

EFFECT OF CYSTEINE AND MANGANESE ON THE CRYSTALLIZATION OF NONCRYSTALLINE IRON(III) HYDROXIDE AT pH 8

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Abstract—To provide a greater understanding of the crystallization of iron oxides under natural aqueous conditions, the combined effect of an inorganic ion (Mn^{2+}) and a reducing organic ligand (L-cysteine) on the conversion of noncrystalline ferric hydroxide to goethite and/or hematite was investigated at pH 8.

At cysteine: Fe ratios ≥ 0.2 , L-cysteine caused noncrystalline iron(III) hydroxide to transform rapidly into goethite at pH 8; in the absence of the organic ligand, hematite was the predominant reaction product. The presence of Mn (≥ 9 mole %) in the cysteine-ferric hydroxide system retarded crystallization and reduced the goethite-promoting effect of cysteine.

Polarographic measurements showed that the adsorption of cysteine on noncrystalline iron(III) hydroxide was immediately followed by the oxidation of cysteine to the disulfide with simultaneous reduction of a proportion of the interfacial ferric ions. The partly reduced noncrystalline iron(III) hydroxide dissolved at pH 8 more rapidly than the original material, thus facilitating the formation of goethite. In Mn(II)-noncrystalline iron(III) hydroxide coprecipitates, the interfacial oxidation/reduction reaction with cysteine (and hence the partial reduction of the noncrystalline phase) was reduced, due to replacement of some interfacial Fe(III) by non-reducible Mn.

At pH 8, uptake of Mn by crystalline iron oxides was low (< 5 mole %). Mn precipitated preferentially as pure Mn phases, either rhodochrosite (in $NaHCO_3$ buffer) or hausmannite (in NH_4Cl/NH_3 buffer).

Key words—Crystallization, Cysteine, Ferrihydrite, Goethite, Iron oxides, Manganese.

INTRODUCTION

In both natural and synthetic systems the initial precipitate from hydrolyzed ferric solutions is noncrystalline iron(III) hydroxide. This material resembles the mineral ferrihydrite (a poorly ordered iron(III) hydroxide) in that both materials are thermodynamically unstable and change with time into goethite (α - $FeOOH$) and/or hematite (α - Fe_2O_3); the main difference between noncrystalline iron(III) hydroxide and ferrihydrite appears to lie in the degree of ordering.

Laboratory studies have shown that the transformation of noncrystalline iron(III) hydroxide into products having greater crystallinity is influenced by the presence of inorganic ions, such as Al^{3+} , Mn^{2+} , or Cu^{2+} , as well as by organic ligands (Lewis and Schwertmann, 1979; Cornell, 1987, 1988; Cornell and Giovanoli, 1988). The forementioned studies concentrated on the effect of a single foreign ion; however, interactions between noncrystalline iron(III) hydroxide and two or more ions or ligands may be more relevant to natural systems, because in aquatic systems, noncrystalline iron(III) hydroxide commonly coexists with organic matter and with numerous inorganic ions.

The objective of the present investigation was to study the combined influence of an organic reducing ligand (L-cysteine) and Mn on the products and ki-

netics of the transformation of noncrystalline iron(III) hydroxide at pH 8. L-cysteine is a powerful reducing ligand, which has been shown to accelerate the conversion of noncrystalline iron(III) hydroxide to goethite at a pH (8) at which, in the absence of this ligand, hematite is the predominant transformation product (Cornell and Schneider, 1989). Mn was chosen for this work because it is frequently associated with Fe in natural systems and because earlier studies have already considered the influence of Mn alone on the transformation of noncrystalline iron(III) hydroxide in detail. Cornell and Giovanoli (1987) showed earlier that in very alkaline media, Mn promotes the conversion of noncrystalline iron(III) hydroxide to goethite and jacobsonite ($MnFe_2O_4$) and reduces the amount of hematite in the product. The principal question of interest was whether or not a combination of Mn and L-cysteine would promote goethite formation at pH 8 and if so, whether the level of Mn incorporation in the goethite product differed from that for Mn-goethite grown at pH 12. A further aim of the study was to determine the products from the reaction of Mn and noncrystalline iron(III) hydroxide in the absence of cysteine, at pHs approaching those in aquatic systems, thereby providing additional information about Fe and Mn formation in nature.

EXPERIMENTAL METHODS

Noncrystalline iron(III) hydroxide was precipitated with 1 M KOH from solutions of Fe(III) nitrate and Mn(II) nitrate having Mn/(Mn + Fe) mole ratios of 0, 0.09, 0.33, and 0.5. The pH of the suspension was adjusted to 7.5–8.5 with NaHCO₃ buffer solution (0.02–0.05 M), or, in some experiments, with NH₄Cl/NH₃ buffer (0.05–0.1 M). Sufficient L-cysteine to give a final concentration of 1×10^{-3} to 4×10^{-3} M (i.e., cysteine:Fe = 0.1–0.4) was then added to the freshly prepared ferric hydroxide. The suspensions (10 mmole Fe/liter) of ferric hydroxide were held in closed polypropylene bottles (headspace 3 cm) at 70°C for as long as 700 hr. No attempt to exclude air was made, inasmuch as the main aim of this work was to investigate the effect of cysteine and Mn under the same conditions as in previous investigations. A temperature of 70°C was used for the transformation experiments to enable crystalline products to be obtained in a reasonable length of time; the mechanism by which noncrystalline iron(III) hydroxide transforms into goethite and/or hematite is independent of temperature (Cornell, 1985), hence, results obtained at 70°C should also apply to natural systems.

The crystalline reaction products were washed and dried at 50°C. X-ray powder diffraction (XRD) patterns were obtained with a Guinier-Enraf camera (Mk IV) using FeK α_1 radiation. If the reaction product consisted of a mixture of goethite and hematite, the proportion of each was estimated by comparison with a series of standards made by mixing known amounts of synthetic goethite and hematite. The 110 and 111 XRD peaks of goethite and the 102 peak of hematite were used for comparison.

Transmission electron micrographs (TEMs) were obtained using a Hitachi H-600 electron microscope operating at 100 kV. For TEM examination the samples were dispersed in twice-distilled water with an ultrasonic treatment, and a drop of suspension was evaporated to dryness on a carbon-coated bronze grid.

The kinetics of the reaction were followed by taking subsamples at intervals and dissolving the unconverted ferric hydroxide by a 30-min extraction with 0.4 M HCl (0.1 g solid/100 ml) at 25°C (cf. Cornell and Schneider, 1989). The acid-oxalate extraction method of Schwertmann (1984) could not be used in the present work, because the combination of oxalate and cysteine led to the dissolution of both the crystalline and the noncrystalline phases. Preliminary experiments showed that the acid treatment adopted provided a satisfactory separation of these phases. The extent of the transformation was expressed as the ratio, Fe_A/Fe_T, where Fe_A is the acid-soluble material (i.e., unconverted, noncrystalline iron(III) hydroxide) and Fe_T is the total iron in the system. Analysis for Fe was carried out using atomic absorption spectroscopy (AA).

The total amount of Fe and Mn in the reaction product was found by completely dissolving the oxide in 4 M HCl. If the reaction product consisted of either goethite or hematite (together with an Mn phase), the level of Mn incorporation was taken as the difference between oxalate soluble Mn (Mn_o) and the total Mn (Mn_t) in the oxide; Mn phases are completely soluble in acid-oxalate solution (pH 3) (cf. Stiers and Schwertmann, 1985). The degree of Mn substitution in goethite or hematite was expressed as the ratio (Mn_t - Mn_o)/[(Mn_t - Mn_o) + (Fe_t - Fe_o)]. Oxalate-soluble Mn and Fe (Fe_o) were found by extracting the oxide in acid-ammonium oxalate solution for 2 hr in the absence of light (cf. Cornell and Giovanoli, 1987). Mn was determined by AA.

The interaction between cysteine and noncrystalline iron(III) hydroxide was followed using differential pulse polarography (polaroid E 506 metrohm polarograph with Ag/AgCl reference electrode) (Cornell and Schneider, 1989). Suspensions of the ferric hydroxide with and without Mn (0.1 g oxide/100 ml, pH 8) were equilibrated for 5 min or 2 hr at 25°C and centrifuged, and the levels of cysteine and cystine (the oxidation product of cysteine) in the supernatant liquid were found by polarography. Standard solutions of cysteine (pH 8 and in 0.1 M NaHCO₃ buffer) were prepared for calibration purposes.

RESULTS

Product mineralogy

The reaction products included goethite, hematite, hausmannite (Mn₃O₄), rhodochrosite (MnCO₃), and manganite (γ -MnOOH) (Figure 1). The composition of the product depended on the concentrations of Mn and cysteine in the system and also on the nature of the buffer ions.

Inasmuch as carbonate/bicarbonate ions are the principal buffering ions in neutral and slightly alkaline waters, most experiments were carried out using a bicarbonate buffer. Under these conditions, however, the initial Mn precipitate was always rhodochrosite. Some experiments, therefore, were performed using NH₄Cl/NH₃ buffer to investigate what other Mn compounds could form in the Mn(II)-ferric hydroxide-cysteine system.

XRD indicated that at pH 8 in NaHCO₃ buffer, noncrystalline iron(III) hydroxide transformed into hematite (Figure 1a); TEM, however, showed the presence of a few percent of goethite crystals. Addition of $\geq 2 \times 10^{-3}$ M cysteine (i.e., cysteine:Fe ≥ 0.2) to the suspension converted the noncrystalline iron(III) hydroxide to 100% goethite within a few hours (cf. Cornell and Schneider, 1989). With lower levels of cysteine, goethite in the product was increasingly replaced by hematite until with 10^{-3} M cysteine, no goethite was detectable by XRD.

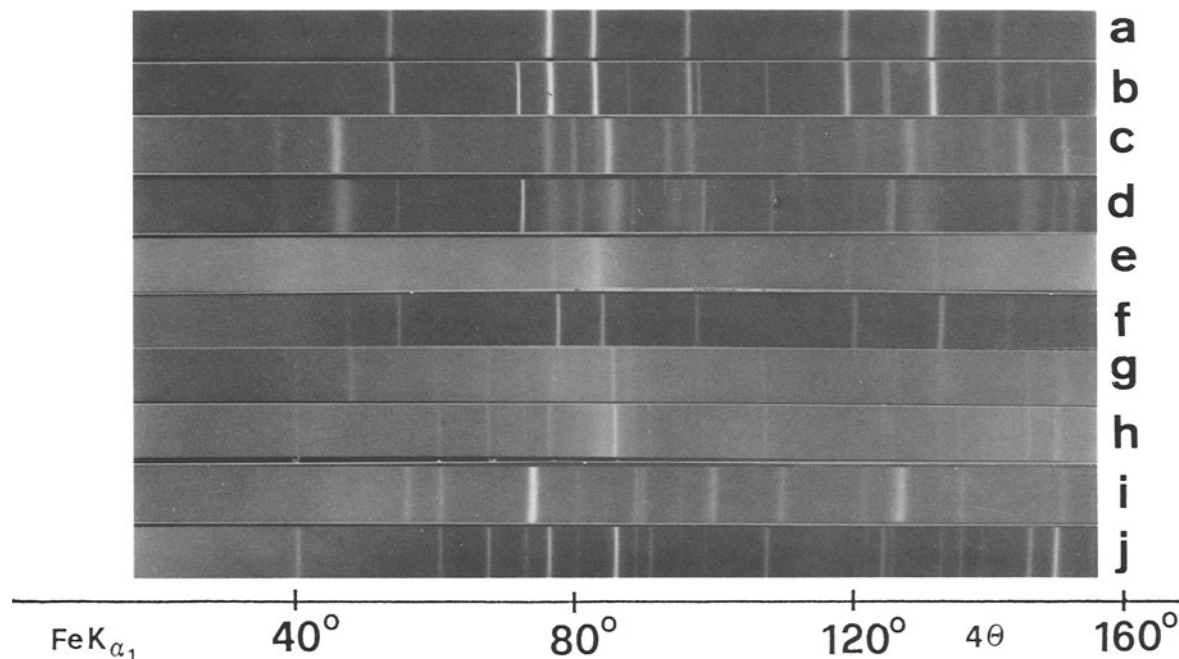


Figure 1. X-ray powder diffraction patterns of the products formed by the transformation of noncrystalline iron(III) hydroxide at pH 8. (a) Hematite (NaHCO_3 buffer); (b) hematite and rhodochrosite from noncrystalline iron(III) hydroxide coprecipitated with 9 mole % Mn (NaHCO_3 buffer); (c) goethite obtained from noncrystalline iron(III) hydroxide with cysteine: Fe = 0.2 (NaHCO_3 buffer); (d) goethite and rhodochrosite from noncrystalline iron(III) hydroxide coprecipitated with 9 mole % Mn and with cysteine: Fe = 0.4 (NaHCO_3 buffer); (e) mixture of hematite, a trace of goethite, and partly ordered iron(III) hydroxide during initial stage of transformation in a system with 9 mole % Mn and cysteine: Fe = 0.2 ($\text{NH}_4\text{Cl}/\text{NH}_3$ buffer); (f) hematite and goethite from the system in (e) after complete crystallization of the noncrystalline phase; (g) goethite and hausmannite from noncrystalline iron(III) hydroxide coprecipitated with 33 mole % Mn ($\text{NH}_4\text{Cl}/\text{NH}_3$ buffer); (h) hausmannite and partly ordered iron(III) hydroxide during the initial stage of the transformation in a system with 33 mole % Mn and with cysteine: Fe = 0.2 ($\text{NH}_4\text{Cl}/\text{NH}_3$ buffer); (i) rhodochrosite and manganite from (0.1 M) Mn^{2+} solution buffered with 0.05 M NaHCO_3 ; (j) hausmannite and manganite from (0.1 M) Mn^{2+} solution buffered with 0.05 M $\text{NH}_4\text{Cl}/\text{NH}_3$.

Effect of Mn

NaHCO₃ system (Table 1). At pH 8 and in the presence of Mn (≥ 9 mole %), the noncrystalline iron(III) hydroxide transformed into well-crystallized Mn-hematite (see below) and rhodochrosite (Figure 1b). The amount of the Mn phase in the product increased as the level of Mn in the system rose. The initial Mn precipitate was rhodochrosite, which, with time, transformed into manganite. In NaHCO_3 buffer, Mn did not have a goethite-promoting effect; regardless of the concentration of Mn in the system, the iron oxide product was hematite.

In the presence of 2×10^{-3} M cysteine, noncrystalline iron(III) hydroxide containing 9–33 mole % coprecipitated Mn, slowly transformed into a mixture of Mn-hematite, rhodochrosite, and manganite (Table 1). Increasing the concentration of cysteine reduced the amount of hematite formed in favor of goethite. A slight increase to 2.5×10^{-3} M cysteine led to a mixture of hematite, goethite, and rhodochrosite, and with 4×10^{-3} M cysteine, hematite was eliminated from the

product, even in systems containing 50 mole % Mn (Figure 1d, Table 1).

NH₄Cl/NH₃ system (Table 2). In the $\text{NH}_4\text{Cl}/\text{NH}_3$ system, Mn reduced the formation of hematite and/or promoted that of goethite in a manner similar to that observed at pH 12 (cf. Cornell and Giovanoli, 1987). XRD showed that noncrystalline iron(III) hydroxide containing 9 mole % Mn transformed into 30% goethite + 70% hematite; the proportion of goethite was larger than for the control system (Table 2). As the level of Mn rose to 33 mole %, hematite was increasingly replaced by goethite, and Mn precipitated as hausmannite (Figure 1g).

With 2×10^{-3} M cysteine, noncrystalline iron(III) hydroxide coprecipitated with 9 mole % Mn transformed to hematite + goethite; complete crystallization was only achieved after 3–4 weeks. During the initial stage of the transformation (one week), the XRD pattern (Figure 1e) showed faint, broad hematite lines, very weak lines of goethite, and a broad diffuse band at 2.4–2.5 Å attributable either to very small crystals

Table 1. Effect of [cysteine] and [Mn] on the transformation products of noncrystalline iron(III) hydroxide in NaHCO₃ (0.05 M) buffer.

[Cysteine] (M)	Mole % Mn	Products
0	0	Hematite + trace goethite
10 ⁻³	0	Hematite
2 × 10 ⁻³	0	Goethite
0	9	Hematite + some goethite + rhodochrosite
0	33	Hematite + rhodochrosite + manganite
2 × 10 ⁻³	9–50	Hematite + rhodochrosite + manganite
4 × 10 ⁻³	9–50	Goethite + rhodochrosite + manganite

pH = 8, 70°C

of magnetite or to noncrystalline iron(III) hydroxide with a degree of local ordering (cf. Feitknecht *et al.*, 1973). As this band disappeared with longer transformation times, and at the same time, the lines arising from goethite and hematite increased in intensity (Figure 1f), the line at 2.4–2.5 Å was probably due to partly ordered iron(III) hydroxide. The same diffuse band was occasionally observed for incompletely transformed iron(III) hydroxide-cysteine systems containing 33 mole % Mn (Figure 1h); TEM showed dense masses of noncrystalline material as well as crystals (Figure 3e). The final reaction product in this system consisted of poorly formed crystals of goethite together with hausmannite.

No jacobsonite was detected in any of these systems. Mn precipitated preferentially as a separate Mn phase instead of coprecipitating with iron oxides.

Precipitates from Mn solutions at pH 8

In NaHCO₃-buffered systems, the precipitate during the first 24 hr consisted of rhodochrosite and some manganite (Figure 1i). During the following 8 days (70°C), most of the rhodochrosite disappeared and was replaced by manganite. The transformation experiments were carried out in closed reaction vessels; under these conditions pO₂ ≤ 0.2 atm, hence, slow oxidation of the precipitate could have taken place. In NH₄Cl/NH₃ buffer, Mn precipitated initially as hausmannite and manganite (Figure 1j); with time, the hausmannite oxidized to manganite. XRD patterns of subsamples

Table 2. Effect of [cysteine] and [Mn] on the transformation products of noncrystalline iron(III) hydroxide in NH₄Cl/NH₃ (0.05 M) buffer.

[Cysteine] (M)	Mole % Mn	Products
0	0	90% Hematite + 10% goethite
0	9	70% Hematite + 30% goethite
2 × 10 ⁻³	9	80% Hematite + 20% goethite
2 × 10 ⁻³	23–33	Goethite + hausmannite

pH = 8, 70°C

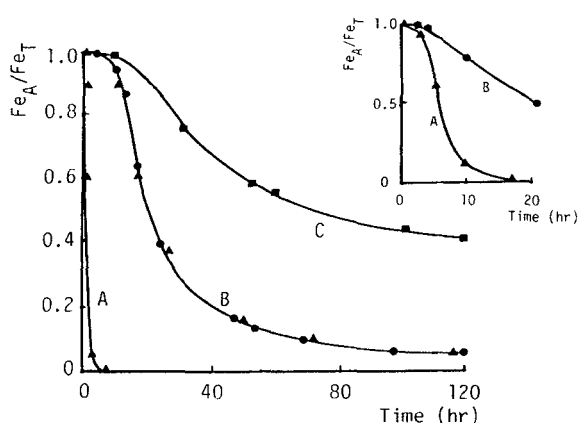


Figure 2. Fe_A/Fe_T as a measure of the degree of transformation of noncrystalline iron(III) hydroxide vs. time (Fe_A = acid-soluble Fe, Fe_T = total Fe). pH 8, 0.05 M NaHCO₃ buffer, 70°C. (A) Noncrystalline iron(III) hydroxide in the presence of 2 × 10⁻³ M cysteine (cysteine: Fe = 0.2); (B) noncrystalline iron(III) hydroxide (●) and noncrystalline iron(III) hydroxide coprecipitated with 9 mole % Mn (▲); (C) noncrystalline iron(III) hydroxide coprecipitated with 9 mole % Mn, in the presence of 2 × 10⁻³ M cysteine. Inset: Fe_A/Fe_T vs. time for noncrystalline iron(III) hydroxide (curve A) and noncrystalline iron(III) hydroxide coprecipitated with 9 mole % Mn, in the presence of 4 × 10⁻³ M cysteine.

taken at intervals during these experiments indicated that manganite formed more slowly from hausmannite than from rhodochrosite.

Crystal morphology

Hematite grown in the NaHCO₃ system consisted of irregular platelets having diameters ranging from 40 to 180 nm (Figure 3a). These crystals were smaller than those grown at pH 10–11 in a KOH medium (diameters = 100–300 nm; cf. Cornell and Giovanoli, 1985). Mn-hematites also grew as platey crystals (Figure 3c). Although these crystals were small, they were more rounded than those of the unsubstituted hematites. Some of these crystals appeared to be agglomerates of much smaller particles.

Goethite crystals grown in the presence of cysteine were usually acicular, having lengths ranging from 200 to 400 nm and widths of 10–30 nm (Figures 3b and 3e). Some crystals were multi-domainic and a few were twinned; these twins were either dendritic or twin pieces. The presence of Mn did not promote additional twinning. The terminal faces of the acicular crystals were usually poorly developed; this may reflect interference in growth by the organic material in the system. A similar effect was noted for goethite grown in the presence of sucrose (Cornell, 1985).

Goethite grown in the absence of cysteine in the NH₄Cl/NH₃ system (with 33 mole % Mn) consisted mainly of acicular crystals as long as 400 nm and as

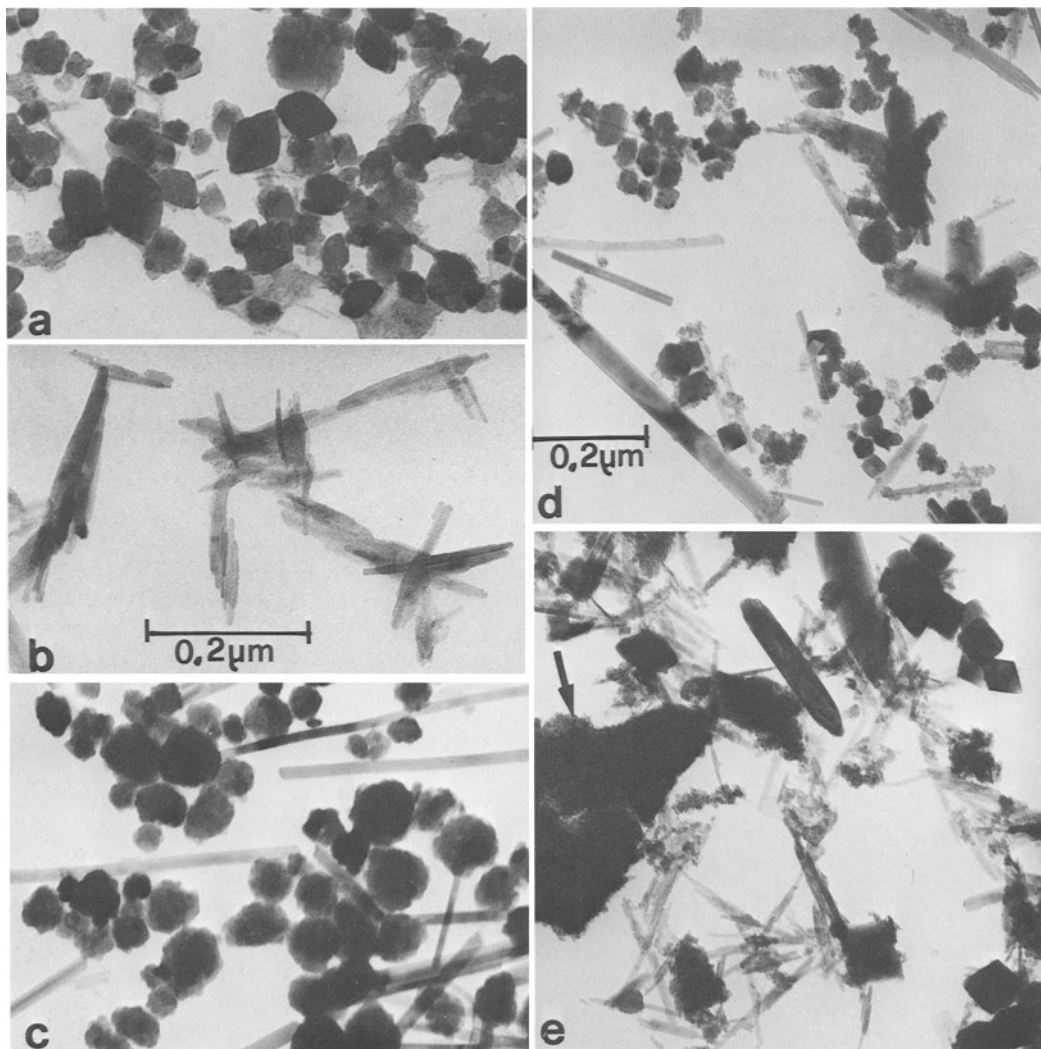


Figure 3. Transmission electron micrographs of Fe and Mn oxides grown at pH 8 from noncrystalline iron(III) hydroxide with and without coprecipitated Mn. (a) Hematite grown in NaHCO_3 buffer; (b) goethite grown in the presence of 2×10^{-3} M cysteine (cysteine : Fe = 0.2); (c) Mn-hematite and manganite (needles) grown in NaHCO_3 buffer; (d) hausmannite (cubes), goethite (twinned and acicular particles), and manganite (needles) grown in $\text{NH}_4\text{Cl}/\text{NH}_3$ buffer; (e) hausmannite, goethite, and noncrystalline iron(III) hydroxide ($\text{NH}_4\text{Cl}/\text{NH}_3$ buffer). Original magnification for (a), (b), and (c) = 100,000 \times ; for (d) and (e) = 75,000 \times .

wide as 50 nm. Some dendritic twins and rare epitaxial twins were observed (Figure 3d).

Manganite crystals grew as needles as long as 1 μm (Figure 3c). Hausmannite was present as typical cubes or bipyramids 40–120 nm across (Figures 3d and 3e). Rhodochrosite grew as rhombohedra.

Substitution of Mn in iron oxides

At pH 8, uptake of Mn by iron oxides was low, and Mn precipitated instead as a pure Mn phase. These results contrast with those reported for pH 12, where as much as 15 mole % Mn was incorporated in the

goethite structure (Stiers and Schwertmann, 1985; Cornell and Giovanoli, 1987).

Chemical analysis showed that Mn-hematite formed both in the presence and absence of cysteine contained 4–5% Mn, which is close to the maximum level of substitution that has been reported for Mn hematites prepared at pH 8 in an oxalate medium (Cornell and Giovanoli, 1987). The additional Mn precipitated as rhodochrosite.

Chemical analysis also showed that no more than 2–3 mole % Mn was taken up by goethite that formed in the presence of 4×10^{-3} M cysteine. Even this low

level of incorporation was sufficient to change the color of the crystals from yellow to olive.

These results refer to the products formed in NaHCO_3 -buffered systems. The iron oxides formed in $\text{NH}_4\text{Cl}/\text{NH}_3$ systems were always mixtures and/or poorly crystalline, so reliable estimates of Mn substitution by chemical analysis could not be obtained. As for the products in the NaHCO_3 systems, shifts in the positions of the XRD lines of goethite and hematite were not detected. The formation of hausmannite, however, at much lower Mn concentrations than at pH 12 (i.e., at 23 mole % Mn instead of 60 mole % Mn) suggests that at pH 8, Mn was not readily taken up by iron oxides.

Davies (1984) showed that adsorption of Mn^{2+} (the predominant Mn species in slightly alkaline media; cf. Lindsay, 1979) on goethite is very low at pH 8, but rises rapidly at pH >8.5. In the present work, the low degree of Mn incorporation in goethite may simply reflect the inability of Mn to adsorb on the goethite nuclei to any extent.

Kinetics

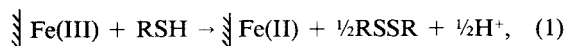
NaHCO₃ system. Curve A in Figure 2 shows that in the presence of 2×10^{-3} M cysteine, noncrystalline iron(III) hydroxide transformed into goethite in a few hours. Without cysteine, the transformation (to hematite) took several days; the plots of extent of transformation vs. time were identical for systems both with and without Mn (Figure 2, curve B).

In systems containing Mn (9 mole %) as well as cysteine (2×10^{-3} M), noncrystalline iron(III) hydroxide displayed an unexpected stability and changed to a crystalline product (hematite) more slowly than in the absence of the organic ligand (Figure 2, curve C). Doubling the concentration of the ligand accelerated the transformation, but the rate of conversion was still slower than in the absence of Mn (Figure 2, inset).

In the $\text{NH}_4\text{Cl}/\text{NH}_3$ system, the presence of Mn strongly retarded the transformation of noncrystalline iron(III) hydroxide; this retarding effect was enhanced in cysteine-containing systems. Quantitative kinetic studies were not made, but XRD and TEM examination of subsamples taken during the transformation indicated that the reaction took weeks rather than days.

Interaction of cysteine with noncrystalline iron(III) hydroxide

On the addition of 2×10^{-3} M cysteine, noncrystalline iron(III) hydroxide immediately changed from light to dark brown. Polarography measurements showed that more than 80% of the cysteine in the system was oxidized to the disulfide (cystine) during the first five minutes of contact with the ferric hydroxide at pH 8 (25°C), i.e.,



where RSH = cysteine and RSSR = cystine. The supernatant liquid from the noncrystalline iron(III) hydroxide-cysteine system showed polarographic peaks at -0.51, -0.63, and -0.94 V. The latter two peaks indicate the presence of the disulfide (Mairesse-Ducarmoir *et al.*, 1974). For a solution of cysteine, only one polarographic peak was noted, at -0.51 V.

Interaction of cysteine with noncrystalline iron(III) hydroxide involves adsorption of cysteine, followed by partial reduction of interfacial ferric sites accompanied by desorption into solution of the organic oxidation products, i.e., the cysteine free radicals (Cornell and Schneider, 1989). The free radicals combine in solution to form the disulfide. Eq. (1) indicates that with an initial cysteine:Fe ratio of 0.2, 20% of the total Fe in the system should be reduced.

Oxidation of cysteine was lower for Mn-noncrystalline iron(III) hydroxide coprecipitates than for the unsubstituted noncrystalline iron(III) hydroxide. Polarography showed that the amount of the disulfide produced during 2 hr of contact of cysteine (2×10^{-3} M) with Mn-noncrystalline iron(III) hydroxide coprecipitates decreased as the level of Mn in the system increased. Unlike Fe^{3+} , Mn^{2+} does not have the ability to catalyze oxidation of cysteine; hence, a mixed Mn(II)-Fe(III) hydroxide surface would be expected to have a reduced oxidizing power compared with that of noncrystalline iron(III) hydroxide.

DISCUSSION

Cornell and Schneider (1989) showed that the presence of cysteine at cysteine:Fe ratios ≥ 0.2 promotes rapid conversion of noncrystalline iron(III) hydroxide to goethite at pH 8. Interaction of cysteine with noncrystalline iron(III) hydroxide involves oxidation of cysteine together with simultaneous reduction of a proportion of the interfacial ferric sites, thus converting the solid phase into a mixed valence compound. Cornell and Schneider (1989) showed that addition of a ferrous solution ($2\text{--}4 \times 10^{-3}$ M Fe^{2+}) to noncrystalline iron(III) hydroxide also leads to the formation of goethite (together with magnetite), but the transformation takes place far more slowly than in the presence of equivalent levels of cysteine. They concluded that the interfacial ferrous ions produced during interaction with cysteine did not reductively dissolve the noncrystalline iron(III) hydroxide; rather the mixed valence compound that resulted dissolved more rapidly than the original ferric material and so permitted formation of goethite from soluble ferric species to outweigh formation of hematite completely. The mixed valence compound cannot be classed as a green rust. It is X-ray and electron amorphous, dark brown, and has a $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.25–0.66, whereas the green rusts are crystalline, greenish blue, and have $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of 3–4.

In the cysteine-noncrystalline iron(III) hydroxide system, the oxidation/reduction reaction and the formation of the disulfide occurred within a few minutes of the organic ligand contacting the ferric compound. The subsequent conversion of the partly reduced noncrystalline iron(III) hydroxide was slower (hours) and was the rate-determining step in the reaction.

The presence of Mn reduced the goethite-promoting effect of cysteine (2×10^{-3} M), apparently due to partial inhibition of the interfacial oxidation/reduction reaction as a result of replacement of some interfacial Fe(III) by Mn(II); the development of mixed-valence character was not sufficient to solubilize the noncrystalline iron(III) hydroxide. Under these conditions, the cysteine actually stabilized the noncrystalline iron(III) hydroxide against dissolution and so permitted the internal dehydration/rearrangement process, by which hematite forms, to be competitive with the dissolution/reprecipitation process, which leads to goethite. This effect was also observed with low levels ($\leq 10^{-3}$ M) of cysteine in the absence of Mn. High enough levels of cysteine could, of course, overcome the stabilizing effect of Mn.

Infrared studies (cf. McAuliffe and Murray, 1972) have shown that in soluble ferric-cysteine complexes formed in alkaline media, the ligand coordinates to Fe via S^- and COO^- groups, forming bidentate chelates; these groups should participate during cysteine adsorption on noncrystalline iron(III) hydroxide. Cysteine can, therefore, behave like other multi-dentate ligands (e.g., citrate, silicate, and maltose; Cornell, 1987), which at ratios of L:Fe = 0.1 strongly retard the transformation of noncrystalline iron(III) hydroxide and, in addition, suppress the formation of goethite. The difference between these ligands and cysteine lies in the presence of a reducing sulphhydryl group in cysteine. With rising cysteine:Fe ratios, reduction of interfacial ferric ions via the adsorbed S^- apparently outweighed stabilization through COO^- coordination, and cysteine changed from a stabilizing to a dissolving ligand. The same effect was noted with a related reducing ligand, glutathione. This compound differs from cysteine in that it possesses two COOH groups; higher glutathione:Fe ratios (~ 0.4) were needed to overcome the stabilizing effect of these groups and to accelerate conversion of noncrystalline iron(III) hydroxide to goethite.

The present work shows that at the pHs of natural systems, noncrystalline iron(III) hydroxide can be converted to goethite quite readily provided that sufficient organic reducing ligand (L:Fe ≥ 0.2) is present; non-reducing organic ligands have a stabilizing and/or hematite-enhancing effect (Cornell, 1987). The goethite-promoting ability of cysteine can be lessened by the presence of inorganic ions. Interference in the formation of goethite appears to proceed by two different routes. Coprecipitated Mn reduces the extent of the

oxidation/reduction reaction at the noncrystalline iron(III) hydroxide surface; preliminary experiments showed that other nonreducible metal ions, such as Zn, behaved similarly. Phosphate and silicate ions, on the other hand, blocked goethite formation by adsorbing on noncrystalline iron(III) hydroxide in preference to cysteine (Cornell and Schneider, 1989). Whether the goethite-promoting effect of the reducing organic ligand or the retarding effect of the inorganic species predominates appears to depend to a large extent on the local (ligand and/or inorganic ion):Fe ratios in the system.

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