

EFFECT OF MANGANESE ON THE TRANSFORMATION OF FERRIHYDRITE INTO GOETHITE AND JACOBSITE IN ALKALINE MEDIA

R. M. CORNELL,¹ AND R. GIOVANOLI²

¹ Institute of Inorganic Chemistry, University of Berne
Freiestrasse 3, CH-3000 Berne 9, Switzerland

² Laboratory of Electron Microscopy, University of Berne
Freiestrasse 3, CH-3000 Berne 9, Switzerland

Abstract—In the presence of Mn(II), ferrihydrite transforms into Mn-goethite and/or jacobsite. Chemical analysis showed that as much as 15 mole % Mn replaced Fe in the goethite structure. If Mn(III) replaced Mn(II), the formation of jacobsite was suppressed; ferrihydrite transformed into Mn-goethite, and, at high Mn(III) concentrations, a 7-Å phyllo-manganate. Low levels of Mn(II) retarded the transformation of ferrihydrite only slightly, whereas in an Mn(III) system the nucleation and growth of Mn-goethite were both hindered. Mn-goethite nucleated in solution, whereas jacobsite appeared to form by interaction of dissolved Mn(II) species with ferrihydrite. Mn suppressed the formation of hematite in these systems; however, Mn-hematite containing as much as 5 mole % Mn was induced to form at pH 8 by adding oxalate to the system. Transmission electron micrographs showed that goethite crystals grown in the presence of Mn were long ($\leq 2 \mu\text{m}$) and thin and commonly contained etch pits. The presence of Mn appears to have promoted twinning.

Key Words—Ferrihydrite, Goethite, Jacobsite, Manganese, Phyllo-manganate, Synthesis, Transmission electron microscopy.

INTRODUCTION

The transformation of ferrihydrite into goethite and/or hematite in alkaline media is strongly influenced by the presence of foreign ions and molecules. In general, foreign species tend to stabilize ferrihydrite and also increase the proportion of hematite relative to goethite in the end product. In some systems, crystal morphology is also modified. Studies of the effects of foreign species have provided further details of the mechanisms by which ferrihydrite transforms into goethite and hematite (Fischer and Schwertmann, 1975; Cornell and Schwertmann, 1979; Cornell, 1985). Most attention to date has been directed to anionic species. The only cationic species to have been considered in detail is Al which, in addition to modifying the kinetics and products of the transformation, has also been incorporated in the crystal structure of both goethite and hematite (Schwertmann *et al.*, 1979; Lewis and Schwertmann, 1979; Fey and Dixon, 1981; Schulze, 1984; Schulze and Schwertmann, 1984).

Another cation that might be expected to influence the transformation of ferrihydrite to goethite and/or hematite is manganese. Fe and Mn are chemically closely related, and the mineral groutite, $\alpha\text{-MnOOH}$, is isostructural with goethite. Manganese has recently been shown to replace as much as 15 mole % of the Fe in the structure of synthetic goethite (Stiers and Schwertmann, 1985). A further reason for interest in manganese is that Mn and Fe precipitates can coexist in marine and terrestrial environments.

This paper presents the results of an investigation into the influence of manganese on the transformation of ferrihydrite in alkaline media at 70°C. These reaction conditions were chosen because they enable crystalline reaction products to be obtained in a reasonable length of time.

EXPERIMENTAL METHODS

Ferrihydrite was precipitated with 1.0 M KOH from solutions of Fe(III) nitrate and Mn(II) nitrate having Mn/(Mn + Fe) mole ratios (henceforth termed x) between 0.01 and 1.0. The pH of the suspensions ranged from 8 to 14, although the majority of transformation experiments were carried out at pH 11–13. The suspensions (1.0 or 10 g ferrihydrite/liter) were held in closed polypropylene bottles at either 70° or 90°C for 48 hr. Although in most experiments Mn(II) and Fe(III) were coprecipitated, experiments were also carried out in which Mn(II) was added after precipitation of ferrihydrite; where necessary, the pH was readjusted after the addition of Mn(II) with KOH. In other experiments, Mn(II) nitrate was replaced by Mn(II) oxalate or Mn(III) acetate. Additional experiments were made in which aluminum nitrate (1×10^{-3} to 2×10^{-3} M) replaced Mn(II) nitrate. Mn-goethite was also grown in the presence of silicate ions (10^{-4} M) or NaNO_3 (2 M). Stock solutions containing 2×10^{-3} M H_4SiO_4 (pH 3) were prepared according to the method of Santschi and Schindler (1974). All chemicals were AR (Merck),

Table 1. Effect of pH, Mn concentration, and source of Mn on the transformation products.¹

[Mn] (M)	x ²	pH					
		8	10	11	12	13	14
0	0	Hm, g	Hm, g	G, Hm	G	G	G
Mn(II) nitrate							
1.5 × 10 ⁻³	0.15	Hm, g	G, hm	G	G	G	G
1.9 × 10 ⁻³	0.18	—	G, hm	G, j	G, j	G, j	—
4.4 × 10 ⁻³	0.30	—	J, G	J, G	J, G	J, G	—
1 × 10 ⁻²	0.50	G, j	—	J, g	J, g	J, g	J, g
Mn(III) acetate							
1.5 × 10 ⁻³	0.15	—	—	—	G	G	—
4.4 × 10 ⁻³	0.30	—	—	—	G, 7-Å phase	—	—
1 × 10 ⁻²	0.50	—	—	—	G, ha, 7-Å phase	—	—
Mn(II) oxalate							
1.5 × 10 ⁻³	0.15	Hm	—	G	G	—	—
1 × 10 ⁻²	0.50	Hm	—	G, J, Ha	J, Ha, g	—	—

¹ G, g = goethite; J, j = jacobsite; Hm, hm = hematite; Ha, ha = hausmanite; 7-Å phase = 7-Å phylломanganate. Capital letter indicates dominant phase, small letter indicates minor phase.

² x = Mn/(Mn + Fe) in the system.

except for Mn(III) acetate, which was only available as technical grade.

Coprecipitation of Mn(II) and Fe(III) led to the instantaneous formation of dark-brown ferrihydrite. On addition of a solution of Mn(II) nitrate to ferrihydrite, the red-brown precipitate gradually darkened over 30 min, indicating a slower interaction than for a coprecipitated system. Analysis of the supernatant liquid showed that in both systems all the Mn added (to 10⁻² M) was taken up by the ferrihydrite.

The kinetics of the transformation to Mn-goethite was followed by taking subsamples during the reaction and dissolving the unconverted ferrihydrite with a 2-hr acid/oxalate (pH 3) extraction in the absence of light (Schwertmann, 1964). The extent of the transformation was expressed as the ratio Fe_o/Fe_t, where Fe_o is the oxalate soluble material (i.e., unconverted ferrihydrite) and Fe_t is the total Fe in the system. Kinetic measurements were only made for systems in which the reaction product was Mn-goethite. Both ferrihydrite and Mn oxides are readily soluble in oxalate; hence, if Mn oxides formed as well as Mn-goethite, the acid/oxalate extraction did not give a reliable estimate of the extent of transformation.

The crystalline product of the transformation was dried at 50°C, and X-ray powder diffraction (XRD) patterns were obtained using a Guinier-Enraf camera (Mk IV) with FeKα₁ radiation. The reaction products usually consisted of Mn-goethite or a mixture of Mn-goethite + jacobsite (MnFe₂O₄). The proportions of Mn-goethite and jacobsite in the product were estimated by comparison with a series of standards made by mixing known amounts of synthetic goethite and

jacobsite. The 110 and 111 XRD peaks of goethite and the 220 and 311 peaks of jacobsite were used for comparison.

Jacobsite was prepared by coprecipitating Mn(II) nitrate and Fe(III) nitrate (x = 0.56) with 1 M KOH to pH 12 and heating the precipitate at 70°C for 24 hr. Careful control of the proportions of Fe(III) and Mn(II) was needed to avoid traces of either goethite or hausmanite (Mn₃O₄) in the product. The black, ferromagnetic jacobsite was washed and dried at 50°C. Its XRD pattern corresponded to that given in JCPDS 10-319 for jacobsite (Figure 1a).

The total amount of Fe and Mn in Mn-goethite was found by dissolving the oxide in 4 M HCl. Where the reaction product consisted only of Mn-goethite, 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. The degree of Mn substitution was expressed as the ratio (Mn_t - Mn_o)/[(Mn_t - Mn_o) + (Fe_t - Fe_o)] (cf. Stiers and Schwertmann, 1985).

Transmission electron micrographs (TEM) were obtained using Hitachi HU-12 A and Hitachi H-600-2 electron microscopes operating at 125 and 100 kV, respectively. For TEM examination the samples were dispersed in twice-distilled water with ultrasonic treatment, and a drop of suspension was evaporated to dryness on a carbon-coated bronze grid.

RESULTS

Product mineralogy

At pH ≥ 10 and in the presence of Mn (as high as x = 0.5), ferrihydrite transformed into Mn-goethite

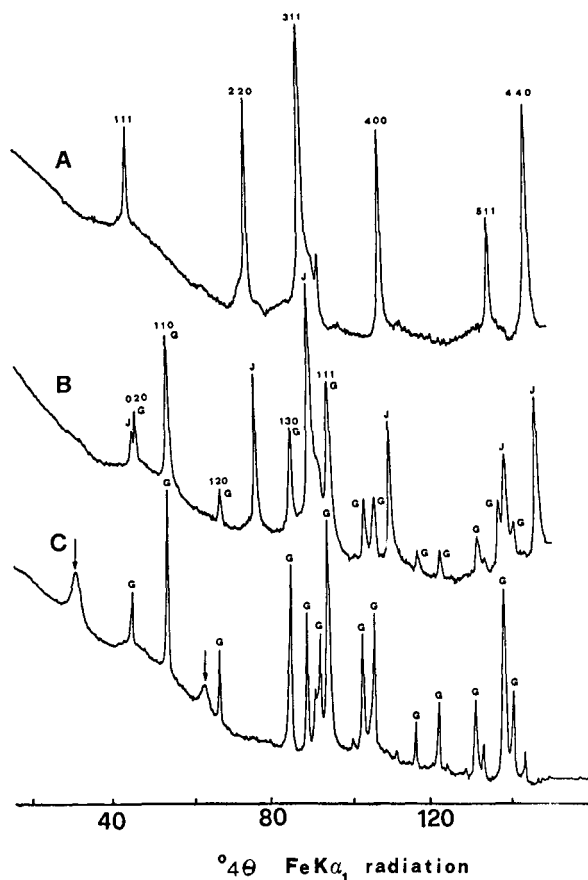


Figure 1. Densitometer traces of $\text{FeK}\alpha_1$ -Guinier patterns of: (A) jacobite; (B) mixture of Mn-goethite and jacobite formed from Mn-ferrihydrite at $\text{Mn}/(\text{Mn} + \text{Fe})$ mole fraction = 0.3; and (C) mixture of Mn-goethite and a 7-Å phyllomanganate formed in a Mn(III)/ferrihydrite system at $\text{Mn}/(\text{Mn} + \text{Fe})$ mole fraction = 0.33. Synthesis conditions at pH 12, 70°C. J = jacobite; G = goethite; arrows show peaks due to 7-Å phyllomanganate.

and/or jacobite (Figure 1b). In some experiments, small amounts of hematite ($\alpha\text{-Fe}_2\text{O}_3$), hausmanite, or a 7-Å Mn(IV) phyllomanganate were also produced. The relative proportions of the two principal reaction products depended mainly upon the level of Mn in the system and the concentration of the suspension.

Effect of pH, concentration of Mn(II), and suspension concentration

Most transformations were carried out in the pH range 11–13. Under these conditions and with Mn additions of as much as 15 mole %, Mn-goethite was the sole reaction product. At lower pH some hematite formed. The presence of Mn, however, suppressed hematite (Table 1). This effect decreased with falling pH and rose with increasing Mn concentration. At pH 8 and with 15 mole % Mn in the system, the amount of hematite in the product was comparable with that of

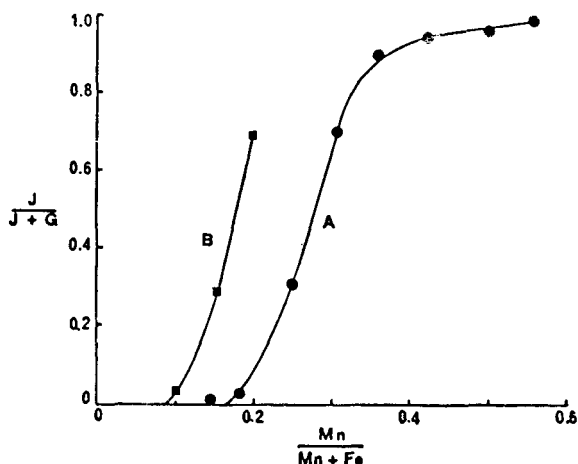


Figure 2. Jacobsite/(jacobite + Mn-goethite) ratios in the reaction product vs. $\text{Mn}/(\text{Mn} + \text{Fe})$ mole fraction initially present in the system. pH 12, 70°C. Curve A = 1 g ferrihydrite/liter system; curve B = 10 g ferrihydrite/liter system.

the control. Increasing the level of added Mn to 30 mole % prevented any hematite formation at pH ≥ 9 .

The proportion of jacobite in the product increased with rising Mn concentration at the expense of Mn-goethite until at $x = 0.55$ goethite was entirely suppressed (Figure 2, curve A). At greater values of x , mixtures of jacobite and hausmanite formed, the proportion of hausmanite increasing to 100% at $x = 1.0$. Varying the pH had little effect on the amount of jacobite produced in the pH range 10–13. Jacobite formed less readily, however, as the pH decreased to 8 (Table 1).

Jacobite has a nominal formula of $\text{Mn}(\text{II})\text{Fe}(\text{III})_2\text{O}_4$. The composition can, however, vary within wide limits. If it is expressed in terms of the $\text{Fe}_3\text{O}_4\text{-Mn}_3\text{O}_4$ system, jacobite covers the range 10–54 mole % Mn_3O_4 (Van Hook and Keith, 1958). In the present work, the composition should range from $\text{Mn}(\text{II})\text{Fe}_2\text{O}_4$ (at $x = 0.18$) to $\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_4$ at $x = 0.55$; in the latter material, some Mn is probably in the trivalent state.

In dilute suspensions (1 g ferrihydrite/liter), only Mn-goethite formed at values of $x < 0.15$; jacobite first appeared at $x = 0.18$ (Figure 2, curve A). A tenfold increase in suspension concentration promoted the formation of jacobite and led to its first appearance at $x = 0.1$ (Figure 2, curve B). Subsequent results refer to the 1 g/liter suspension.

Effect of Mn(III) vs. Mn(II)

The majority of experiments were carried out using divalent Mn. If Mn(III) replaced Mn(II), the formation of jacobite was markedly suppressed. The predominant reaction product was Mn-goethite, although with increasing Mn(III) concentration, manganese oxides were also produced (Table 1). With the addition of

Table 2. Effect of source of Mn on degree of incorporation of Mn in Mn-goethite.¹

Source of Mn	Mn (Mn + Fe)	$\frac{(Mn_i - Mn_o)}{[(Mn_i - Mn_o) + (Fe_i - Fe_o)]}$
Mn(II) nitrate coprecipitated	0.15	0.14
Mn(II) nitrate added to ferrihydrite	0.15	0.08
Mn(III) acetate coprecipitated	0.15	0.07

¹ $Mn/(Mn + Fe)$ = mole fraction Mn added at the start of the transformation; $(Mn_i - Mn_o)/[(Mn_i - Mn_o) + (Fe_i - Fe_o)]$ = degree Mn substitution in goethite.

more than 30 mole % Mn(III), a 7-Å phyllosmanganate appeared in the product (Figure 1c), and at $x = 0.5$, small amounts of Mn_3O_4 formed as well. At $x = 1.0$ the product consisted of the 7-Å phyllosmanganate and a trace of Mn_3O_4 .

Effect of temperature, order of precipitation, and seeding

Increasing the reaction temperature from 70° to 90°C did not enhance the formation of jacobsonite, nor did it promote the formation of hematite. Mn-goethite and jacobsonite grown at 90°C were less crystalline than oxides grown at 70°C, as indicated by the broader XRD peaks of the higher temperature products.

At low additions of Mn(II), the order of precipitation did not influence the reaction product; with as much as 15 mole % Mn(II), only Mn-goethite formed regardless of the order of precipitation. At higher concentrations of Mn(II), the amount of jacobsonite in the product was lower if Mn(II) was added to ferrihydrite instead of being coprecipitated with Fe(III). For example, at $x = 0.36$, 90% of the product from a coprecipitated system was jacobsonite, compared with 30% for a system in which Mn(II) was added after precipitation.

Seeding Mn-ferrihydrite with 10% (by weight) goethite increased the proportion of goethite to jacobsonite in the product. At $x = 0.3$, seeding increased the amount of goethite formed to 85% (25% without seeding). At even higher values of x , the effect of seeding appeared to be outweighed by the high level of Mn(II) in the system. Seeding with 10% jacobsonite (at $x = 0.15$) did not result in the formation of additional jacobsonite.

Hematite

Even 5×10^{-4} M Mn(II) (i.e., $x = 0.05$) suppressed hematite at pH 11. The inhibiting effect increased with rising concentration of Mn(II). This behavior contrasted with that of Al(III); 2×10^{-3} M Al strongly promoted hematite at pH < 12.2 (control, pH < 11.3).

The earlier results of Fischer and Schwertmann (1975) suggest that as oxalate promotes hematite formation

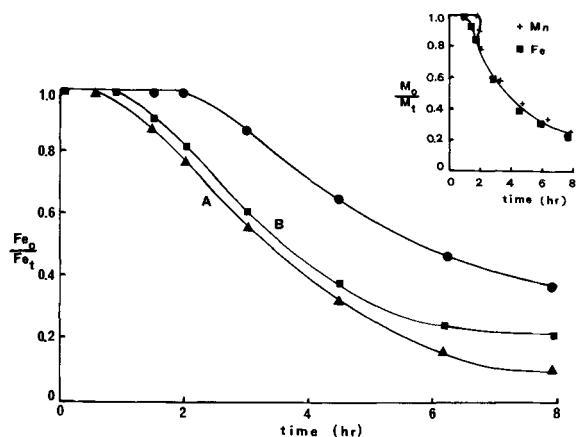


Figure 3. Fe_o/Fe_t as a measure of the degree of transformation of Mn-ferrihydrite coprecipitates (Mn/(Mn + Fe) mole fraction = 0.15) into Mn-goethite vs. time (Fe_o = oxalate soluble Fe, Fe_t = total Fe). pH 12.5, 70°C. (A) control; (B) with Mn(II); (C) with Mn(III). Inset: Mn_o/Mn_t and Fe_o/Fe_t vs. time for system with Mn(II) (Mn_o = oxalate soluble Mn, Mn_t = total Mn).

at pH 8, the inhibiting effect of Mn might be overcome by the presence of oxalate. An attempt, therefore, was made to grow pure Mn-hematite from coprecipitates of Mn(II) oxalate and Fe(III) nitrate (Table 1).

At pH 8 and at $x \leq 0.05$, pure, well-crystallized Mn-hematite was obtained. Less well crystallized Mn-hematite was produced at higher values of x . At $x = 0.5$, the main product was hematite.

Oxalate promotes hematite formation because it adsorbs on ferrihydrite and serves as a template for the nucleation of hematite (Fischer and Schwertmann, 1975). The hematite-promoting effect decreases with rising pH because at pH > 9–10, adsorption of oxalate on iron oxides is negligible (cf. Parfitt *et al.*, 1977). At pH 11 and at $x = 0.15$, only Mn-goethite formed. At the same pH and at $x = 0.5$, the product consisted mainly of jacobsonite and traces of goethite and hausmanite.

Incorporation of Mn in goethite and hematite

Chemical analysis of coprecipitates of Mn(II) and Fe(III) showed that at $x < 0.15$, the bulk of the Mn added was incorporated in goethite (Table 2). XRD line shifts also indicated that substitution of Mn in goethite had taken place: for example, for $x = 0.15$, $d(111) = 2.435$ Å and $d(020) = 5.00$ Å. The maximum level of incorporation was ~15 mole %, which is in accord with the results of Stiers and Schwertmann (1985). Additional Mn formed a separate Mn phase.

Addition of Mn after precipitation of ferrihydrite led to incorporation of only about half the original Mn(II) in goethite (Table 2). No detectable Mn remained in solution after the transformation of ferrihydrite to Mn-goethite; thus the additional Mn was probably ad-

sorbed on the Mn-goethite (no jacobsonite was present). This adsorbed Mn could be extracted by a brief acid/oxalate treatment, whereas extraction of Mn incorporated in the goethite required complete dissolution of the goethite with HCl. Incorporation of Mn in goethite was much less if Mn(III) rather than Mn(II) was coprecipitated with Fe(II) (Table 2). Here again, about half of the Mn added to the system was adsorbed on the goethite.

Incorporation of Mn in goethite caused the color to darken. Unsubstituted goethite was yellow, but even as little as 1 mole % Mn produced an olive color, and highly substituted goethite was gray.

The maximum amount of Mn that could be incorporated in hematite was about 5 mole %. Below $x = 0.05$, almost all Mn added to the system was incorporated in the hematite, whereas at higher Mn concentrations, additional Mn was adsorbed on the surface of the oxide. Mn-substituted hematite was almost black.

The ability of goethite to accommodate more than twice as much Mn as did hematite is due to the higher occupancy of octahedral cation sites in the hematite structure; more Mn can be accommodated and still be surrounded by Fe nearest neighbors (thereby minimizing lattice strain) in goethite than in hematite, as has also been shown for aluminous goethites and hematites (Schwertmann, 1985).

Kinetics

The rate of transformation of ferrihydrite in the presence of as much as 1.5×10^{-3} M Mn(II) ($x = 0.15$) was slightly lower than that of the control (Figure 3). Both during and after the reaction, no Mn was detected in solution; hence, it must have been taken up by the solid phase. Incorporation of Fe and Mn into goethite was congruent over the bulk of the reaction, although at the beginning of the transformation, Mn was incorporated less readily than Fe (Figure 3, inset). This initial discrepancy arose because Mn released by dissolution of ferrihydrite before goethite had nucleated, reabsorbed on the remaining ferrihydrite.

A plot of the extent of transformation of ferrihydrite (expressed as Fe_o/Fe_t) vs. time shows an initial induction period which corresponds to the stage during which goethite nuclei are forming (Cornell and Giovanoli, 1985). If Mn(III) replaced Mn(II), the induction period lengthened; at pH 12.5, it increased from 0.5 to 2 hr (Figure 3). Experiments in which seed crystals of goethite (10% by weight) were added to the suspension confirmed that Mn(III) interfered with the nucleation of goethite. Seeding reduced the induction time to the same value as for the control; it did not, however, accelerate the subsequent reaction, indicating that there was interference in crystal growth as well as nucleation.

In dilute suspensions (1 g ferrihydrite/liter), the transformation of ferrihydrite into more crystalline

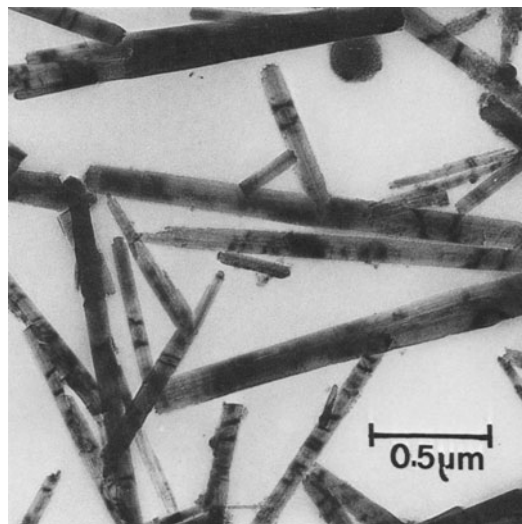


Figure 4. Transmission electron micrographs of Mn-goethite (15 mole % Mn) grown at pH 12.5, 70°C.

products was essentially complete within 48 hr. In more concentrated suspensions, small amounts of ferrihydrite (10–15%) persisted for longer periods. Kinetic measurements were only made for systems for which the entire reaction product was Mn-goethite. The increase in the proportion of jacobsonite in the product with increasing x indicates, however, that higher levels of Mn(II) retard goethite formation.

Crystal morphology

Mn-goethites. Low levels of Mn(II) ($x \leq 0.1$) led to the formation of well-developed acicular crystals. Incorporation of small amounts of Al in the goethite structure also improves crystal growth (Schulze and Schwertmann, 1984). Mn-goethites with the maximum degree of substitution retained the acicular habit, whereas Al-goethites with ≥ 15 mole % substitution commonly develop a platy morphology (Mann *et al.*, 1985).

Higher levels of both Mn(II) and Mn(III) in the system interfered with the growth of goethite as indicated by the numerous long, thin crystals (as long as $2 \mu\text{m}$) having average width/average length ratios of < 0.1 (Figure 4). Goethite grown at $x \geq 0.2$ contained etch pits and had poorly developed or ragged ends (Figure 5). Imperfections in the crystals increased with increasing x , although the level of substitution in Mn-goethite did not increase. Furthermore, goethites grown in Mn(III) systems contained more irregularities than those grown in Mn(II) systems of similar values of x , despite less substitution. The imperfections observed in goethites grown in the presence of Mn were probably the result of adsorbed, rather than incorporated Mn. Somewhat similar effects have been observed for goethites grown at $[\text{OH}^-] = 2$ M and have been attributed to

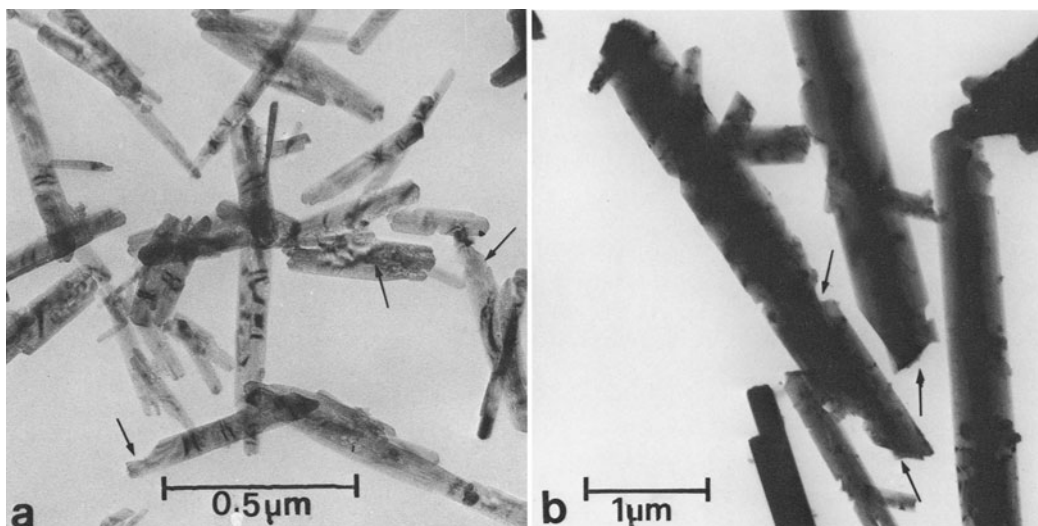


Figure 5. Transmission electron micrographs of Mn-goethites grown (a) in an Mn(II) system of $\text{Mn}/(\text{Mn} + \text{Fe}) = 0.4$; (b) in an Mn(III) system with $\text{Mn}/(\text{Mn} + \text{Fe}) = 0.25$; pH 12.5, 70°C. Imperfections are arrowed.

interference in growth by OH^- (Cornell and Giovanoli, 1985).

The presence of Mn promoted twinning of goethite, mainly as star-shaped and dendritic twins. Epitaxial twins (i.e., goethite outgrowths on hematite centers) were not observed because there was no hematite in the product. Mn(II) promoted twinning in the pH range 11–12 (Figure 6a), although high levels of x (e.g., 0.3) led to some twin formation at higher pH. Levels of Mn(III) greater than $x = 0.15$ enhanced twin formation as high as pH 13 (Figure 6b).

Dendritic twins (i.e., acicular crystals with two or

three outgrowths) were rare in the control system and have been observed mainly when high levels of NaNO_3 (5 M) were present (Cornell and Giovanoli, 1985); accommodation of impurities can promote twinning (Azaroff, 1960). Accordingly, adsorbed Mn species were probably responsible for the dendritic twinning of Mn-goethites.

Figure 7a shows Mn-goethites ($x = 0.15$) that were grown at pH 12 in the presence of 10^{-4} M silicate ion. In natural systems, many different interfering species, including Si, are present and may interact to modify crystal morphology. The presence of silicate ion retards

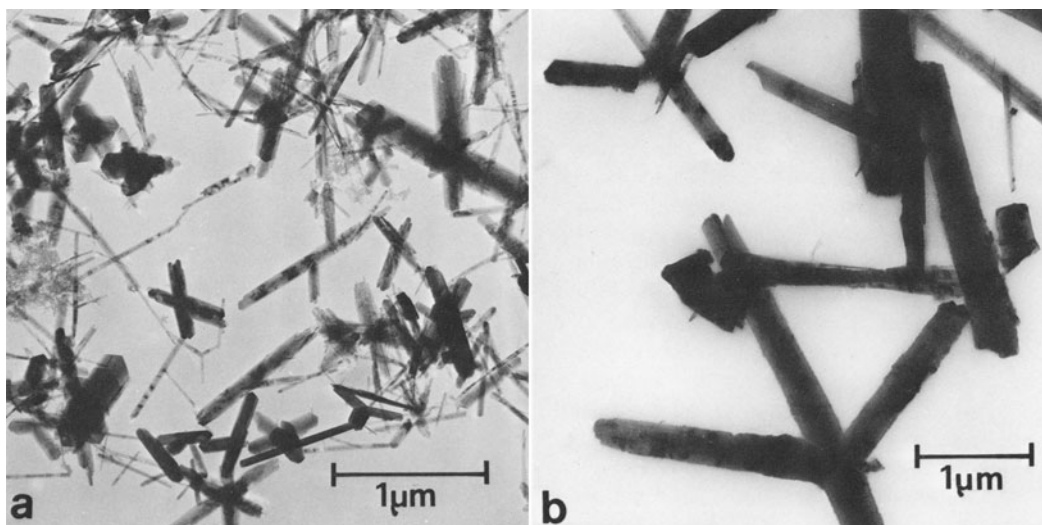


Figure 6. Transmission electron micrographs of mixtures of twinned and acicular goethites (a) grown in Mn(II) system ($\text{Mn}/(\text{Mn} + \text{Fe}) = 0.15$), pH 11.3, 70°C; (b) grown in Mn(III) system ($\text{Mn}/(\text{Mn} + \text{Fe}) = 0.15$), pH 12.7, 70°C.

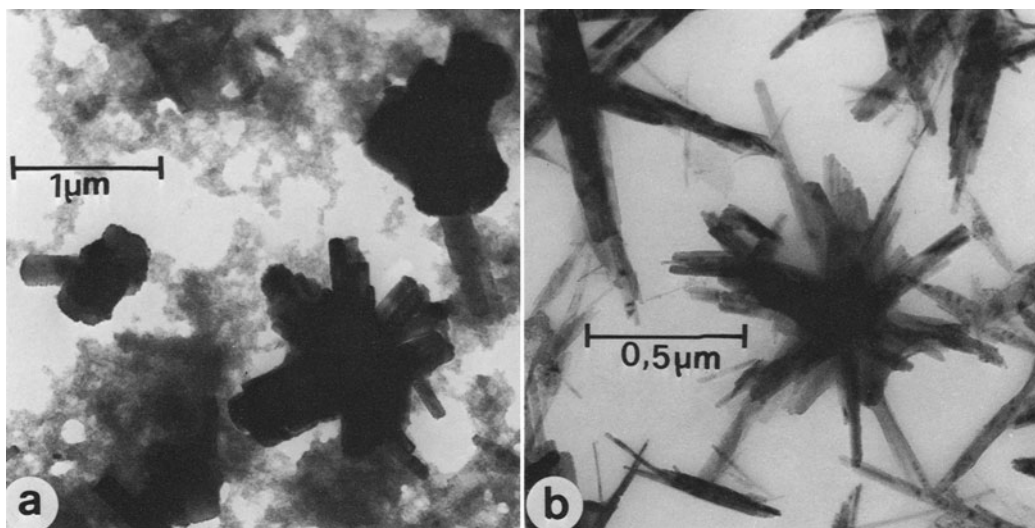


Figure 7. Transmission electron micrographs of Mn-goethites ($Mn/(Mn + Fe) = 0.15$) (a) grown in the presence of 10^{-4} M silicate ion, pH 12, 70°C (shapeless background material is ferrihydrite); (b) grown in the presence of 2 M NaNO_3 , pH 12.5, 70°C .

crystallization (indicated by the presence of unconverted ferrihydrite after 60-hr reaction time; cf. Cornell *et al.*, 1987). The combined effect of the silicate ion and Mn was to produce large (as much as $1\text{-}\mu\text{m}$ diameter), chunky, twinned goethites. Mn-goethites grown in the presence of 2 M NaNO_3 were also extensively twinned (Figure 7b); in this system, star-shaped twins with numerous arms predominated.

Jacobsite. In addition to needles of goethite, the TEM in Figure 8 shows cubes and bipyramids of jacobsonite. The latter crystals are similar in appearance to the habit of Mn_3O_4 . In some experiments, jacobsonite crystals showed outgrowths of what appeared to be goethite, suggesting that jacobsonite may serve as a seed for goethite.

Mn-hematite. Mn-hematite grown at $x = 0.05$ consisted of round or ellipsoidal platelets having a granular surface (Figure 9a). As x increased to 0.15, the ellipsoidal shape of the crystals became more pronounced and the surfaces more granular. The habit of the crystals can be attributed to the presence of oxalate, rather than to the incorporation of Mn (Fischer and Schwertmann, 1975).

DISCUSSION

Mn-goethite formed, like unsubstituted goethite, by dissolution of ferrihydrite followed by nucleation and growth of goethite in solution. Although some of the Mn in the Mn-ferrihydrite coprecipitate might be expected to have been oxidized to Mn(III), the presence of jacobsonite as one of the reaction products indicates that the bulk of the Mn associated with ferrihydrite is in the divalent form. Dissolution of ferrihydrite re-

leased Mn and Fe species (probably $\text{Fe}(\text{OH})_4^-$ and $\text{Mn}(\text{OH})_3^-$) into solution. Adsorption of $\text{Mn}(\text{OH})_3^-$ on goethite was probably followed by oxidation at the surface to Mn(III) and incorporation into the goethite structure. Adsorption of $\text{Mn}(\text{OH})_3^-$ on goethite should have been competitive with that of $\text{Fe}(\text{OH})_4^-$ because both species are monovalent (cf. Schwertmann and Murad, 1983). Kinetic studies showed that, except during the initial stage of the reaction, uptake of Fe(III) and Mn(II) species by goethite was congruent. During the initial stage, when goethite nuclei were forming,

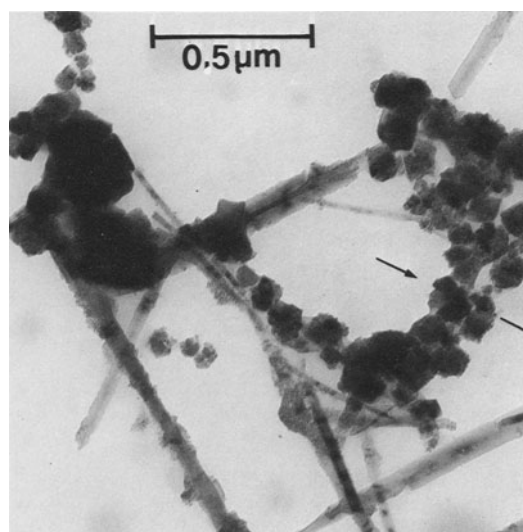


Figure 8. Transmission electron micrograph of a mixture of jacobsonite (arrowed) and Mn-goethite. $Mn/(Mn + Fe) = 0.36$, pH 12, 70°C .

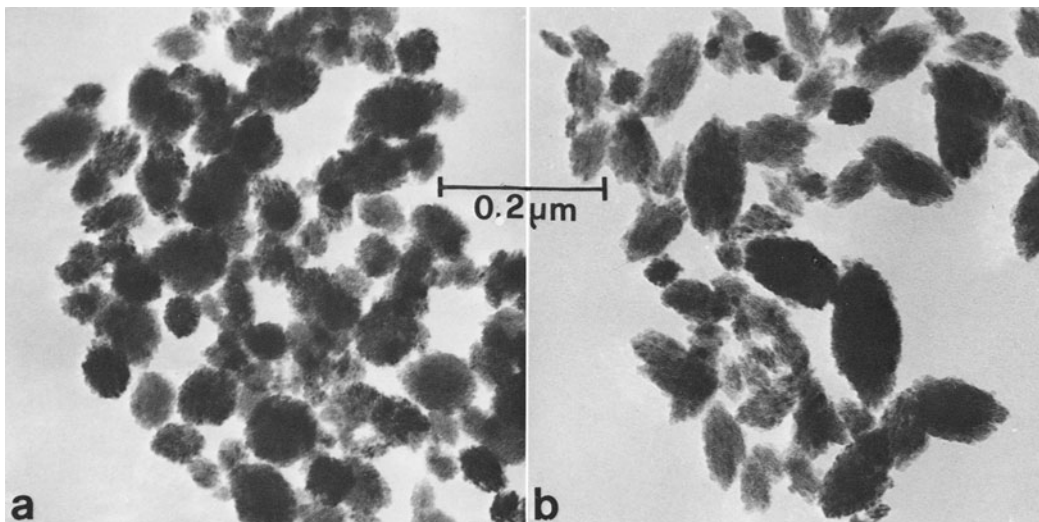


Figure 9. Transmission electron micrographs of Mn-hematite grown at pH 8 (a) $\text{Mn}/(\text{Mn} + \text{Fe}) = 0.05$; (b) $\text{Mn}/(\text{Mn} + \text{Fe}) = 0.15$.

dissolved Mn(II) species apparently re-adsorbed on ferrihydrite.

In the present experiments, oxygen was not passed into the system during the transformation reaction. The transformations were carried out in closed vessels at 70°C ; hence, $p\text{O}_2 \leq 0.2$ atm. Slow oxidation could still have taken place under these conditions, being promoted by high $[\text{OH}^-]$ and high temperatures and, in addition, being catalyzed by the presence of solids such as goethite (Stumm and Morgan, 1981; Davies, 1984). Probably, small amounts of Mn(II) released by slow dissolution of ferrihydrite were adsorbed and oxidized at the goethite surface quite readily, but larger quantities (i.e., higher x), allowed a separate Mn(II) phase to be formed.

Jacobsite became competitive with goethite as the amount of Mn(II) in the system increased. In jacobsonite, Mn is in the divalent form, and the essential prerequisite for jacobsonite formation appears to be a high enough level of dissolved Mn(II). Comparison with mechanisms by which both Fe_3O_4 and Mn_3O_4 form in alkaline media suggests that jacobsonite formed by interaction of dissolved Mn(II) with ferrihydrite (Tamura *et al.*, 1981; Giovanoli, 1976). Support for this hypothesis comes from a number of observations. Neither increasing the temperature of synthesis, nor pHs of 7–8 promoted jacobsonite formation; both factors should have favored jacobsonite if it formed by an aggregation-rearrangement mechanism (similar to that by which hematite forms) within ferrihydrite. Furthermore, jacobsonite was favored by high pH which promotes dissolution of ferrihydrite and release of Mn(II) species. Although seeding should have promoted the transformation if it took place in solution, such an effect was not noted for jacobsonite. Therefore, jacobsonite

probably nucleated in the water layer adsorbed on the surface of the ferrihydrite in the same way that Mn_3O_4 nucleates in the water layer on $\text{Mn}(\text{OH})_2$ (Giovanoli, 1976).

If Mn was added as Mn(III) instead of Mn(II), substitution of Mn in goethite was reduced and, in addition, jacobsonite was suppressed. In a Mn(III) system, dissolution of Mn-ferrihydrite released Mn(III). This species is unstable in solution, however, and probably disproportionated to equal amounts of Mn(II) and Mn(IV). The Mn(II) was incorporated in goethite, but as it accounted for only half the total Mn in the system, incorporation at any given x was less than if Mn had been added in the divalent form. Furthermore, a higher initial concentration of Mn(III) was necessary for the production of sufficient Mn(II) for the formation of an Mn(II) oxide; neither jacobsonite nor hausmanite formed at $x < 0.5$. At $x > 0.3$, the Mn(IV) produced by disproportionation of Mn(III) gave rise to a 7-Å phyllo-manganate. At lower x , Mn(IV) probably adsorbed on the Mn-goethite, possibly as a noncrystalline coating. It may be this species that was responsible for the particularly large number of imperfections and also the dendritic twinning in goethites grown in a Mn(III) system.

The lesser incorporation of Mn in goethite if Mn(II) were added to ferrihydrite instead of being coprecipitated with it may have been due to a greater proportion of Mn adsorbed on ferrihydrite being oxidized (because of its mode of adsorption), thus reducing the concentration of Mn(II) available for adsorption (and subsequent oxidation and incorporation) on goethite.

Stiers and Schwertmann (1985) showed from the continuous change in unit-cell size between goethite and groutite (α - $\text{Mn}(\text{III})\text{OOH}$) that substituted Mn is

in the trivalent rather than the divalent state in goethite. In view of the larger radius of Mn(II) (0.96 Å) compared with that of Mn(III) (0.79 Å) or Fe(III) (0.78 Å) (Shannon and Prewitt, 1969), the presence of Mn(III) in the goethite structure is to be expected. Nevertheless, Mn(III) does not fit as readily into the goethite structure as does Fe(III) because owing to its four d electrons, Mn(III) has a tetragonally distorted coordination sphere. This distortion is reflected in the increase in b_0 as the level of Mn substitution rises (Stiers and Schwertmann, 1985). The goethite structure is made up of double chains of $\text{Fe}(\text{O},\text{OH})_6$ octahedra parallel to the c axis. The distortion caused by the presence of Mn(III) in this type of structure can be expressed as the ratio of the undistorted to the distorted edges of the octahedron i.e., a''/a' (Feitknecht *et al.*, 1960; Giovanoli and Stähli, 1970). Here, a' is the length of the octahedron along the c axis, whereas a'' , the distorted edge, has a length $a'' = \frac{1}{2}\sqrt{b^2/4 + c^2}$. The ratio a''/a' is 0.964 for unsubstituted goethite and 1.058 for groutite. Using the unit-cell dimensions given by Stiers and Schwertmann (1985) for their most Mn-rich goethite, a''/a' for Mn-goethite is 0.97. To be significant, this ratio should be greater than 1.0; the low value for Mn-goethite can be attributed to the comparatively low level of substitution.

Mn behaved rather differently from Al in its effect on the transformation of ferrihydrite. Only half as much Mn as Al was accommodated in goethite or hematite, probably due to the distorted coordination sphere of Mn(III). Another difference lies in the end product. At high levels of both Al and Mn, phases other than goethite (or hematite) can be produced; however, gibbsite and bayerite only appear in Al-ferrihydrite systems at pH 7–8. At pH 12, they dissolve and much Al remains in the supernatant liquid (Lewis and Schwertmann, 1979). Jacobsite, on the other hand, precipitates at high pH.

Unlike Al, Mn suppressed the formation of hematite. The reasons for this are not entirely clear. Structural factors may act against hematite. No Mn compound having a corundum structure exists, perhaps because the high occupancy of cation sites in this structure is not compatible with the accommodation of Mn(III) with its distorted coordination octahedron.

Mn substituted goethites are rare in natural systems; only one reference to such goethites appears to exist (Thiry and Sornein, 1983). The natural Mn-goethites mentioned by these authors appear to have formed from the Fe(II) rather than the Fe(III) system. In the present work, preliminary experiments with the Mn(II)/Fe(II) system have shown that goethites with 2–3% Fe replaced by Mn can be prepared under milder conditions than from ferrihydrite/Mn systems; from aerated Fe(II) sulphate/Mn(II) nitrate suspensions (pH 5–7, 25°C), well-formed crystals of Mn-goethite developed in 24 hr. These results suggest that the Fe(II) pathway may be the predominant one in natural systems. Fur-

ther experiments with Fe(II)/Mn(II) systems are in progress.

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