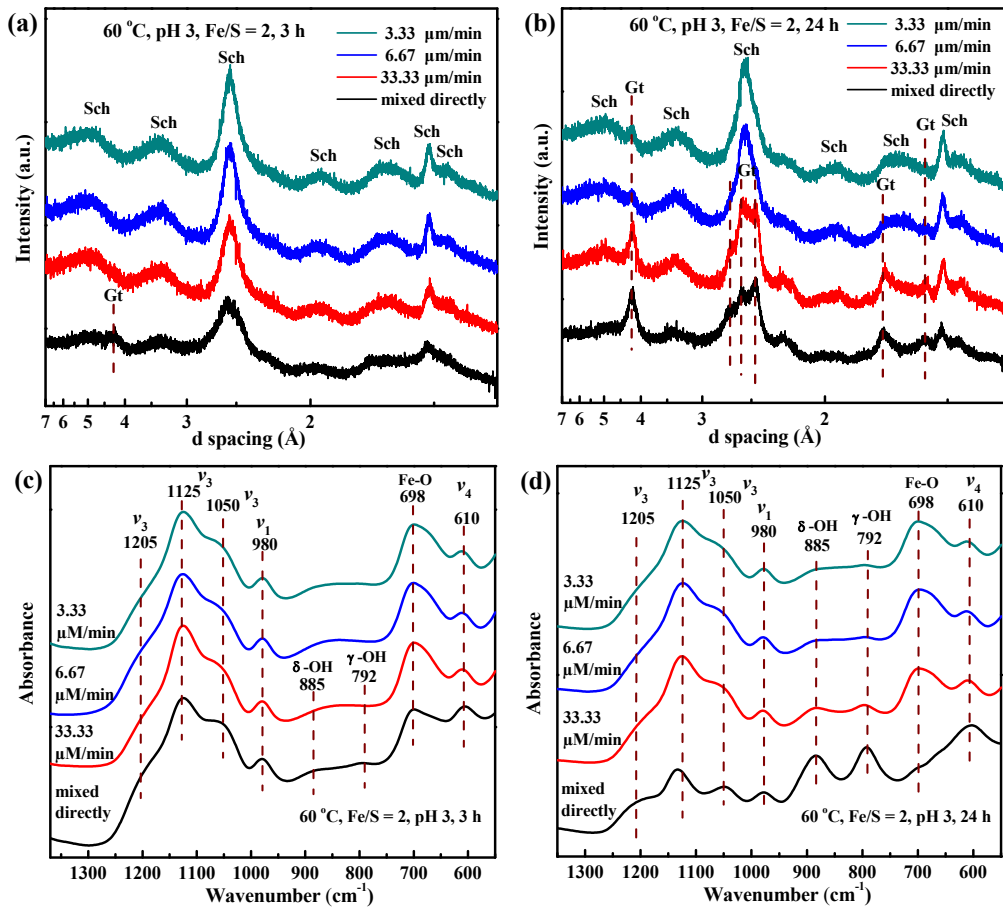


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701 **Fig. 4.** XRD patterns (a) and SEM images (b) of the initial products obtained from702 direct Fe^{3+} hydrolysis at different Fe^{3+} hydrolysis rates (mixed directly, 33.33, 6.67, and703 3.33 $\mu\text{M}/\text{min}$) and pH 3.

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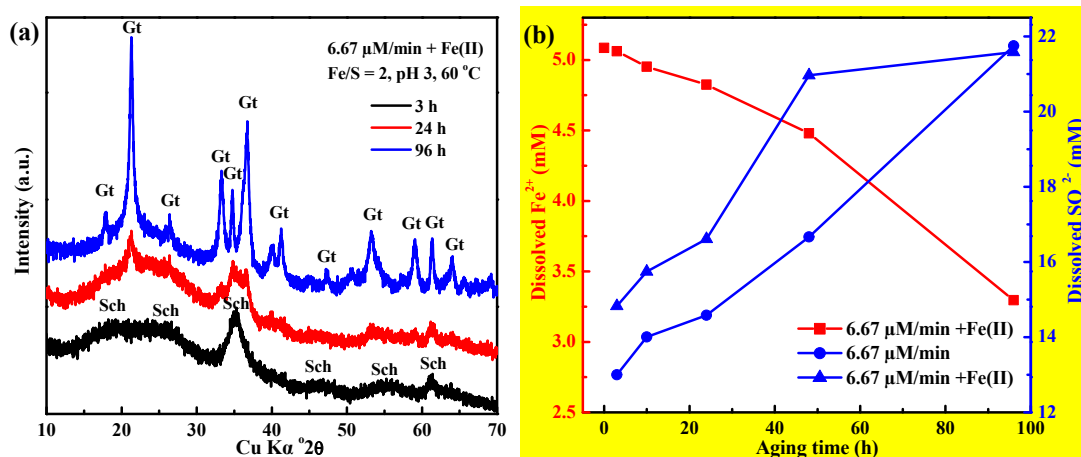
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707 **Fig. 5.** Synchrotron-based XRD patterns and FTIR spectra of the products obtained
 708 from direct Fe³⁺ hydrolysis at different Fe³⁺ hydrolysis rates after aging for 3 h (a and c)
 709 and 24 h (b and d) at 60 °C and pH 3 (Gt = goethite; Sch = schwertmannite).



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Fig. 6. XRD patterns of the transformation products of schwertmannite, obtained from

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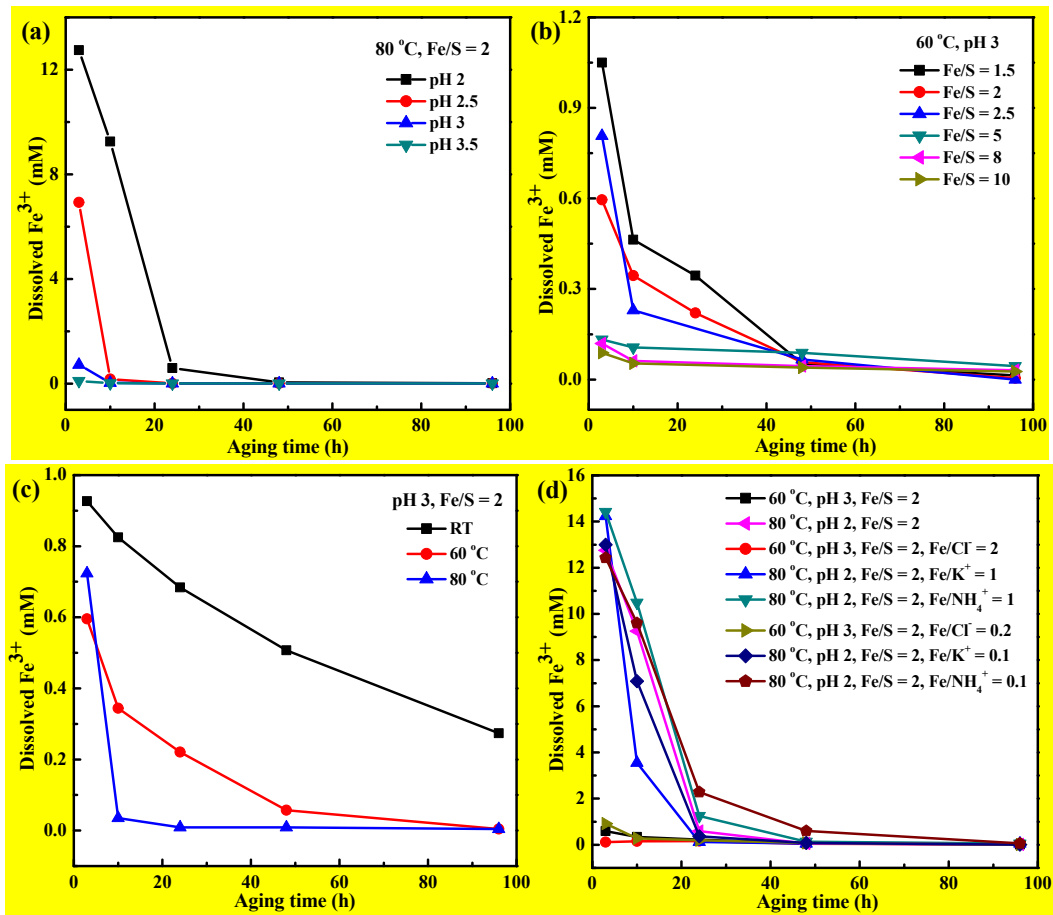
Fe^{3+} hydrolysis rate of 6.67 $\mu\text{M}/\text{min}$, at pH 3 and 60 $^{\circ}\text{C}$ in the presence of Fe^{2+} (a) and

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the concentrations of dissolved Fe^{2+} and SO_4^{2-} (mM) during the transformation (b)

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($\text{Fe}^{3+}/\text{Fe}^{2+} = 10$; Gt = goethite; Sch = schwertmannite).



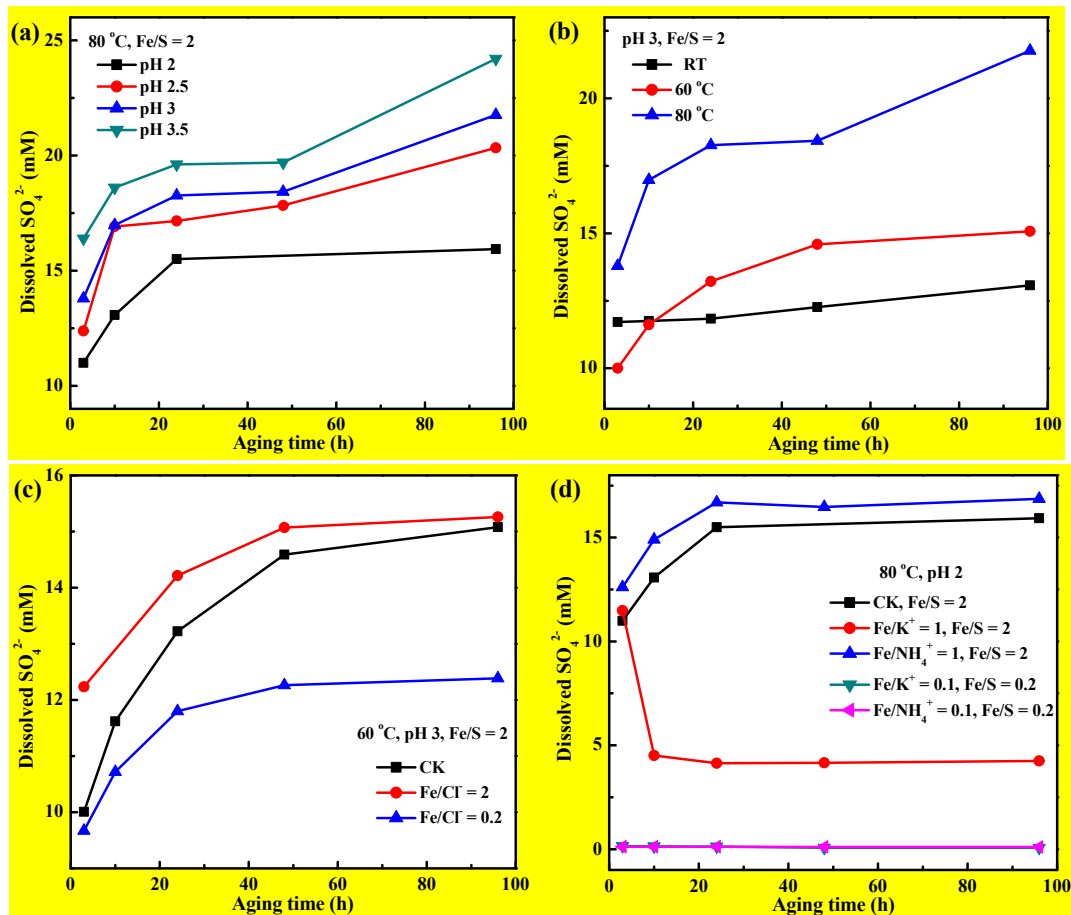
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Fig. 7. Concentration of dissolved Fe^{3+} (mM) during the transformation of schwertmannite, obtained from the quick Fe^{3+} hydrolysis (mixed directly), over the pH range of 2.0 - 3.5 (a), Fe/S molar ratios of 1.5 - 10 (b), the temperature range of 25 - 80 °C (c) and in the presence of Cl^- , K^+ or NH_4^+ (d).

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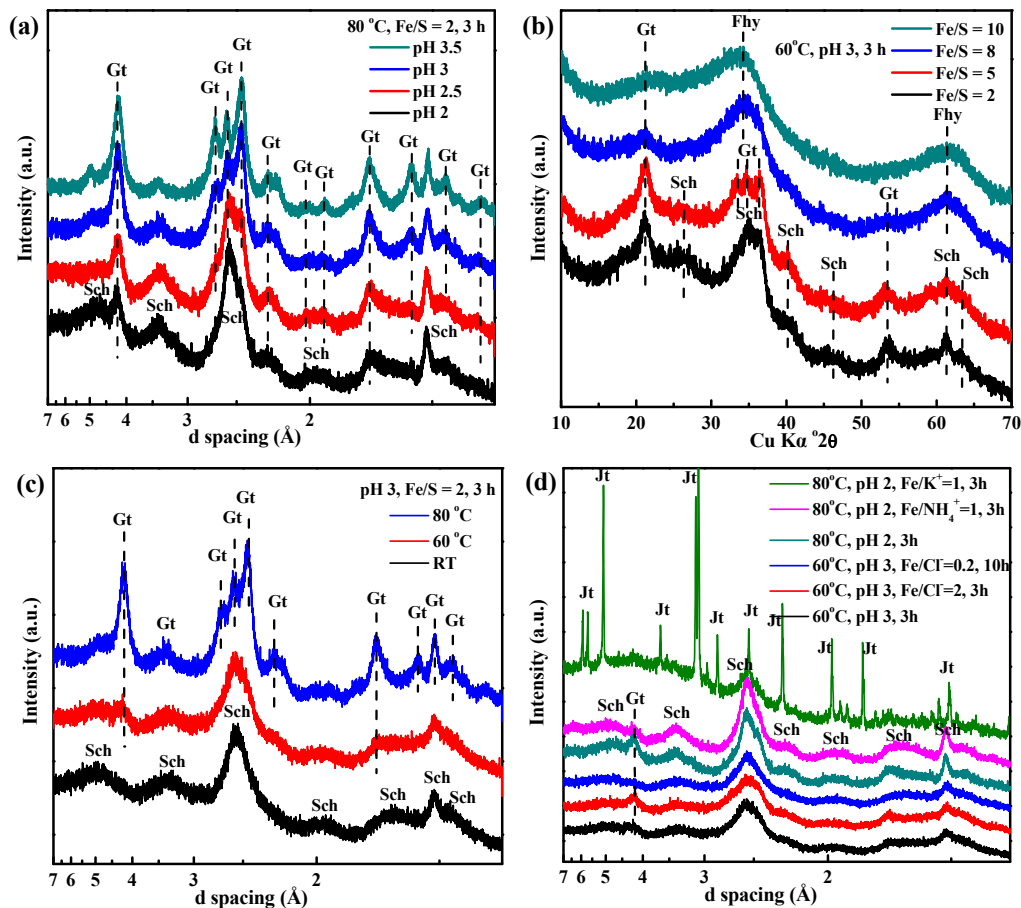
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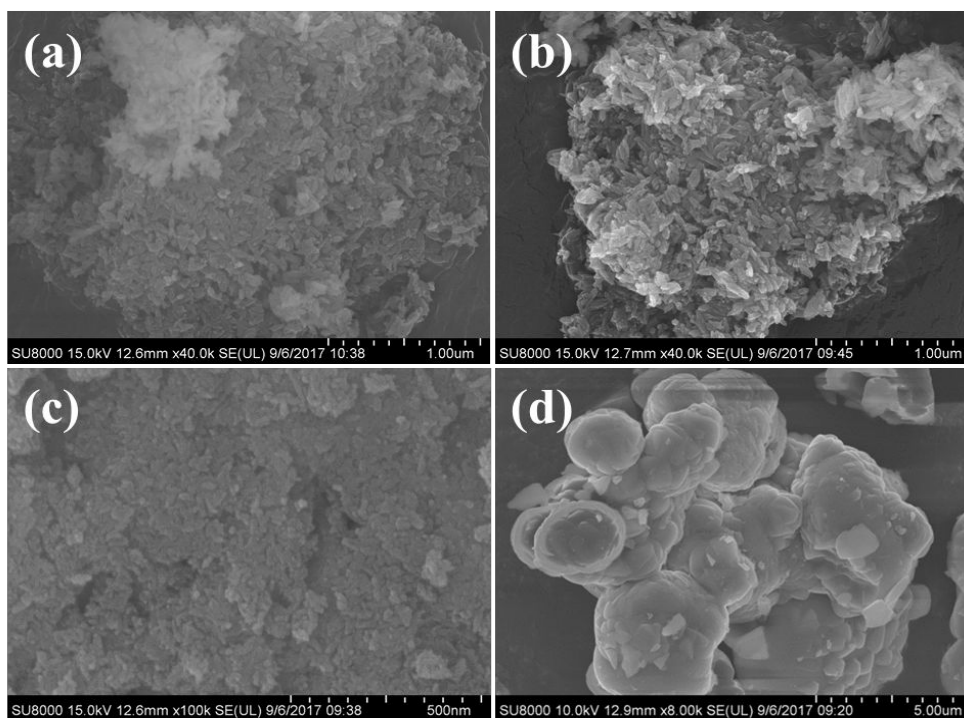
725 **Fig. 8.** Concentration of dissolved SO_4^{2-} (mM) during the transformation of
 726 schwertmannite, obtained from the quick Fe^{3+} hydrolysis (mixed directly), at different
 727 pHs (a), different temperatures (b), in the presence of Cl^- (c) and K^+ or NH_4^+ (d).



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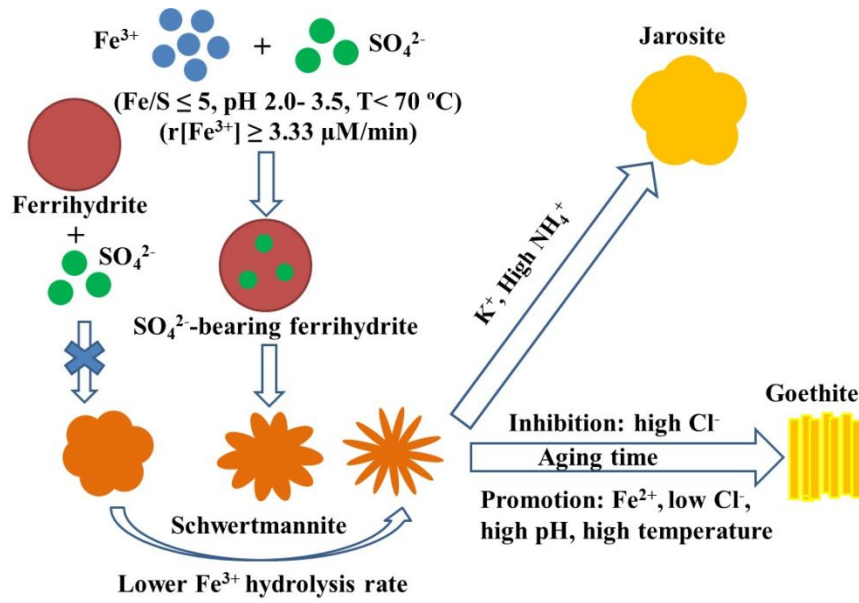
730 **Fig. 9.** XRD patterns of the mineral phases obtained from quick hydrolysis of Fe³⁺ and
 731 SO₄²⁻ (mixed directly) aged for 3 h at different pHs (a), different Fe/S molar ratios (b),
 732 different aging temperatures (c) and in the presence of Cl⁻, K⁺, or NH₄⁺ (d) (Gt =
 733 goethite; Sch = schwertmannite; Fhy = ferrihydrite; Jt = jarosite).



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735 **Fig. 10.** SEM images of mineral phases obtained from the quick hydrolysis of Fe^{3+} and736 SO_4^{2-} (mixed directly) in the presence of Cl^- at 60 °C or in the presence of K^+ or NH_4^+ at737 80 °C after aging for 96 h (a: $\text{Fe}/\text{NH}_4^+ = 1$; b: $\text{Fe}/\text{NH}_4^+ = 0.1$; c: $\text{Fe}/\text{Cl}^- = 0.2$; d: $\text{Fe}/\text{K}^+ =$

738 0.1).



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740 **Fig. 11. Schematic diagram** of schwertmannite formation and transformation through741 direct Fe^{3+} hydrolysis under various geochemical conditions.

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4 1 **Electronic supplementary information**

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9 3 **Formation and transformation of schwertmannite through direct Fe³⁺ hydrolysis**
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11 4 **under various geochemical conditions**

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14 5 Hong Ying^a, Xionghan Feng^a, Mengqiang Zhu^b, Bruno Lanson^c, Fan Liu^a, Xiaoming
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16 6 Wang^{a,*}

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19 7 ^a Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze
20
21 8 River), Ministry of Agriculture, College of Resources and Environment, Huazhong
22
23 9 Agricultural University, Wuhan 430070, China

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25
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27 10 ^b Department of Ecosystem Science and Management, University of Wyoming,
28
29 11 Laramie, WY, 82071

30
31
32 12 ^c Univ. Grenoble Alpes, Univ. Savoie-Mont Blanc, CNRS, IRD, IFSTTAR, ISTERre,
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39 15 Supplementary data includes 1 table and 5 figures.

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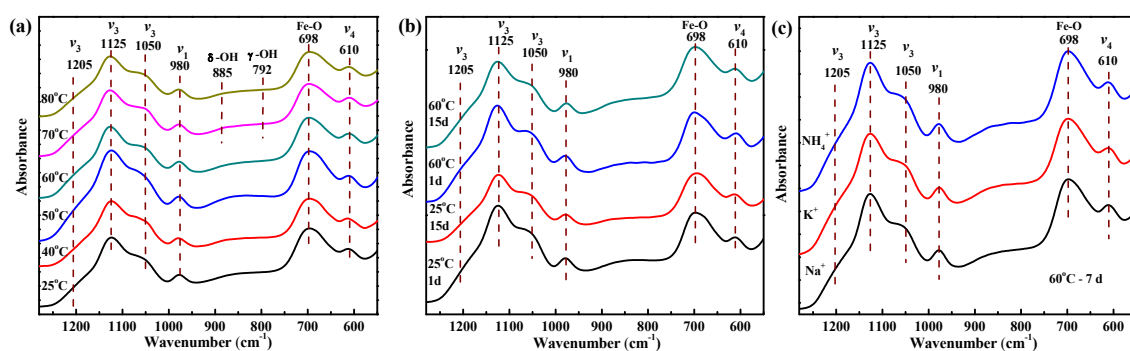
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49 19 Xiaoming Wang, Tel: +86 27 87280271; Fax: +86 27 87288618; E-mail:
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51 20 wangxm338@mail.hzau.edu.cn

21 **Table S1.** Experimental conditions on formation and transformation of schwertmannite
 22 through direct Fe³⁺ hydrolysis

Sample	Fe ³⁺ (mM)	SO ₄ ²⁻ (mM)	pH	Temperature	Co-existing ions (mM)	Dialysis time
(a) Schwertmannite formation through Fe³⁺ 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 Fe³⁺ 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) Fe³⁺ 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)	-

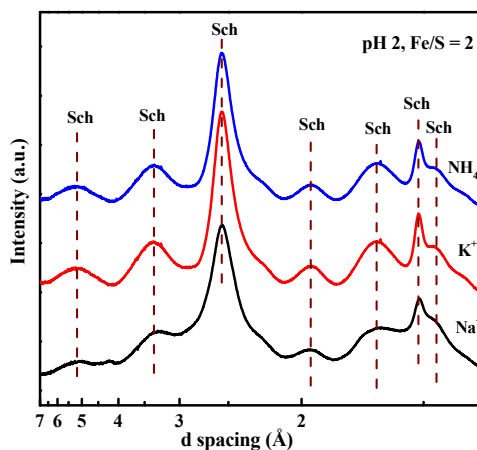
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Fig. S1. FTIR spectra of the products obtained from Fe³⁺ hydrolysis-dialysis at different Fe³⁺ hydrolysis temperatures followed by dialysis for 7 d (a), from Fe³⁺ hydrolysis at 25 °C and 60 °C followed by dialysis for 1 d and 15 d (b), and from Fe³⁺ hydrolysis at 60 °C in the presence of K⁺ or NH₄⁺ followed by dialysis for 7 d (c).

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Fig. S2. Synchrotron based XRD patterns of the products obtained from quick

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hydrolysis of Fe^{3+} and SO_4^{2-} (mixed directly) in the presence of K^+ or NH_4^+ ($\text{Fe}/\text{S} = 2$, Fe/K^+ or $\text{NH}_4^+ = 1$) at pH 2 and 25 °C (Sch = schwertmannite).

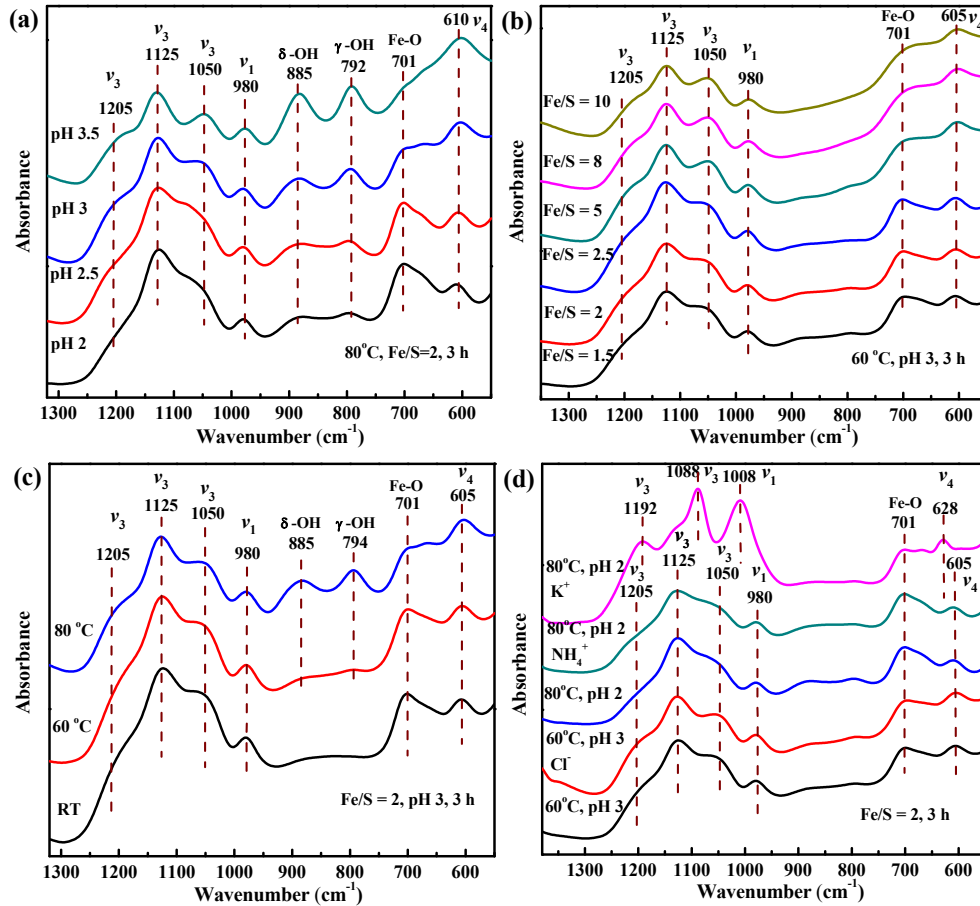
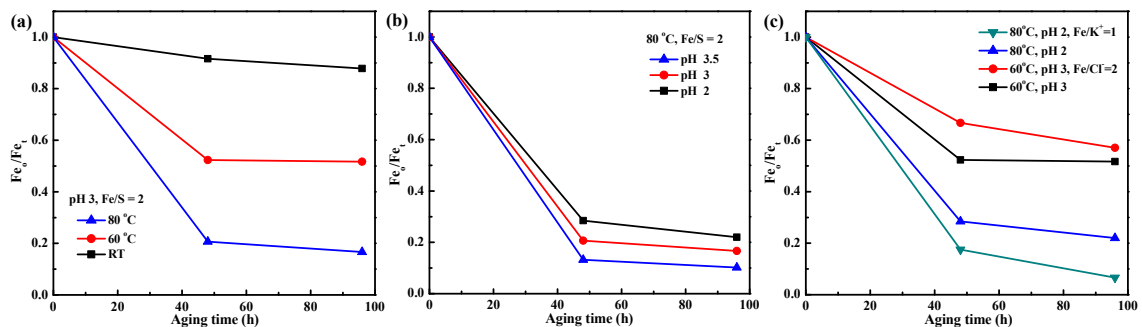
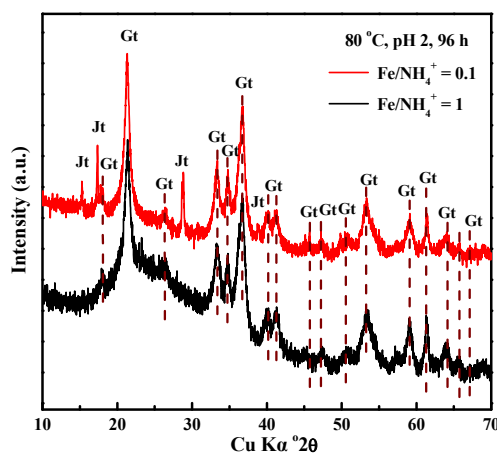


Fig. S3. FTIR spectra of the mineral phases obtained from quick hydrolysis of Fe^{3+} and SO_4^{2-} (mixed directly) aged for 3 h at different pHs (a), different Fe/S molar ratios (b), different aging temperatures (c) and in the presence of Cl^- , K^+ or NH_4^+ (d).



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42 **Fig. S4.** The transformation rate described as Fe_o/Fe_t of schwertmannite obtained from
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6 quick hydrolysis of Fe^{3+} and SO_4^{2-} (mixed directly) during aging at different
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8 temperatures (a), at different pHs (b) and in the presence of Cl^- or K^+ (c) (Fe_o : weak
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10 crystalline iron, dissolved by 0.2 M acidic ammonium oxalate; Fe_t : total iron, dissolved
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12 by 4 M HCl).
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49 **Fig. S5.** XRD patterns of the mineral phases obtained from quick hydrolysis of Fe^{3+} and
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51 SO_4^{2-} (mixed directly) in the presence of NH_4^+ ($Fe/NH_4^+ = 0.1$ or 1) at 80 °C and pH 2
after aging for 96 h (Gt = goethite, Jt = jarosite).
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