

LETTER

The effect of zinc sulfide on phase transformations of ferrihydrite

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ABSTRACT

The addition of ZnS particles to suspensions of ferrihydrite promotes the formation of the more crystalline phases goethite [ $\alpha$ -FeO(OH)] and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) at pH ~ 2–3 and 85 °C. This previously undocumented effect appears to arise from surface-mediated reduction of Fe<sup>3+</sup> species to Fe<sup>2+</sup> with associated dissolution of ZnS.

INTRODUCTION

The hydrolysis of Fe<sup>3+</sup> and Fe<sup>2+</sup> ions in solution to yield iron oxides and oxyhydroxides is sensitive to various reaction conditions, and the control of such reactions is of great importance in the synthesis of iron oxides with specific particle properties for applications in advanced material technologies (Cornell and Schwertmann 2003). It is also of relevance to understanding the mechanisms of iron oxide formation in soils, biomineralization, and hydrometallurgical processing industries, where iron oxides often must be removed from process streams as an unwanted byproduct. Formation of iron oxides in soils is sensitive to several pedoenvironmental factors including temperature, soil hydrology, pH, the presence of dissolved ions, and the nature of other minerals present in the soil. The effects of such factors on the precipitation kinetics and product morphology of iron oxide and oxyhydroxide phases under laboratory conditions can thus provide useful models for the pedogenesis of iron minerals in relevant soil environments (Cornell and Schwertmann 2003).

The first phase to precipitate in hydrolysis of iron is usually ferrihydrite—a poorly crystalline oxide that is given the nominal formula 5Fe<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O. Ferrihydrite is metastable, and under the right conditions it will transform to more crystalline and thermodynamically more stable phases, such as goethite [ $\alpha$ -FeO(OH)] and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The effect of pH on the formation of goethite and hematite from ferrihydrite is well documented. As a means to understanding the formation of goethite and hematite in soils, Schwertmann and Murad (1983) measured the relative amounts of these two phases formed at ambient temperature and pH ranging from 2.5 to 12, with reaction times of up to 3 years. They found that hematite formation is generally promoted at pH near neutrality, and at high temperatures, whereas goethite is the more stable phase at acidic pH (roughly pH 2 to 5) and at moderate temperatures (Schwertmann and Murad 1983; Schwertmann et al. 1999).

Several studies have investigated the effects of organic ligands on the products of Fe<sup>3+</sup> hydrolysis (Schwertmann 1969;

Cornell and Schwertmann 1979; Cornell 1985; Cornell and Schneider 1989; Reeves and Mann 1991; Jones et al. 2003), but so far none has examined the influence of sulfides as solid-phase additives for iron oxide formation.

This paper describes the effect of addition of sphalerite (ZnS) particles to an Fe<sup>3+</sup> sulfate system, at a pH where the transformation from ferrihydrite to goethite is normally very slow and considerably favored over hematite formation. The results have important implications for the understanding of possible mechanisms of iron oxide precipitation in soils and acidic mine drainage environments, and provide insight into potential means of controlling the formation of iron oxide phases in mineral processing streams.

EXPERIMENTAL PROCEDURE

The transformation of ferrihydrite under the standard conditions of our batch experiments was first investigated in the absence of any ZnS, at three different pH values (1.9, 2.86, and 3.5). The purpose of these experiments was to determine which phases formed at each solution pH, and to assess the crystallinity of those phases after a 5 hour reaction time at a fixed temperature of 85 °C. In these experiments, Fe<sup>3+</sup> sulfate solutions (300 mL, 0.25 or 0.16 mol/L Fe<sup>3+</sup>) were prepared in a batch reactor and warmed to 85 °C with agitation provided by an overhead stirrer. The solution was then neutralized to the desired pH by addition of a small volume (~10–15 mL) of 10 mol/L NaOH solution. The resulting 2-line ferrihydrite suspension was then kept at 85 °C, with stirring, for a period of 5 hours, while the pH was maintained via drop-wise additions of dilute H<sub>2</sub>SO<sub>4</sub> or NaOH solutions when required. The iron oxide precipitate was then collected by filtration, washed with de-ionized water and dried in air at 55 °C. Filtrates were retained for inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis.

The effects of ZnS on the transformation of ferrihydrite were investigated in a set of experiments at pH 3.5, where the only variation to the above method was the addition of a specific concentration of ZnS powder to the reaction mixture immediately before neutralization with NaOH. ZnS was added at concentrations of 0.5, 1.0, and 10.0 g/L. The ZnS powder was supplied by Pasmenco Ltd., and was ground and sieved to less than 63  $\mu$ m before use. Its purity was confirmed by XRD analysis. In one experiment, with 1.0 g/L ZnS added, the reaction mixture was sampled at regular intervals over the 5 hours of the experiment, but in other experiments only the final reaction products were collected.

Powder X-ray diffraction patterns of the precipitates were recorded with a Phillips X'pert X-ray Analytical Powder Diffractometer using CoK $\alpha$  radiation. Total iron and zinc concentrations in filtrate solutions were determined by ICP-AES analysis. The Fe<sup>2+</sup> concentration was determined by titration with potassium dichromate. Transmission electron micrographs (TEM) were recorded with a JEOL 2011 TEM operating at 200 kV. The samples were dispersed in de-ionized water with the aid of ultra-sonication, then cast and dried onto a conventional holey carbon-coated copper grid.

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## RESULTS AND DISCUSSION

By contrasting the results of the batch precipitation experiments performed both in the presence of added ZnS and in its absence we found that the product phases and the degree of crystallinity of the products are influenced by both the solution pH and the concentration of added ZnS. The first set of experiments investigated the effects of varying pH in the range 1.9 to 3.5 and as expected (Cornell and Schwertmann 2003), the final product phase in this pH range was goethite, with progressively more of this phase being formed as the pH was decreased. This difference in reaction product is demonstrated by the series of XRD patterns presented in Figure 1. At pH 3.50, the product displays the characteristic broad reflections of 2-line ferrihydrite (Schwertmann et al. 1999). At lower pH, however, the pattern begins to resemble more closely that of goethite, although it is clear from the broad reflections that the material is still poorly crystalline. As pH was decreased to 2.86 and 1.9 in separate experiments, we observed increasing crystallinity in the goethite product. We infer that the product obtained at pH 1.9 does, however, still contain some 2-line ferrihydrite, which can be identified from the XRD pattern by background modeling (Loan et al. 2002).

In Figure 2 we show the XRD patterns of hydrolysis products obtained after five hours at pH 3.5, with increasing amounts of ZnS added to ferrihydrite suspensions prepared in the same manner as those shown in Figure 1.

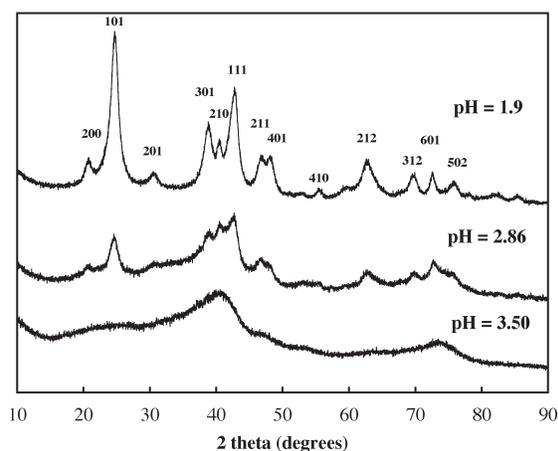
The XRD pattern of the product precipitated in the absence of any ZnS displays the broad, low-intensity reflections characteristic of 2-line ferrihydrite, the same as seen in Figure 1. At pH 3.5, a reaction time of 5 hours is insufficient for any detectable amount of ferrihydrite to convert to a more stable iron oxide. The sharper peaks (marked with an asterisk) in the 0 g/L ZnS pattern are due to the presence of a small amount of residual sodium sulfate arising from the background electrolyte. As the concentration of ZnS particles was increased from 0 to 1 g/L and

10 g/L, we observed significant changes in the mineralogy and crystallinity of the precipitation products.

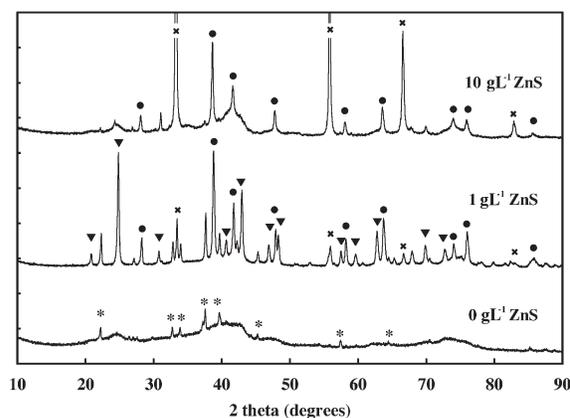
When 1 g/L ZnS was added to the system, we obtained a crystalline product with reflections indicative of goethite as the major phase precipitated, but also containing hematite in significant quantities. The sharpness of the goethite peaks in this pattern suggests a product with considerably greater crystallinity than any of the precipitation products obtained in the absence of ZnS (Fig. 1). The reaction products were sampled at regular time intervals during the 1 g/L ZnS experiment, and XRD patterns of the solids revealed that 2-line ferrihydrite was the first phase precipitated, with goethite reflections becoming evident in the XRD patterns after about 40 minutes. Hematite peaks were not clearly discernable in the patterns until 2 hours after neutralization.

In the experiment containing ZnS at a level of 10 g/L, we found that hematite was the most significant product phase in the final precipitate. It should be noted, however, that in all cases ferrihydrite was still present, as evidenced by the difficulty in filtering and washing of the products, and the broad reflections observed in background modeling of the XRD patterns<sup>1</sup> (Loan et al. 2002). Therefore the phase transformation of ferrihydrite is not complete under the conditions we have in this study. Nonetheless, the effect of ZnS is striking in its tendency to promote the transformation of ferrihydrite, and in the crystalline nature

<sup>1</sup> The broad reflections of 2-line ferrihydrite can often be masked in XRD patterns containing a mixture of other crystalline phases. The techniques for identifying the ferrihydrite phase in such cases are thoroughly described in Loan et al. (2002).



**FIGURE 1.** Powder XRD patterns of iron oxyhydroxide samples precipitated from a 0.16 mol/L  $\text{Fe}^{3+}$  solution in the absence of ZnS and aged at 85 °C for 5 hrs. The formation of poorly crystalline goethite becomes more evident in samples prepared at lower pH. Goethite reflections are indexed in the diffractogram of the product obtained at pH = 1.9.

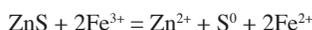


**FIGURE 2.** Powder XRD patterns showing the effect of adding increasing amounts of ZnS to ferrihydrite suspensions aged at 85 °C for 5 hrs. The ferrihydrite suspensions were obtained by neutralization of a 0.25 mol/L solution of  $\text{Fe}^{3+}$  sulfate to pH 3.5. Note that experimental conditions for the lower diffractogram in this figure were essentially identical to those for the lower diffractogram in Figure 1. Reflections of some of the phases observed are marked with symbols as follows: triangle = goethite ( $\alpha\text{-FeO}(\text{OH})$ ); circle = hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ); crosses = sphalerite (ZnS); and asterisk =  $\text{Na}_2\text{SO}_4$  (background electrolyte).

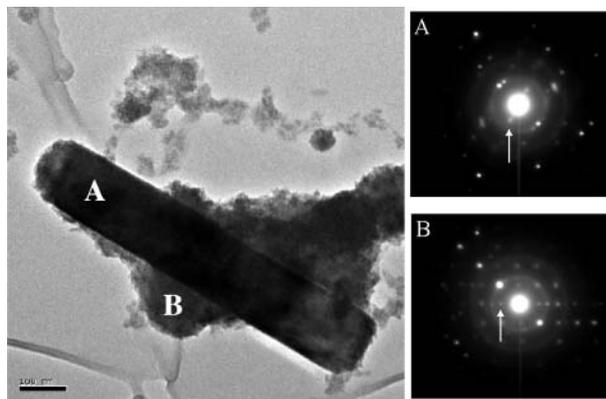
of the goethite and hematite products.

The morphology of the crystalline iron oxide phases is shown in the TEM micrograph in Figure 3, which shows the mixed hematite/goethite/ferrihydrate product obtained by addition of 1 g/L ZnS. The large acicular crystal labeled "A" is typical of the goethite particles observed in the sample. These particles were on the order of hundreds of nanometers in length and did not appear to be comprised of smaller crystallites, as is often the case with goethite (Cornell and Giovanoli 1986). Indeed, their morphology seems to have much in common with that of goethite formed in basic systems at high temperature and/or after long ageing times, rather than with the poorly crystalline forms usually precipitated from acid media (Schwertmann et al. 1985; Cornell and Schwertmann 2003). The hematite particles, of which an example is labeled "B" in Figure 3, appear as dense aggregates, and seem to be closely associated with 2-line ferrihydrate. This observation is consistent with the recently described mechanism of hematite formation involving solution-mediated formation of hematite nuclei within 2-line ferrihydrate aggregates (Schwertmann et al. 1999; Schwertmann and Cornell 2000).

To investigate the soluble species present during the ageing process, we sampled the reaction mixtures and analyzed the filtered solutions for  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$ . The results confirmed that ZnS dissolves readily under the reaction conditions employed in our experiments. One would expect that this dissolution process involves a redox couple comprising simultaneous reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  as has been proposed for  $\text{Fe}^{3+}$  ion leaching of sphalerite (Crundwell 1987).



Concentrations of dissolved zinc correlated well with levels of added ZnS, but very little  $\text{Fe}^{2+}$  was detected in the reaction solutions, with the exception of the 10 g/L ZnS experiment, where



**FIGURE 3.** TEM micrograph (scale bar = 100 nm) showing typical products of ferrihydrate transformation in the presence of 1 g/L ZnS. A selected area electron diffraction (SAED) pattern for crystal A is shown at top right with the 101 reflection of goethite at 0.41 nm marked with an arrow. In the same way, the dense aggregate B was found to be hematite. Its SAED pattern is shown at lower right, and the hematite 012 reflection (0.35 nm) is marked with an arrow. The remaining aggregated nanoparticulate material is 2-line ferrihydrate as evidenced by the diffuse rings in both SAED patterns.

$[\text{Fe}^{2+}]$  was found to be about 0.014 mol/L. Given the very low total dissolved iron concentration after ferrihydrate precipitation, it is perhaps not surprising that  $\text{Fe}^{2+}$  was not detected in systems with lower ZnS loading, and it is also likely that any  $\text{Fe}^{2+}$  ion so formed would be rapidly re-oxidized in the bulk solution, although it may well be more stable when formed within ferrihydrate aggregates. We have investigated the effects of  $\text{Zn}^{2+}$  ion (as zinc sulfate) on the transformations of ferrihydrate under similar conditions to those studied here, and found very little observable effect. This is perhaps not surprising given that many other studies examining the effects of cationic species on ferrihydrate transformation have found an inhibitory effect on transformation kinetics (Cornell and Schwertmann 2003), and thus we are led to suspect that the promotion of goethite and hematite formation owes more to the presence of a small amount of  $\text{Fe}^{2+}$  ion in the system than to the presence of dissolved  $\text{Zn}^{2+}$  ion.

Cornell and Schneider (1989) found that cysteine can promote transformation of ferrihydrate to goethite by acting as a reductant, through a mechanism involving adsorption of cysteine, followed by reduction of surface  $\text{Fe}^{3+}$  on ferrihydrate, and then desorption of a cysteine radical. It is reasonable therefore, to propose that ZnS might play a similar role, but in this case, the ferrihydrate nanoparticles adsorb onto the ZnS surface, allowing the oxidative dissolution of ZnS to couple with reduction of  $\text{Fe}^{3+}$  on the ferrihydrate surface. Oxidative dissolution of ZnS by  $\text{Fe}^{3+}$  has been well characterized in sulfate solutions under conditions similar to those employed in our experiments (Crundwell 1987; Markus et al. 2004).

The formation of goethite and hematite should therefore be a matter of the chemical environment (pH and temperature) during the re-oxidation of  $\text{Fe}^{2+}$ . It is well established that goethite is the main product of hydrolysis of  $\text{Fe}^{2+}$  in solution under acidic (and aerobic) conditions (Cornell and Schwertmann 2003), so the role of ZnS as a reductant goes some way toward explaining the formation of goethite in our experiments. It does not, however, explain the formation of hematite, or the remarkable morphology and crystallinity of the goethite particles. One possible explanation is that the reduction process just described not only promotes goethite formation, but also leads to more rapid transformation of ferrihydrate aggregates to hematite, perhaps by promoting hydrolysis of bridging hydroxyl groups according to the general scheme shown in Figure 4, representing a half reaction coupled with electrolytic oxidation of ZnS to produce  $\text{Zn}^{2+}$  and elemental sulfur.

This reaction describes a surface process that is essentially the first of a series of steps that could lead to the precipitation of goethite/hematite, or their formation via transformation from ferrihydrate. If the above reduction step is followed by the release of  $\text{Fe}^{2+}$  into solution, goethite and/or hematite precipitation can be envisaged as the end result of subsequent reaction steps including reoxidation to  $\text{Fe}^{3+}$ , and formation of goethite and hematite nuclei. Thus, ZnS provides a means to dissolve ferrihydrate by virtue of the higher solubility of  $\text{Fe}^{2+}$  relative to  $\text{Fe}^{3+}$ , and dissolution of ferrihydrate makes more iron available in solution for precipitation of the more thermodynamically stable phases. The higher crystallinity observed in the goethite and hematite products, relative to that seen in precipitates formed in the absence of ZnS, suggests that this mechanism allows formation of



**FIGURE 4.** A possible mechanism for dehydration of ferrihydrite, represented as a half-reaction that must be coupled with electrolytic oxidation of ZnS.

a more ordered structure than that arising from non-reductive transformation.

In conclusion, we have demonstrated that the addition of ZnS particles to a ferrihydrite suspension in the pH range 2 to 4 has a dramatic effect on the rate of ferrihydrite phase transformation. The goethite phase so formed is of considerably enhanced crystallinity compared with the product formed in the absence of ZnS. Furthermore, we observe formation of crystalline hematite, even though these reaction conditions would not be expected to favor formation of this phase. The ability of ZnS to act as a reductant would seem to be the key to its effectiveness in increasing the rate of formation of these crystalline phases.

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