On the crystal growth of nanoscale schwertmannite

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Abstract

Schwertmannite ($Fe_{16}O_{16}(OH)_{12}(SO_4)_2$), commonly found in acidic aqueous systems, forms rapidly into a "hedge-hog" morphology, where nano-dimension whiskers project outwards from an electron-dense interior. Schwertmannite whiskers were recently found to contain the highly-disordered and maghemite-like structural components present in ferrihydrite, and on this basis, schwertmannite was postulated to be an intermediate phase (in terms of crystallinity and kinetics of formation) to the least and most crystalline forms of ferrihydrite, 2- and 6-line, respectively. To test this hypothesis and help elucidate the schwertmannite growth mechanism, we reduced supersaturation (a function of pH and ferric concentration) during the crystallization of 2-line ferrihydrite from ferric sulfate liquors. Lower supersaturations resulted in schwertmannite formation, often in an admixture or possibly nucleated on 2-line ferrihydrite aggregates. Alternate experiments performed in the presence of arsenic (as a crystal growth modifier) produced X-ray diffraction (XRD) patterns consistent with admixed ferrihydrite and schwertmannite, but with a morphology where aligned ferrihydrite nanoparticles appeared to approximate the structure of schwertmannite whiskers. We postulate that as similar structural components constitute 2-line ferrihydrite and schwertmannite, but are only minor components in 6-line ferrihydrite, the proportion of each component (with the maghemite-like phase dominating) permits the specific alignment and growth of the intriguing schwertmannite morphology.

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1. Introduction

Schwertmannite ($Fe_{16}O_{16}(OH)_{12}(SO_4)_2$) is a nanoscale and poorly crystalline iron oxyhydroxysulfate mineral found in acidic water systems, acid mine drainage and mineral processing wastes. Schwertmannite is known to form rapidly (within minutes) into a single identifiable and consistent, but complex morphology (Figure 1), described as "hedge-hog". Fine needles or whiskers (2-10 nm in width; 60-100 nm in length) project outwards from an electron-dense interior, forming rounded aggregates 200-500 nm in diameter [1]. From a crystal growth point of view, the nano-dimension morphology of schwertmannite is intriguing. By electron nanodiffraction [1], schwertmannite has recently been found to share structural-likeness with ferrihydrite ($5Fe_2O_3.9H_2O$), a ubiquitous and natural nanomaterial. Ferrihydrite is the mineral of choice for storage and transport of iron (as solid phase) in the human body [2]. The nomenclature 'ferrihydrite' actually refers to a range of minerals, variant in crystallinity, size and structure; the number of reflections in an XRD pattern provides the basis for identification, nominally as 2- or 6-line ferrihydrite [3]. Fast rates of crystallization produce the poorly-ordered 2-line ferrihydrite, with slower rates forming the more crystalline 6-line ferrihydrite [4]. Both these phases consist of several structural components. A mixture of cubic (maghemite-like), hexagonal and highly-disordered structural components are present in 2-line ferrihydrite, but these occur less commonly in 6-line ferrihydrite, where an alternate hexagonal component dominates [3]. Schwertmannite whiskers have also been found to contain the highly-disordered and maghemite-like structural components [1], and on this basis schwertmannite was postulated to be an intermediate phase (in terms of crystallinity) to 2- and 6-line ferrihydrite. To test this hypothesis we took three different paths. Firstly, we reduced supersaturation (a function of pH and ferric concentration) during the crystallization of 2-line ferrihydrite from ferric sulfate liquors. Then we performed experiments in the presence of arsenic (as a crystal growth modifier). Finally, we have performed some 'preliminary' time-resolved Transmission Electron Microscopy (TEM) experiments looking at the growth and formation of schwertmannite aggregates.

2. Experimental

The methods of characterisation and elemental analyses are detailed in previous publications [1,5]. To determine the effect of supersaturation on 2-line ferrihydrite formation, solutions of 100 ml of Fe(III) [ranging from 5.2-0.7 g l^{-1} as $Fe_2(SO_4)_3.xH_2O$, dissolved in MillQ^{TM} water] were acidified to pH 1.5 with concentrated H_2SO_4 (to avoid nucleation on heating). These were placed in 250 ml Nalgene^{TM} bottles and equilibrated at 85°C in a water bath. A pre-determined concentration of NaOH (as a minimal volume 6 ± 2 ml) was added with one addition to neutralise to the desired pH. The samples were placed in a mechanical bottle roller/water bath at 85°C for 5 hours, which is conducive to gentle mixing. On completion, the solids were filtered through 0.45 μm Gelman Supor^{TM} membranes, washed with MillQ^{TM} water, and dried for 24 hours at 65°C. The experiments involving precipitation in the presence of arsenic are detailed in a previous publication [5], where the required amount of arsenic (at a Fe:As molar ratio of 12) was added to the initial solution as sodium arsenate.

3. Results

3.1 Effect of supersaturation on 2-line ferrihydrite formation

Schwertmann et al. [4] demonstrated the precipitation of ferrihydrite and its more crystalline analogues to be governed by crystallization kinetics, rather than any other factor (i.e. thermodynamics). Although the ferrihydrite precipitation mechanism is dominated by fast nucleation, control of the rate permits the formation of ferrihydrite with a range of structural ordering and sizes. The ferrihydrite nucleation rate is created by very high supersaturations, due to the very low equilibrium solubility of iron and hence ferrihydrite, which at a fixed temperature is dictated by pH. Supersaturation is generally expressed as the dimensionless ratio $S = c/c^*$, where c is the concentration of the solute and c^* is the equilibrium solubility of the solute. Measurement of the equilibrium solubility of ferrihydrite is experimentally challenging; ferrihydrite primary particles have a diameter of 5 nm, can pass through conventional filter papers and skew analyses towards artificially high iron concentrations [3].

Hence, data over an entire pH range at 85 °C is not available, but also due to the propensity for ferrihydrite to transform to hematite during the long equilibration times (200 hours) required. For the purpose of this study, the supersaturation ratio was not estimated, but is defined by the Fe(III) concentration at a particular pH, considering that at pH ~ 4 the ferric concentration is almost negligible [3].

At a fixed pH (3.5) the effect of the initial Fe(III) concentration and hence supersaturation on the crystal structure of ferrihydrite is shown in Figure 2. XRD patterns of these experiments demonstrate that 2-line ferrihydrite was not discretely formed. It appears that intermediate structures between 2- and 6-line ferrihydrite were precipitated. These XRD patterns indicate higher supersaturations to favour the formation of 2-line ferrihydrite, but as the supersaturation is reduced these reflections become more representative of schwertmannite admixed with 2-line ferrihydrite. This is exhibited in the alternate symmetry and relative intensity of the major ferrihydrite reflection (~ 41° 2-theta); the 2nd major ferrihydrite reflection (~ 74° 2-theta) appearing to split into two separate reflections (alternate intensity ratio to 6-line ferrihydrite); and, the weak reflections (45-70° 2-theta) being more similar in intensity and position to schwertmannite than 6-line ferrihydrite. It should be noted that a further decrease of the ferric concentration resulted in the crystallization of small proportions of goethite and hematite.

TEM and selected area electron diffraction (SAED) analyses were consistent with XRD interpretations. In all samples primary ferrihydrite particles were not larger than 4 nm (1.6-3.8 nm), with most being smaller than 3 nm (Figure 1). These ferrihydrite particle sizes are intermediate to those commonly observed for 6-line ferrihydrite and 2-line ferrihydrite [3], and indicate that both particle size and crystallinity increased at lower supersaturations. TEM analysis of the 0.7 g l^{-1} sample suggested the increased XRD reflection symmetry was due to schwertmannite-like morphologies co-existing with ferrihydrite aggregates (Figure 1). The typical *hedge-hog* morphology of schwertmannite was not present (see Figure 1a), but

schwertmannite-like whiskers appeared to coat or possibly have nucleated on the surface of ferrihydrite aggregates. SAED analysis did not confirm the presence of schwertmannite, as ring intensities were too diffuse to resolve in comparison to the major ferrihydrite bands. If schwertmannite whiskers coat ferrihydrite aggregates, then the proportion of each phase can be modelled mathematically. Various levels of ferrihydrite and schwertmannite XRD patterns were added and compared to that of the 0.7 g l^{-1} sample (Figure 3). Figure 3 demonstrates that if present as a mixture, the sample would contain as much as 25% schwertmannite.

The effect of pH on supersaturation and 2-line ferrihydrite formation was less obvious in the 0.7 g l^{-1} samples, only having an observable effect at lower pH, which induced goethite formation. In the higher pH 0.7 g l^{-1} samples, all reflection positions and symmetry were consistent, being schwertmannite-like.

3.2 Effect of Arsenic

In a previous study [5] we showed that even in the presence of arsenic, schwertmannite-like crystal structures form at lower supersaturations (Figure 4). Arsenic was not observed to alter the effect of supersaturation on structural order, however, elemental analyses of the solids showed the ratio of iron to arsenic in all samples to be similar [5]. Changes in the degree of crystallinity in these samples were therefore due to the change in the driving force for precipitation (i.e. supersaturation), and not incorporation as arsenic adsorbs on ferrihydrite surfaces. At 0.7 g l^{-1} XRD patterns were again consistent with admixed ferrihydrite and schwertmannite. However, in TEM analyses the schwertmannite aggregates did not consist of whiskers, but rather were composed of individual ferrihydrite crystallites of ~ 5 nm diameter aligned to form irregular whiskers (Figure 5). Although the morphology closely resembled schwertmannite, selected area electron diffraction patterns of these aggregates gave only the two diffuse rings characteristic of 2-line ferrihydrite; surprising, given that the powder XRD pattern of this sample showed clear signs of reflections attributable to schwertmannite. Previously we suggested that these aggregates represented some form of precursor to the

typical schwertmannite morphology [5], however, it is more likely that the aligned crystals are terminated with adsorbed arsenic blocking complete whisker formation.

3.3 Time-resolved schwertmannite growth: Preliminary results

Using the Loan et al. [1] schwertmannite formation method, a colloidal precipitate was found to form between 5 and 10 minutes, which completely settled (i.e. non-colloidal) after 1 hour. The settled precipitate, and that formed after 15 minutes were found by XRD analyses to be schwertmannite. However, between 1 and 5 hours the liquor reverted to a colloidal state, indicating a new nucleation and precipitation event, corresponding to the formation of goethite. Thus, goethite forms from schwertmannite via a dissolution re-precipitation mechanism, rather than by structural re-arrangement, or gradual structural ordering of the schwertmannite crystal lattice [6]. To further elucidate the schwertmannite growth mechanism, samples taken from 2 to 60 minutes during schwertmannite formation, were analysed by TEM, which will be documented in a subsequent publication [6]. The sample began as a mixture of non-structured amorphous material (like paint thrown on canvas), which appeared to coalesce very rapidly by 5 minutes into dense balls made up of very small particles. These gradually decreased in size, where whiskers started to appear on the surface. However, whiskers were at first short and broad (like triangles), but gradually became thin and increased in length, including a decrease in ball density [6]. More structural analyses are underway to determine what occurs between 2 and 15 minutes during schwertmannite formation. This will help to ascertain if a structural change occurs, and determine if schwertmannite forms *via* a self-assembly process, or *via* nucleation on the surface of an alternate material.

4. Discussion

At constant pH the crystal structure of 2-line ferrihydrite can be altered via supersaturation control, where lower ferric concentrations increase crystallinity. By reducing the driving force for precipitation (i.e. pH and Fe^{3+}) in ferric sulfate media, this results in the formation of

schwertmannite, often admixed with ferrihydrite. Such a reduction in supersaturation is more likely to promote the formation of alternate ferrihydrite structural component. A feasible possibility, as schwertmannite and both 2- and 6-line ferrihydrite contain a mixture of closely related structural components [1,2]. 6-line ferrihydrite was not produced in these experiments, which is contrary to the observations of Schwertmann et al. [4]. This may be due to the ferric sulfate media impacting on species formation. The dimer ($Fe_2(OH)_2^{4+}$) is the precursor to 6-line ferrihydrite formation [3,4], and has also been found to form in highly concentrated sulfate solutions, but associated with sulfate, forming a $Fe_2(OH)_2.(SO_4)_x^{4-2x}$ sulfato dimer species [4]. This may help explain why schwertmannite will form in preference to 6-line ferrihydrite in lower supersaturation sulfate solutions.

The experiments involving crystallization in the presence of arsenic provide the most interesting insight. On the basis of previous As-ferrihydrite studies ([5] and refs. therein) it can be assumed that the adsorption of arsenic on ferrihydrite nanoparticles blocks the complete alignment and formation of schwertmannite whiskers, which occurred in its absence. Our preliminary time-resolved TEM studies [6] also suggest that the initial triangular schwertmannite whiskers grow and elongate, involving a reduction in the volume of the precursor 'ball-like' structure. In light of these results, and as 2-line ferrihydrite and schwertmannite are composed of similar structural components [1,2], we propose the following hypothesis. For schwertmannite formation the maghemite-like structural component must dominate. Hence, when this occurs at low supersaturations, it promotes the alignment, self-assembly and growth of schwertmannite whiskers.

5. Conclusion

Our studies demonstrate that in ferric sulfate media schwertmannite is an intermediate phase in the ferrihydrite crystallinity and crystallization series, specifically governed by supersaturation. Lower supersaturations result in the formation of schwertmannite, often in an admixture or nucleated on 2-line ferrihydrite aggregates. Our studies suggest that controlling

supersaturation dictates the proportion of each ferrihydrite/schwertmannite structural component. Alternate experiments performed in the presence of arsenic (as a crystal growth modifier) produced XRD patterns consistent with admixed ferrihydrite and schwertmannite, but with a morphology intermediate to ferrihydrite and schwertmannite. Whiskers did not radiate out from an electron-dense interior; the morphology was more consistent with nanoparticles of ferrihydrite aligning to approximate the bulk structure of schwertmannite. This is thought to be immature schwertmannite, where crystals are terminated with arsenic, which blocks complete whisker formation.

We postulate that as similar structural components constitute 2-line ferrihydrite and schwertmannite, but are only minor components in 6-line ferrihydrite, the proportion of each component (with the maghemite-like phase dominating) must permit the specific alignment and self-assembly and growth of the intriguing schwertmannite morphology.

6. Acknowledgements

7. References

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Figure captions

Figure 1: a) TEM image of typical schwertmannite aggregates; b) TEM image of a ferrihydrite aggregate formed from an initial Fe(III) concentration of 5.2 g l^{-1} and at pH 3.5 (scale bar is 20 nm); c) TEM image of aggregates formed from an initial Fe(III) concentration of 0.7 g l^{-1} and pH 3.5 (scale bar is 0.5 µm).

Figure 2: The effect of reducing supersaturation at pH 3.5 on the XRD patterns (crystal structure) of ferrihydrite, producing intermediate structures between 2- and 6-line ferrihydrite. The major 2-line ferrihydrite reflections are indicated by the dotted lines.

Figure 3: Mathematical proportional mix of ferrihydrite and schwertmannite XRD patterns demonstrating that the sample of initial ferric concentration 0.7 g l^{-1} may contain as much as 25% of schwertmannite. a) 5.2 g l^{-1} sample; b) 0.7 g l^{-1} sample; c) 1: 4 Mixture; d) 1: 3 Mixture; e) 1: 2 Mixture; f) 1: 1 Mixture; g) schwertmannite.

Figure 4: Powder XRD patterns of arsenic-ferrihydrite composites precipitated from a Fe^{3+} solution at various concentrations. In each case the pH was 5.5 and the Fe: As molar ratio was 12.

Figure 5: TEM images of ferrihydrite precipitated at low supersaturation (corresponding to the bottom XRD pattern in Figure 4); a) A group of large spherical aggregates with schwertmannite-like morphology; b and c) Higher magnification images of these aggregates showing the "whiskers" composed of individual ferrihydrite crystallites ~ 5nm in diameter.
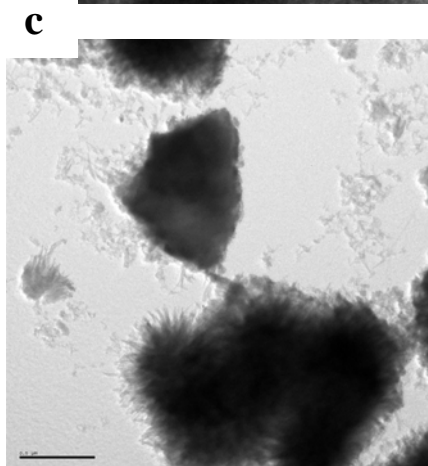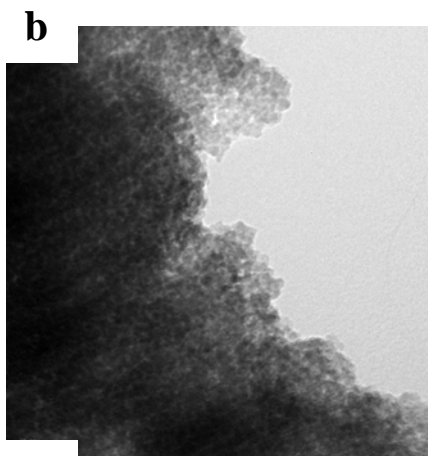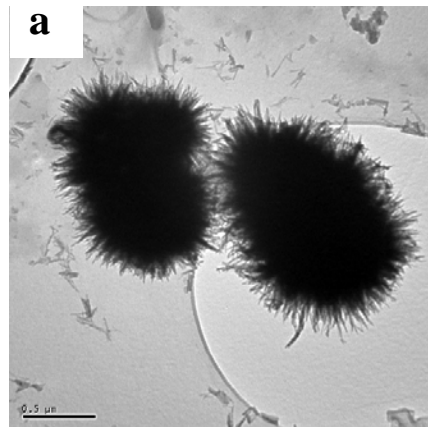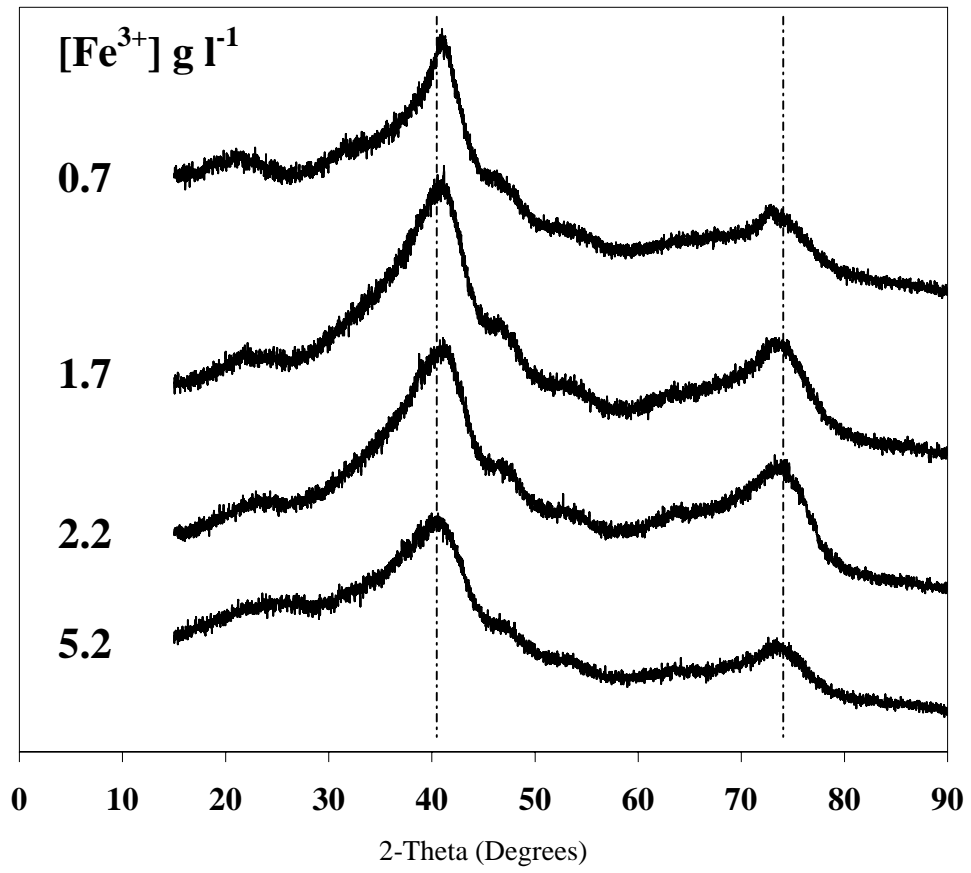
Figure 1

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