Anionic effect on nanostructure and morphology of bio-schwertmannite dynamically produced within cellular reproduction

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Abstract
Schwertmannite has been considered as the host mineral and potentially excellent adsorbent of contaminants from waters, and it has various morphologies of spheroid with pincushions, whiskers, hedge-hogs, and needles. In this work, using the (high-resolution transmission and field-emission scanning) electron microscopes, we studied nanostructure, morphological evolution, and difference in chemical composition for the produced schwertmannites in the cell-rich iron solutions. All analysis results showed within cellular 36-h reproduction period, the production of only schwertmannite was examined in iron solutions at the Cl⁻/SO₄²⁻ molar ratios of 0–10 and pH 3.0 ± 0.1. There were differences in two typical morphologies of “pincushions” (Cl⁻/SO₄²⁻ = 0 and 3) and “hedge-hogs” (Cl⁻/SO₄²⁻ = 6 and 10) for the schwertmannite nanostructures. And all final schwertmannite particles had the chemical formulas of Fe₈O₈(OH)₈x(SO₄)x(1.08 ≤ x ≤ 1.66), especially as Cl⁻/SO₄²⁻ = 0, the visible “pincushions” only being the outermost sections of the whole needles existing in a tightly spherical assemblage of schwertmannite. Moreover, the absence of ferrihydrite and goethite was determined in the nanodimension of these needles, though the initial Fe and SO₄²⁻ were 5600 and of 9600 mg/mL, respectively. It could be induced by the amounts and activities of aqueous Fe, SO₄²⁻, and Cl⁻ associated with cellular activities and mineral precipitation. This study will be useful for understanding the actual occurrence of iron oxyhydroxide nanostructure and better developing its potential environmental application.

Keywords
Sulfate, chloride, schwertmannite, cellular reproduction, biomineralization

Introduction
Schwertmannite is a poorly crystalline ferric oxyhydroxy-sulfate mineral, which commonly occurs in acid sulfate systems.¹⁻³ The key issues for schwertmannites, such as synthetic strategies, structure–property relationships, potential environmental applications, and related mechanisms, have been recently overviewed.⁴ It has been accepted that schwertmannites are effective scavengers⁵⁻⁸ and environmentally potential adsorbent materials of metals.
metalloys,\textsuperscript{9–13} rare earth elements,\textsuperscript{14} and fluoride.\textsuperscript{15} However, schwertmannites as an unstable phase will progressively transform into other stable iron mineral phases of jarosite and goethite, releasing an appreciable amount of acidities and bound trace metals, due to variation of pH and acid concentration,\textsuperscript{22,23} and the presence of aqueous Fe(II) and dissolved organic matter.\textsuperscript{16–20} On the other hand, the presence of phosphate at high loadings of 800 \(\mu\)moles/g can stabilize schwertmannite surface against dissolution.\textsuperscript{21} Also, as schwertmannites presented as a stable phase by inhibiting nucleation of goethite, their morphologies are hardly modified.\textsuperscript{22,23}

Obviously, environmental function and phase stability of schwertmannites are closely related to their crystal phases and specific structures, especially nanoscale particle structures.\textsuperscript{1–4} As we have known, nanoparticles, typically defined as solids less than 100 nm, can display various properties.\textsuperscript{24} Meanwhile, studies of iron (oxy)hydroxide nanoparticles, including schwertmannite, akaganéite, goethite, maghemite, magnetite, and hematite, have attracted enormous attention, due to their interesting properties and associated potential applications.\textsuperscript{24–27} Especially, their research have focused on the development of the novel synthesis methods. Schwertmannites have chemical formulas \(\left(\text{Fe}_x\text{O}_y\text{(OH)}_z\right)_{\text{k}(\text{SO}_4)_{\text{n}}/\text{H}_2\text{O}}\ 1 \leq x \leq 1.86\) with a Fe/S molar ratio range of 4.3–8.\textsuperscript{1–3} Generally, schwertmannites with various crystal structures and chemical formulas can display different morphologies of spheroids with nanoscale particles, such as pincushions, whiskers, hedge-hogs, and needles.\textsuperscript{28–33}

Therefore, the synthesis of schwertmannites and their compounds by chemical and biological methods have been systematically investigated to recognize their morphologies and nanostructures. Generally, schwertmannite needles (60–90 nm in length) can coalesce to form rounded aggregates (200–500 nm in diameter) in FeCl\(_3\) solutions with 7.8–20.8 \(\mu\)moles/L of sulfate at 60\(^\circ\)C.\textsuperscript{1} Another chemical schwertmannite (ball-and-whisker) can be prepared in \(\text{Fe}_2(\text{SO}_4)_{3}\) solutions at 85\(^\circ\)C.\textsuperscript{28} And schwertmannite nanocrystals morphologically resemble those of ferrihydrite and are proposed to be an intermediate phase in the ferrihydrite crystallization series, with their formation specially governed by ferric supersaturation.\textsuperscript{29} Recently, the detailed nanometric investigations on the whole nanoparticle structures of chemical schwertmannites have been conducted under different approaches.\textsuperscript{34} Also, schwertmannite@akaganéite with the core/shell nanostructure can be achieved from hydrochloric pickling waste liquor.\textsuperscript{35}

These documents are mainly related with the structure–property relationship of chemical schwertmannites. However, there is little information elaborated on the nanometric particle structure for bio-schwertmannite. In the past decade, though biosynthesis methods have been developed in our previous studies to produce microstructural schwertmannites at various cellular incubation times, which involved preparing in cell-rich ferrous solutions\textsuperscript{36,37} and bacterial cultures.\textsuperscript{38,39} Schwertmannites as the only phase with different sizes can bioform after 96-h reaction, when chloride and sulfate at various molar ratios are added into the solutions. Also, the presence of chloride seems to decrease sizes of the newly bioformed schwertmannite aggregates.\textsuperscript{36} But, except for schwertmannite phase, it is not testified whether there is an occurrence of other iron mineral phase in an initial period of cellular 36-h reproduction. Also, there is still a little document of morphological evolution of particles with various chemical formulas for these bio-schwertmannites. And it is also necessary to recognize influences of the factors (such as sulfate, Fe, and Cl\(^-\)/SO\(_4^{2-}\) molar ratios) on their morphological structures, especially exploring high-resolution transmission electron microscopy (HRTEM) morphology and nanostructure, when cellular 36-reproduction ends. These studies will be useful for understanding the actual occurrence of ferric oxyhydroxide nanostructures. In the work presented here, we mainly investigate and explore the nanostructures and evolved morphologies of the obtained iron mineral precipitates within cellular 36-h reproduction.

**Materials and methods**

**Experimental bacterium and cell suspension**

*Acidithiobacillus ferrooxidans* isolated from sewage sludge was grown in modified 9 K media.\textsuperscript{39} Bacterial cultures (5\% v/v) were inoculated into 9 K media with pH 2.5 and incubated at 28\(^\circ\)C for about 36 h with continuous aeration. After bacterial reproduction was completed, the cells were harvested by the reported method\textsuperscript{40} and then resuspended in distilled water prior to the formation experiments of iron minerals.

**Formation experiments of iron minerals under various Cl\(^-\)/SO\(_4^{2-}\) molar ratios**

According to results of preliminary experiments, the development of biogenic iron minerals were performed in triplicate with 270 mL of ferrous solutions involving 0.1 mole/L of Fe\(^{2+}\) as forms of FeCl\(_2\) and FeSO\(_4\) followed by the Cl\(^-\)/SO\(_4^{2-}\) molar ratios (see Table 1) as well as approximately 5.0 \(\times\) 10\(^7\) cells/mL of fresh cells in a 500-mL glass flask. The flasks were shaken in a horizontal shaker at 180 r/min and 28\(^\circ\)C. The contents of evaporated water from these flasks were replenished with distilled water by weight method.

During the experimental procedures, the samples were collected at given intervals, centrifuged at 12,000 r/min, and then filtered through a Whatman no. 4 filter paper to remove solid substances. The collected solutions were acidified to about pH 2.0 using 6 M HCl and stored at 4\(^\circ\)C for Fe\(^{2+}\) determination. In addition, the collected iron precipitates by filter paper were washed repeatedly with...
distilled water, then naturally dried, and finally analyzed and characterized.

Characterization and analytical methods

The pH values of the reaction solutions were determined using a pHS-3C model digital pH meter. Fe$^{2+}$ determination by a colorimetric procedure was performed using 1,10-phenanthroline, as described in standard methods, and percent Fe$^{2+}$ oxidation was calculated and expressed as the ratio of the oxidized Fe$^{2+}$ to initial Fe$^{2+}$ in reaction solutions. Sample morphologies were examined by a Hitachi S-4800 field emission-scanning electron microscope (FESEM, operated at 15.0 kV accelerating voltage under a high vacuum) and equipped with an energy-dispersive spectrometer (EDS), and by a Philips Tecnai-12 transmission electron microscope (TEM, the prepared samples were deposited on carbon-copper grids). Local morphologies were further observed by a multipurpose JEM-2100 with scanning transmission electron microscope (STEM) at atomic resolution function integrated in PC control system and an excellent LaB6 electron gun at 200 kV. The EDS analysis of samples was typically applied to quantitative identification of major elements with rough estimates of composition based on relative peak intensities. The powdered X-ray diffraction (XRD) was collected on a German Bruker AXS D8 Advance Model diffractometer with a Cu target at 40 kV and 200 mA. The Fourier transform infrared reflectance spectra were collected on a Nicolet 740 spectrometer at a resolution of 4 cm$^{-1}$ using a KBr beamsplitter, a DTGS detector with KBr window, and a sample shuttle for the transmittance measurements.

Results and discussion

Changes of pH value and Fe(II) oxidized percentage

Under various Cl$^{-}$/SO$_4^{2-}$ (R) molar ratios, the extents of Fe(II) bio-oxidation followed by the precipitate formation over two main growth phases (i.e. exponential phase of 0–16 h and stable phase of 16–36 h) of cellular reproduction are shown in Figure 1(a). After the exponential phase ended (at 16 h), their Fe(II) were mostly bio-oxidized and the percentage orderly were 90, 70, 56, and 47 (as R equal to 0, 3, 6, and 10). Within the stable phase of cellular reproduction, Table 1. Experimental conditions and elemental analysis for the obtained schwertmannites at 36 h (* as a reference).

| Systems | R = Cl$^{-}$/SO$_4^{2-}$ (mmole/L) | FeCl$_2$ | FeSO$_4$ | Cl$^-$ (wt%) | Fe/S (molar ratio) | Chemical formulas |
|---------|-----------------------------------|---------|----------|-------------|-----------------|------------------|
| R0      | 0                                 | 0       | 100      | 65.1        | 7.72            | 65.1 8O8(OH)4.68(SO$_4$)1.66 |
| R3      | 3                                 | 60      | 40       | 61.5        | 5.26            | 61.5 8O8(OH)5.6(SO$_4$)1.21 |
| R6      | 6                                 | 75      | 25       | 57.6        | 4.54            | 57.6 8O8(OH)5.8(SO$_4$)1.1 |
| R10     | 10                                | 83      | 17       | 58.8        | 4.53            | 58.8 8O8(OH)5.84(SO$_4$)1.08 |

*Ideal formula for schwertmannite

![Figure 1. Changes of (a) percent Fe$^{2+}$ oxidation and (b) the pH value in the iron solutions with the different Cl$^{-}$/SO$_4^{2-}$ (R) molar ratios.](image-url)
reproduction, the percentage of Fe(II) oxidized slowly increased to the final values of 99, 79, 63, and 54. The main reason for a difference in Fe(II) oxidized percentage was an increasing restrictive effect on the cellular activities following the enhancement of initially added chloride amounts.\textsuperscript{36,38} Also, at \( R = 0 \) and 3, the reaction mixtures were reddish brown, while at \( R = 6 \) and 10, those were yellowish orange. At the same time, solution pH values declined to their constant values nearing 1.7 from initially about 3.0 (Figure 1(b)). Obviously, the combined change results of the color, pH, and Fe(II) oxidized percentage of the mixtures showed that there were iron minerals dynamically forming in iron solutions following cellular reproduction.

Identification of schwertmannites

In the initial period of cellular reproduction, to testify what mineral phase forming in sulfate-containing systems (R0–R10), their iron precipitate products collected after cellular 1-h cultivation were selected as candidates for XRD and infrared (IR) determinations in this study. Their identification results are shown in Figure 2, the four specimens from systems R0–R10 were inferred to be schwertmannites with poor crystalline nature, according to some typical broad peaks (with \( d \) values of 5.09, 3.37, 2.56, 1.68, and 1.48 \( 	ext{Å} \)) in XRD patterns (Figure 2(a)). Also, the presence of the three common \( \text{SO}_4^{2-} \) absorption bands (at 1122 cm\(^{-1}\); \( v_3 \) (\( \text{SO}_4 \)); 977 cm\(^{-1}\); \( v_1 \) (\( \text{SO}_4 \)), and 610 cm\(^{-1}\); \( v_4 \) (\( \text{SO}_4 \))) for typical schwertmannite was observed in IR spectra (Figure 2(b)), and the other two absorption bands at 842 and 689 cm\(^{-1}\) were assigned to the Fe–O vibrational modes in schwertmannite.\textsuperscript{36} Therefore, it was testified after cellular 1-h cultivation that schwertmannite was only initial mineral phase produced in these systems (R0–R10).

Morphological evolution of schwertmannites

Since the similar morphology evolutions were determined for schwertmannites from systems R0 and R3 (R6 and R10), only two groups of images (Figure 3 for R0 and Figure 4 for R10) were provided for analysis and discussion hereinafter. Evolutions of field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) morphologies for schwertmannite from R0 are shown in Figure 3(a) and (b), respectively. Schwertmannite surfaces (images A–D) were initially lubricous (1–4 h) and then granulated (8–16 h) within the cellular exponential phase. Successively developing to cellular exponential phase (24–36 h), their surfaces were covered by “pincushions” (images E and F), and their spherical diameters (\( \mu \text{m} \)) gradually increased from approximately 0.4 to 0.8, and finally to approximately 1.2. Also, in TEM morphology of schwertmannite, the absence of “pincushions” in image T-A (1 h) was observed, while the obviously evolved “pincushions” mainly appeared in images T-E and T-F (24–36 h). Further, its final schwertmannite spheres (36 h) had a chemical formula of \( \text{Fe}_8\text{O}_8(\text{OH})_{6.68}(\text{SO}_4)_{1.66} \) and the Fe/S molar ratio was 4.82 (Table 1).

While for the final schwertmannite from another system (R10 with the highest \( \text{Cl}^-/\text{SO}_4^{2-} \) molar ratio of 10), there was the chemical formula of \( \text{Fe}_8\text{O}_8(\text{OH})_{5.48}(\text{SO}_4)_{1.08} \) with a Fe/S molar ratio of 7.42 (Table 1). Also, as shown in its independently homogeneous spheres with the granulated surfaces (images A and B) and then within 8–36 h of cellular reproduction, their morphologies evolved as “hedge-hogs” (images C–F), and their diameters (\( \mu \text{m} \)) gradually increased from approximately 0.2 to 0.4, and finally to approximately 0.6. Also, a TEM image (inset in F) for schwertmannite at 36 h presented the same “hedge-hog” morphology.

EDS data for the final schwertmannites are exhibited in Table 1. Their chemical formulas may be orderly expressed as \( \text{Fe}_8\text{O}_8(\text{OH})_{4.68}(\text{SO}_4)_{1.66}, \text{Fe}_8\text{O}_8(\text{OH})_{5.6}(\text{SO}_4)_{1.2}, \text{Fe}_8\text{O}_8(\text{OH})_{5.84}(\text{SO}_4)_{1.1}, \text{and Fe}_8\text{O}_8(\text{OH})_{5.84}(\text{SO}_4)_{1.08} \) with the corresponding Fe/S molar ratios of 4.82, 6.68, 7.25, and 7.42, according to the general chemical formula of schwertmannite \( \text{Fe}_8\text{O}_8(\text{OH})_{x-2x}(\text{SO}_4)_{2x}, 1 \leq x \leq 1.86 \) with a Fe/S mole ratio ranging in \( 4.3–8.0 \). Also, EDS data showed that within a shorter cellular cultivation period of 36 h, the absence of \( \text{Cl}^- \) was examined in all schwertmannite products.

Summarily, all characterization and analysis results consistently showed an initial period of cellular reproduction, the presence of schwertmannite as the only phase in sulfate-containing iron solutions with various \( \text{Cl}^-/\text{SO}_4^{2-} \) ratios. Indeed, it has been confirmed that the kinetic precipitation of environmental or laboratory schwertmannites can be accelerated by the relatively abundant species of Fe(III)–OH and...
Fe$^{3+}$–SO$_4$ in sulfate-rich media, but it can be inhibited by the presence of a certain amount of chloride ions. For instance, it is testified that Fe$^{2+}$, Fe$^{3+}$, and SO$_4^{2-}$ orderly being 1.68, 84, and 816 µg/mL in surface waters of acidic mining lake can facilitate the natural schwertmannite formation. Also, schwertmannite can be synthesized by hydrolyzing of 0.02 M FeCl$_3$ solutions containing 2130 µg/mL Cl$^-$ and 750–2000 µg/mL SO$_4^{2-}$ for 12 min at 60°C. In the present study, three Cl$^-$/SO$_4^{2-}$ containing systems (R3, R6, and R10) had Cl$^-$ ions at their concentrations ranging in 4260–5890 µg/mL and also had SO$_4^{2-}$ ions at a declined range of 3840–1630 µg/mL. It obviously favored the formation of pure schwertmannite, but particle sizes and structures could be influenced by the presence of chloride.

In addition, both FESEM observations for evolved schwertmannites and ED analysis for the final products combinedly indicated that the differences in structural morphologies were typical nanostructures of “pincushions” and “hedge-hogs” covering their spherical surfaces. This could be induced by the presence of various SO$_4^{2-}$, Cl$^-$, Fe$^{2+}$, and Cl$^-$/SO$_4^{2-}$ ratio in these solutions. And it was also elaborated that the morphologies of spheres (~0.5 µm) or typical “hedge-hogs” for schwertmannites were examined from the acidified coastal lowlands involving the higher concentrations of Fe$^{2+}$ (408 µg/mL, equal to 97% of total Fe), SO$_4^{2-}$ (3072 µg/mL), and Cl$^-$ (15265 µg/mL). Moreover, it has been confirmed that SO$_4^{2-}$ is presumably related to its higher charge and its ability to form inner-sphere complexes with structural Fe. This just is a reason

**Figure 3.** (a) FESEM and (b) TEM images for schwertmannite products from R0 system with R = 0. FESEM images A–F for the products orderly collected at 1, 4, 8, 16, 24, and 36 h. T-(A, E, or F) notes a TEM image for the same product. FESEM: field emission scanning electron microscope; TEM: transmission electron microscope.
for the difference between this study and previous work. In this work, the lower amounts of $SO_2$ were incorporated in structures of schwertmannites ($Fe_8O_8(OH)_{8-2x}(SO_4)_x$ with $1.08 \leq x \leq 1.66$) from systems $R10-R0$ at 36 h. While at 96 h, their schwertmannites had the formulas as $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ (1.09 $\leq x \leq 1.79$). Also, ED analysis data showed within the wholly cellular reproduction period of 36 h that the absence of $Cl^-$ was examined in all schwertmannites. Comparatively, it was inferred that $Cl^-$ ions could be only adsorbed by the schwertmannites produced at 96 h.

**Nanostructures and morphologies of schwertmannite pincushions**

It has been accepted that schwertmannites have sphere-with-“pincushions” morphology. Therefore, as shown in the HRTEM images and selected area electron diffraction (SEAD) patterns (Figure 5), we further explored their nanostructures and morphologies for the pincushions of schwertmannite spheroids obtained from $R0$ system at 36 h. Several bundles of independently pincushions (image A) resembled needles, and the outermost sections of these pincushions easily fractured (inset in A). Length of these needles approximately was equal to radius of their aggregated spheroid (image D). Also, the sizes of “pincushions” seemed to gradually become larger with the evolvement of spherical assemblage. It could be inferred that the visible “pincushions” were only the outermost sections of the whole needles and the sphere was a tight assemblage composed by schwertmannite needles. It was coincident with the results described by Loan et al. that pincushions (also called whiskers) seemed to radiate from the center of the spherical structure, rather than coated on an internal or core structure. The other HRTEM images (B and C) for the outer end and center sections of the needles (circled in A) displayed their unclear lattice fringes and spacing, respectively.

Figure 5 also displays SEAD results for the center sections of schwertmannite needles, their SEAD pattern (P-C) was composed of the eight discontinuous rings without bright dots (their $d$ at 1.48, 1.51, 1.68, 1.95, 2.28, 2.56, 3.37, and 5.09 Å), indicating that these needles were polycrystalline powder particles. It was consistent with the XRD result (Figure 6(a)) for the corresponding schwertmannite spheres. Its diffractogram and IR spectrum, as shown in Figure 6, and some typical schwertmannite diffractogram peaks ($d$) at 1.46, 1.51, 1.66, 1.95, 2.28, 2.55, 3.39, and 4.86 Å were seen. Apparently, the spectrum for this product from $R0$ system exhibited the bands at 842 and 689 cm$^{-1}$ being the vibrating modes of two O–H...SO$_4$ hydrogen bonds, as the representative characteristics of SO$_4$-containing schwertmannite. Further analyzing nanostructures of the outermost ends of the raw spherical assemblage composed of schwertmannite needles (circled in D), their HRTEM images (E and F) and the related SEAD patterns (P-E and P-F) revealed that the lattice fringes and spacings were about 0.51/0.44 (nm) and 1.95/2.28 (Å) in the zone axis orientations in the needles, respectively. Also, there were discontinuous rings distributed by many irregular bright dots for crystalline particles. This indicated that the outermost ends of the examined needles were polycrystalline powder particles, but some lattice planes had a good growth trend.
Summarily, there was still little evidence for goethite present in the outward sections of the present needles.

However, the chemical schwertmannite “hedge-hogs” and aggregates studied by Loan et al.\textsuperscript{29} and Hockridge et al.,\textsuperscript{30} and their results on the structure and crystal growth of the nanoscale needles showed that the nanodimension whiskers were outward from an electron-dense interior and contained the highly disordered and maghemite-like structural component present in ferrihydrite. Also, schwertmannite aggregates formed initially as spherical agglomerates of

\textbf{Figure 5.} HRTEM images (A–F) and SAED patterns for schwertmannite from R0 system at 36 h. P notes pattern, and P-C, P-E, and P-F orderly note the patterns for the correlative pincushions in their morphology images C, E, and F. Inset in A displays the fractured sections of needles (i.e. their outermost ends) and had the same scale mark as A image. HRTEM: high-resolution transmission electron microscope.
ferrihydrite crystallites and then began to grow characteristic needles on their surfaces. So, it was considered that the formation of these needles on schwertmannite aggregates could be the first stage in the phase transformation of schwertmannite to goethite. Comparatively, it was obvious in this study that ferrihydrite and goethite were unobserved in the nanodimension needles of schwertmannite aggregates produced in FeSO₄ solutions after cellular 36-h cultivation.

Analysis of possible mechanism for schwertmannite formation

Under the acid conditions (initial pH 3.0 ± 0.1) in this work, the consumption of H⁺ ions could be rapidly supplied by Fe³⁺ hydrolysis followed by schwertmannite precipitation and decrease of solution pH values. Especially, within the final period of cellular reproduction (16–36 h), only less than 13% of all oxidized Fe²⁺ was not completed, which favored Fe³⁺ hydrolysis and rapid generation of schwertmannite precipitates. Within this period, the requirement of sulfate ions is also an important factor for schwertmannite precipitation, therefore, there is the below reaction in competition with the hydrolysis reaction, and its formula is

\[
8\text{Fe}^{3+} + x\text{SO}_4^{2-} + (16 - 2x)\text{H}_2\text{O} \rightarrow \text{Fe}_8\text{O}_8(\text{OH})_{2-4}(\text{SO}_4)_x + (24 - 2x)\text{H}^+ \tag{1}
\]

in which the relative abundance of the Fe³⁺–OH and Fe³⁺–SO₄ species kinetically facilitated precipitation of four schwertmannites as Fe₈O₈(OH)₈–₂x(SO₄)ₓ (1.08 ≤ x ≤ 1.66) from the systems of R10–R0. Additionally, in this study, the higher amounts of SO₄²⁻ and aqueous Fe³⁺ ions in iron solutions induced the presence of only schwertmannite phase within cellular 36-h reproduction period.³⁶

Conclusions

All analysis results showed within cellular 36-h reproduction period, the production of only schwertmannite in 0.1 M of iron solutions initially with the Cl⁻/SO₄²⁻ molar ratios of 0–10. The differences in two typical morphologies of “pincushions” and “hedge-hogs” for the nanostructures in the schwertmannite-spheres (Fe₈O₈(OH)₈–₂x(SO₄)ₓ, 1.08 ≤ x ≤ 1.66) could be induced by the amounts and activities of aqueous Fe, SO₄²⁻, and Cl⁻ associated with cellular activities and mineral precipitation. In addition, the HRTEM and SEAD analysis results of two types of needles deduced the absence of ferrihydrite in sphere particles, and little evidence for the presence of goethite in needles under an insufficiently reducing condition, due to the acidic cell-rich iron solutions with initial pH 3.0 ± 0.1. This study will provide useful insight into the production of synthetic iron oxyhydroxide nanoparticles in technological settings.

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