TRANSFORMATION OF AKAGANÉITE INTO GOETHITE AND HEMATITE IN THE PRESENCE OF Mn

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Abstract—The interaction of Mn and akaganéite in neutral to alkaline media has been investigated using X-ray powder diffraction and transmission electron microscopy. Akaganéite transformed into goethite and/or hematite, whereas Mn precipitated as hausmannite and birnessite at pH > 12 and as manganite at pH 7.5–8.5. Mn influenced the kinetics of the transformation of akaganéite: the rate-determining step, i.e., the dissolution of akaganéite, was retarded by adsorbed Mn species. Hematite formation was not suppressed. By catalyzing the air oxidation of adsorbed Mn(II), akaganéite promoted the formation of birnessite. Akaganéite did not retard recrystallization of the Mn phases. The incorporation of Mn in the structure of goethite formed in this system was negligible, and jacobsite ($MnFe_2O_4$) did not form. The formation of mixed Mn-Fe phases appeared to require a ratio of Mn^{2+} : Fe $_{total}$ > 0.02; this ratio was not achieved due to the oxidation of Mn^{2+} at the akaganéite surface.

Key Words—Akaganéite, Goethite, Hematite, Manganese, Transmission electron microscopy, X-ray powder diffraction.

INTRODUCTION

In natural systems, iron oxides seldom form in isolation; the precipitation of both crystalline and noncrystalline iron oxide phases is commonly influenced to some degree by the presence of foreign ions (Carlson and Schwertmann, 1981; Schwertmann and Murad, 1988). The effects of soluble foreign species on the crystallization of Fe oxides from ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) has been investigated in the laboratory (Lewis and Schwertmann, 1979; Cornell and Schwertmann, 1979; Cornell 1985; Cornell *et al.,* 1987; Cornell and Schneider, 1989). These studies have provided valuable information about the mechanisms of crystallization of two of the most widespread iron oxides in the environment, goethite (α-FeOOH) and hematite (α-Fe_2O_3). Less attention has been given as yet to interactions between solid phases and the effects of such interactions on recrystallization processes although both crystalline and noncrystalline solid phases commonly coexist in soils.

In recent years, Mn-Fe interactions, particularly the influence of Mn from different sources on the formation of iron oxides, has attracted considerable interest (Stiers and Schwertmann, 1985; Cornell and Giovanoli, 1987; Krishnamurti and Huang, 1988, 1989; Ebinger and Schulze, 1989). In soils and sediments Mn and Fe oxides may intimately coexist (Halbach *et al.,* 1982), and this coexistence, together with the chemical similarity of the elements is the reason for the interest in their interactions.

A previous study showed that poorly ordered coprecipitates of Mn and ferrihydrite transformed in alkaline media to Mn-goethite and a spinel phase, jacobsite ($MnFe_2O_4$) (Cornell and Giovanoli, 1987). The present work considered the effect of Mn oxides on the kinetics and products of the transformation of a *crystalline* iron oxyhydroxide, akaganéite (β-FeOOH), over the pH range 7.5–13. The objective here was to compare recrystallization reactions in this system with similar reactions in the ferrihydrite-Mn system in order to obtain further details of the mechanisms of formation of iron oxides. Two specific questions were: (1) does the effect of Mn on the transformation of akaganéite depend on whether Mn is added as Mn^{2+} solution or as a crystalline solid, hausmannite (Mn_3O_4); and (2) does Mn directly suppress hematite formation. In the absence of Mn, akaganéite transforms at pH > 12 into goethite and/or hematite (Cornell and Giovanoli, 1990). Mn could interfere in hematite formation either by stabilizing its precursor or by directly hindering nucleation of hematite. Inasmuch as hematite forms from ferrihydrite by a solid-state transformation (Schwertmann and Fischer, 1966) and from akaganéite by a dissolution-reprecipitation process (Cornell and Giovanoli, 1990), comparing the effect of Mn on the recrystallization of both ferrihydrite and akaganéite could indicate at what stage Mn interferes in the formation of hematite.

EXPERIMENTAL METHODS

The transformation experiments were carried out by reacting 0.1 g of akaganéite in 100 ml of KOH at 70°C for as long as 1200 hr. The concentration of KOH ranged from 0.1 to 1 M. Experiments were also carried

out at pHs between 7.5 and 8.5; here, the pH was adjusted with KOH. Mn was added to the system as Mn(II) nitrate solution (Mn/(Mn + Fe) = 0.1 to 0.5) or as hausmannite (0.1 g, i.e., Mn/(Mn + Fe) = 0.5). The transformation of akaganéite to goethite and hematite is slow, even in 0.01 M KOH and at 70°C (Cornell and Giovanoli, 1990); at pHs close to those in natural systems, the reaction may require years to reach completion, particularly in the presence of retarding species. Transformation of a related iron oxyhydroxide, ferrihydrite, to hematite and goethite at room temperature and pH 7–8, required over one year to reach completion (Schwertmann and Murad, 1983). Therefore, to obtain transformation products within a reasonable time period and also to facilitate comparison with the previous study of the transformation of akaganéite alone (Cornell and Giovanoli, 1990), the majority of experiments was carried out at high pH. Experiments performed at pH 7.5–8.5 suggested that similar transformation mechanisms were involved both in highly alkaline media and at neutral pH. The reaction products were washed, dried at 50°C, and examined by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

XRD patterns were obtained using a Guinier-Enraf camera (Mk IV) with $FeK\alpha_1$ radiation. The proportions of goethite and hematite in the product were estimated by comparison with a series of standards made by mixing known amounts of goethite and hematite, using the 110 and 111 reflections of goethite and the 102 reflection of hematite.

The kinetics of the transformation were followed using a series of Mn/akaganéite suspensions; at predetermined intervals, a sample was removed for XRD and TEM examination. The extent of the transformation was expressed in terms of the extent of conversion of akaganéite. The proportion of akaganéite remaining at any time was estimated with the aid of a calibration curve made by mixing known amounts of synthetic akaganéite, goethite, and hematite. The 110 reflection of akaganéite was used.

TEMs were obtained with a Hitachi H-600-2 (100 kV) electron microscope. The samples were dispersed ultrasonically in twice-distilled water, and a drop of suspension was dried on a carbon-coated bronze grid.

The total amount of Fe and Mn in the Mn-goethite product of the transformation was found by dissolving the reaction product completely in 4 M HCl. Any separate Mn phase or surface Mn adsorbed on the Mn-goethite was removed by a 2-hr extraction in the absence of light with 0.2 M oxalic acid-ammonium oxalate buffer solution (pH 3); this treatment left the Mn-goethite intact (cf. Stiers and Schwertmann, 1985; Cornell and Giovanoli, 1987). The extent of Mn incorporation in goethite was taken as the difference between the oxalate soluble Mn (Mn_o, i.e., Mn coming from adsorbed, surface Mn and any pure Mn phase)

and the total Mn, Mn_t, in the sample. The degree of Mn substitution was expressed as the ratio,

$$(Mn_t - Mn_o)/[(Mn_t - Mn_o) + (Fe_t - Fe_o)].$$

Fe and Mn were measured using atomic absorption spectroscopy. Ultraviolet spectra were measured using a Perkin Elmer $\lambda 3$ spectrophotometer.

Spindle-shaped crystals of akaganéite (BET surface area = 30 m^2/g) were prepared by hydrolyzing 0.1 M $FeCl_3$ solution at 60°C for 8 days. This material was used for most experiments. A high surface area (111 m^2/g) sample of rod-shaped akaganéite crystals was prepared by heating a partly hydrolyzed $FeCl_3$ (OH:Fe = 2.75) system at 60°C for 8 days. Hausmannite was prepared by passing O_2 through a suspension formed by mixing 0.5 M $MnCl_2$ with 1 M NaOH (OH:Mn = 2) at 60°C. All oxides were washed by dialysis and dried at 50°C.

Transformation experiments with ferrihydrite were carried out by coprecipitating Mn(II) nitrate solution and ferric nitrate solution (Mn/(Mn + Fe) = 0.1) with 1 M KOH to pHs between 12 and 13.9. The coprecipitates were held in closed polypropylene bottles at 70°C for 60 hr. In other experiments, Mn(II) nitrate solution was added to a suspension of ferrihydrite with a pH of 11 and the system held at 70°C for 60 hr. The reaction products were washed and dried at 50°C.

Surface areas were measured by the BET method using N_2.

RESULTS

Interactions between akaganéite and Mn

Adsorption of Mn^{2+} on iron oxides in alkaline media is well documented (Hem, 1977; Davis and Morgan, 1989). In the present work, however, the exact level of adsorption of Mn on akaganéite could not be measured because a separate Mn phase (identified by XRD as pyrochroite, $Mn(OH)_2$) precipitated as well. During the entire transformation of akaganéite the concentrations of Mn and also Fe in solution were <0.02 ppm.

A suspension of akaganéite (pH > 12) to which Mn(II) nitrate solution was added turned blackish within 30 min. A suspension of akaganéite alone (pH 12), and also the precipitate resulting from addition of Mn(II) nitrate solution to KOH (0.01–1 M) in the absence of iron oxide, were brownish yellow and cinnamon colored, respectively. The suspension darkened only if Mn interacted with akaganéite. This darkening can be attributed to partial oxidation by dissolved oxygen of Mn(II) adsorbed on the surfaces of the akaganéite crystals: an iron oxide surface catalyzes air oxidation of adsorbed Mn(II) (Hem, 1977). If hausmannite (instead of Mn^{2+} solution) was added to an alkaline suspension of akaganéite, the suspension also darkened, but only after several hours. Hausmannite dissolved in KOH (Cornell and Giovanoli, 1988), and, presumably, the

Table 1. Reaction products in the akaganéite-Mn system.

Form of Mn added	pH	Products
none	13.9	Goethite
	13.0	Goethite, hematite (20%)
Mn^{2+}	13.9	Goethite, birnessite, hausmannite
$(Mn/(Mn + Fe) = 0.5$	13.0	Goethite, hematite (50%), birnessite, hausmannite
$(Mn/(Mn + Fe) = 0.1$	7–8	Akaganéite,[1] manganite
Hausmannite	13.9	Goethite, birnessite

The reaction was carried out at 70°C.

[1] Akaganéite was not transformed during the period of the experiment (six weeks).

soluble Mn species released were readsorbed on the crystals of akaganéite where surface oxidation led to darkening of the system.

Oxidation of Mn(II) should produce Mn(III) and possibly Mn(IV). Some evidence for Mn(III) was obtained by immediately separating the blackish akaganéite from the suspension, washing and drying it, and carrying out an acid-oxalate extraction (pH 3). The extraction solution was initially a deep rose color and showed an ultraviolet absorbance band at $\simeq 500$ nm, which is indicative of the presence of an Mn(III)-tris-oxalate complex (Olliff and Odell, 1964). On exposure to light, the rose color gradually faded, (due to photochemical reduction of Mn(III) by oxalate) and a white precipitate of Mn(II) oxalate formed.

Reaction products (Table 1)

The transformation products of the akaganéite-Mn system were goethite, hematite, birnessite (a 7-Å phyllomanganate), hausmannite, and manganite (γ-Mn-OOH). No jacobsite ($MnFe_2O_4$) was detected in the product. The relative proportions of the different products depended on the pH of the system and on the source of Mn.

Akaganéite transformed into goethite in 1 M KOH and into a mixture of goethite and hematite at [KOH] < 0.1 M, regardless of whether or not Mn was present in the system. The amount of hematite in the transformation product increased as [OH⁻] decreased. Mn did not suppress the formation of hematite. High levels of Mn, in fact, appeared to promote additional hematite formation in 0.1 M KOH; with an initial Mn/(Mn + Fe) ratio = 0.5, the ratio of hematite/(hematite + goethite) in the product increased from 0.2 (no Mn present) to 0.5. Seeding akaganéite-Mn systems with
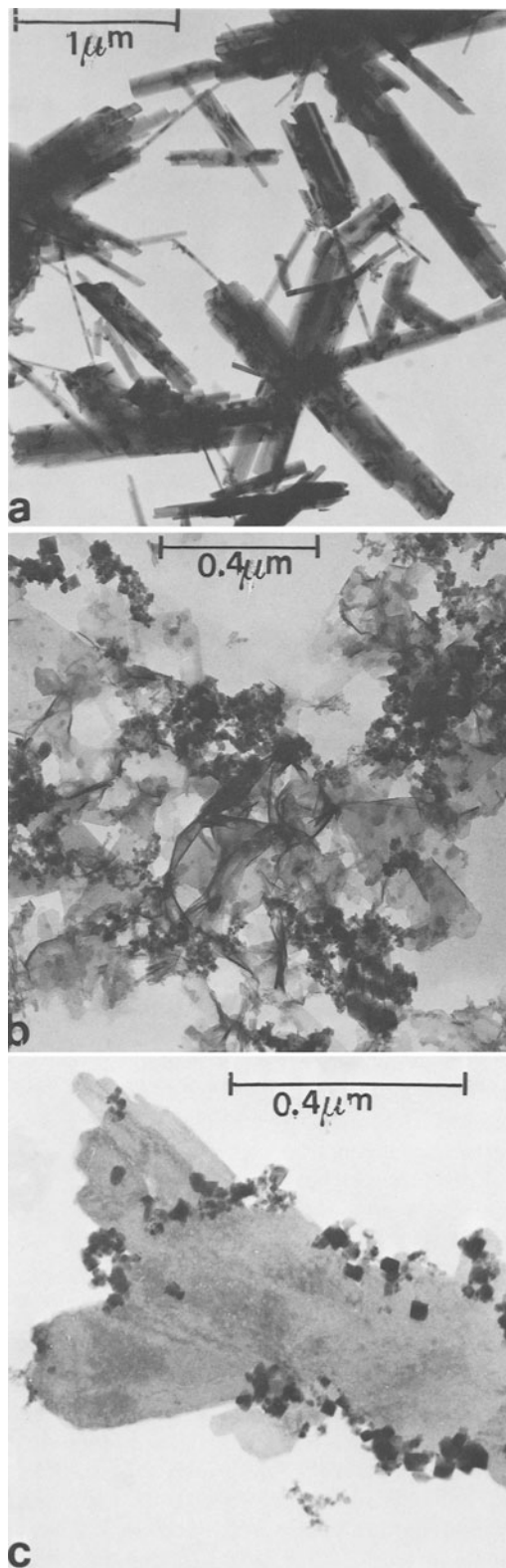

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Figure 1. Transmission electron micrographs of (a) goethite formed from akaganéite at Mn/(Mn + Fe) = 0.1, 1 M KOH, 70°C; (b) birnessite films and hausmannite cubes formed in the akaganéite-Mn system after 24 hr. 1 M KOH, Mn/(Mn + Fe) = 0.2 (Mn added as Mn^{2+}, 70°C; (c) as in (b) after 3 weeks. The birnessite has recrystallized to a thick, plate-like crystal.

goethite did not promote the formation of additional goethite.

In highly alkaline media, the Mn transformation products (with Mn(II) nitrate solution as the Mn source) were hausmannite and birnessite. If the source of Mn was hausmannite, this compound gradually recrystallized to birnessite. The XRD lines of these reaction products were weak compared to the XRD lines arising from goethite and hematite, even in systems having Mn/(Mn + Fe) = 0.5. The Mn products were, however, clearly visible in electron micrographs. The weak XRD lines presumably reflected the thinness of the birnessite platelets and the small size of the hausmannite cubes (Figure 1b), rather than the amount of product in the system. TEMs of samples taken during the earliest stages of the reaction showed that birnessite formed simultaneously with or even before hausmannite. Apparently, this birnessite formed by disproportionation from Mn(III) produced by oxidation of Mn(II) at the akaganéite surface: earlier studies (Cornell and Giovanoli, 1987) showed that addition of Mn^{3+} solution (0.01 M) to KOH (0.01–1 M) led to rapid precipitation of birnessite. In the present work, more birnessite formed initially in the presence of high-surface-area, than low-surface-area akaganéite, which is consistent with more extensive adsorption and, hence, oxidation of Mn(II) by the high-surface-area iron oxide.

In neutral to slightly alkaline media, the initial precipitate formed by addition of Mn^{2+} solution to the akaganéite suspension transformed to manganite within 24 hr, whereas the akaganéite remained unchanged for weeks.

Coprecipitates of Mn and ferrihydrite (Mn/(Mn + Fe) = 0.1) transformed over the pH range 12–12.9 into Mn-goethite. Addition of the same level of Mn^{2+} solution to ferrihydrite at pH 11 led to the formation of a mixture of Mn-goethite and 5–10% hematite, i.e., about the same level of hematite as in the absence of Mn.

Incorporation of Mn in goethite

Visually, the products of the akaganéite-Mn system (1 M KOH) consisted of a mixture of bright, yellow particles (goethite) and a dark-colored Mn phase. Chemical analysis indicated that uptake of Mn in the goethite structure was negligible, in accord with the color of the goethite; even 2–3 mole % Mn substitution gives goethite an olive color (Cornell and Giovanoli, 1987). On the other hand, Mn-goethite synthesized from ferrihydrite-Mn coprecipitates over the pH range 12–13.9 contained 8–9 mole % Mn. Over this pH range, therefore, pH had no effect on the ability of Mn to replace Fe in the structure of goethite.

Crystal morphology

Goethite formed by transformation of akaganéite in 1 M KOH grew as acicular crystals as long as 2.5 μm.

These crystals terminated in irregular or rectangular faces; some displayed intergrowths and extinction contours. Similar goethite crystals formed in the presence of Mn, but were usually dendritically twinned (Figure 1a). Hematite grew as large, thick platelets as much as 2 μm across both in the presence and absence of Mn. These large crystals gave rise to XRD patterns containing sharp lines.

TEM showed that on addition to an alkaline suspension of akaganéite, Mn^{2+} precipitated as round to hexagonal crystals of pyrochroite (Figure 2a). These crystals were replaced within hours by films of birnessite and cubes of hausmannite (Figure 2b). At this stage the akaganéite crystals appeared intact, but with time (several days) the ends of the crystals became frayed, and signs of surface attack were apparent (Figure 2c).

Hausmannite formed small bipyramids or cubes 0.01 to 0.14 μm across (Figure 1b). Birnessite formed initially as thin films or very thin plates $\simeq$100 Å in thickness and 2000–5000 Å across (Figure 1b), which with time, recrystallized to larger, plates several hundred Ångstroms thick (Figure 1c).

Kinetics

Even small amounts of Mn, e.g., Mn/(Mn + Fe) = 0.01, retarded the conversion of akaganéite to goethite and hematite to some extent. The degree of retardation increased with the level of Mn in the system. For Mn/(Mn + Fe) = 0.5, for example, the conversion of akaganéite to goethite in 1 M KOH was incomplete after four weeks, whereas in the absence of Mn, all akaganéite had transformed after 48 hr. Seeding these systems with goethite did not accelerate the transformation, indicating that Mn interfered by retarding the dissolution of akaganéite, not by hindering the nucleation of goethite. Further support for this mechanism comes from the observation that at any stage of the transformation, the level of Fe in solution was low ($\sim$0.02 ppm). This result agrees with earlier observations that the presence of Mn (at least to a Mn/(Mn + Fe) ratio of 0.2) did not retard the formation of goethite from ferrihydrite (Cornell and Giovanoli, 1987).

Figure 3 shows a plot of the extent of the transformation of akaganéite vs. time in 0.1 M KOH in both the presence and absence of Mn. The shapes of both plots are similar, but for Mn/(Mn + Fe) = 0.1, the overall reaction was retarded, again suggesting that Mn retards the dissolution of akaganéite.

Although the rates of recrystallization of the Mn phases were not quantified, TEMs taken at intervals during the conversion of akaganéite in systems with Mn/(Mn + Fe) = 0.5, indicated that birnessite and hausmannite formed within 24 hr, whereas even after one week, XRD and TEM indicated that little or no transformation of akaganéite had taken place. These results show that whereas Mn retarded the transformation of akaganéite, recrystallization of the Mn phas-
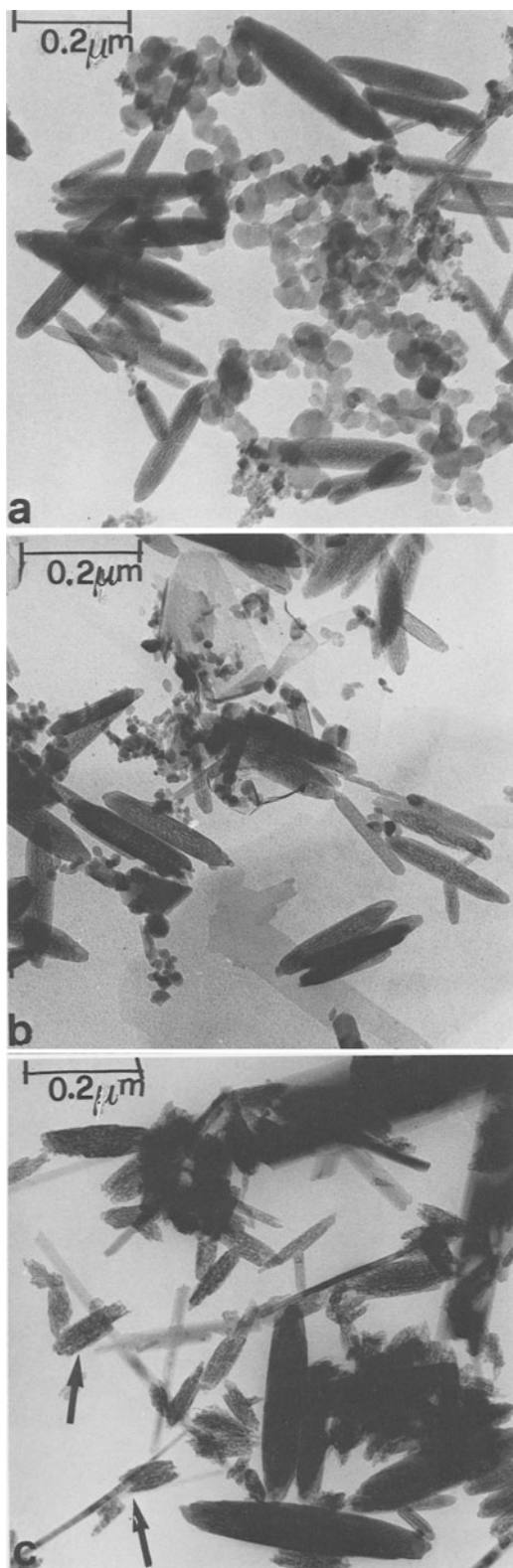
Figure 2. Transmission electron micrographs of (a) akaganéite (spindle crystals) and plates of pyrochroite after 1 hr interaction in 1 M KOH at 70°C; (b) as in (a) after 24 hr. The
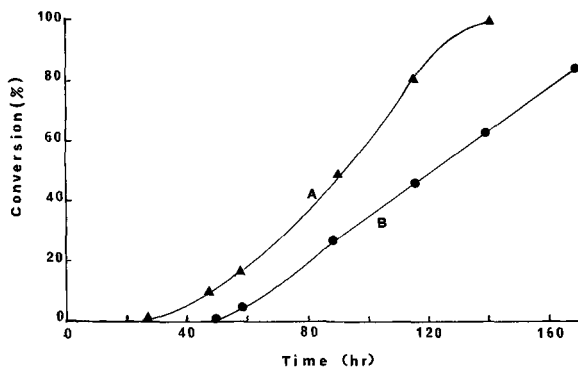

Figure 3. Extent of transformation of spindle-shaped akaganéite vs. time at 70°C in 0.1 M KOH; (A) control; (B) Mn/ (Mn + Fe) = 0.1. Mn added as Mn^{2+} solution.

es proceeded unhindered. Note that hausmannite started to recrystallize to birnessite almost at once and continued over weeks (*cf.* Cornell and Giovanoli, 1988). The transformation involved dissolution of hausmannite with the release of soluble Mn species, some of which adsorbed on akaganéite, thus retarding its dissolution over long periods.

Mn retarded the transformation of akaganéite whether it was added as Mn^{2+} solution or as well-crystallized hausmannite. In the former case, some Mn^{2+} immediately adsorbed on akaganéite and the remainder precipitated as pyrochroite, which subsequently dissolved, thereby providing a further source of Mn species available for adsorption on akaganéite.

DISCUSSION

The presence of even small amounts of Mn markedly retarded the transformation of akaganéite to goethite and hematite. The rate-determining step in the transformation process was the dissolution of akaganéite. Adsorbed Mn species retarded the dissolution process. Davies and Morgan (1989) showed that Mn adsorbs on goethite and on lepidocrocite (γ-FeOOH) as a binuclear surface species, i.e.,

$$\begin{array}{c} Fe\text{–}O \\ \diagdown \\ \qquad\qquad Mn; \\ \diagup \\ Fe\text{–}O \end{array}$$
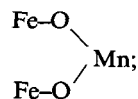
similar surface species should exist in the akaganéiteMn system. Although *bidentate* surface complexes may promote dissolution of an oxide, *binuclear* surface species appear to stabilize a substrate (Stumm *et al.,* 1983); this concept could account for the retarded dissolution of akaganéite in the presence of Mn.

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pyrochroite has been replaced by birnessite (films) and hausmannite (cubes); (c) partly dissolved crystals of akaganéite (arrowed) and some goethite after one week. 1 M KOH, 70°C, Mn/(Mn + Fe) = 0.1

Mn retarded the formation of hematite by retarding dissolution of akaganéite and, hence, release of soluble ferric species from which hematite nucleated. With high levels of Mn in the system, however, the amount of hematite in the reaction product actually increased relative to goethite, i.e., Mn did not directly suppress formation of hematite. This result, together with the observation that Mn did not suppress formation of hematite from ferrihydrite if Mn was added to ferrihydrite (and not coprecipitated with it), indicates that Mn does not influence hematite nucleation *directly*; instead Mn acts by influencing the rate of formation of the competing product, goethite. Hematite nucleates less readily than goethite (Cornell and Giovanoli, 1990). By retarding the dissolution of akaganéite, Mn reduces the supersaturation relative to goethite and, hence, its rate of nucleation, thus enabling hematite to form more competitively.

Cornell and Giovanoli (1987) reported that hematite did not form from ferrihydrite-Mn coprecipitates at pH > 10; they suggested that Mn directly suppressed hematite formation. In view of the present results, however, it now seems likely that in this system Mn promoted the competing product, goethite. In the ferrihydrite-Mn system, a certain amount of Mn(II) was oxidized to Mn(III) by dissolved oxygen (shown by the rose color of the oxalate extraction solution). Simultaneous reduction of some Fe(III) does not occur (Hem, 1977), but the distorted coordination sphere of the Mn(III) ions (Jahn-Teller effect) may have partly destabilized the ferrihydrite structure, thereby leading to more rapid dissolution and, hence, more rapid precipitation of goethite. Ferrihydrite consists of particles 200–400 Å in diameter containing some thousands of Fe atoms (Schneider, 1988); hence, in a ferrihydrite-Mn coprecipitate, a proportion of Mn atoms should be located on the internal sites. If Mn was added *to* ferrihydrite, on the other hand, all Mn was adsorbed at the surfaces of the ferrihydrite spheres; hence, destabilization due to internal Mn(III) ions did not occur, and hematite formation was competitive with that of goethite to the same extent as in the control system, i.e., to pH 11.3 (cf. Cornell and Giovanoli, 1985).

The formation of Mn phases was not retarded by the presence of akaganéite, in agreement with earlier observations that the recrystallization of hausmannite to birnessite proceeded without apparent interference in the presence of ferrihydrite (Cornell and Giovanoli, 1988). Akaganéite appeared, in fact, to promote the formation of birnessite from the initial precipitate of pyrochroite by catalyzing air oxidation of Mn(II) adsorbed at the iron oxide surface. The presence of the iron oxide, therefore, provided another route to birnessite formation, in addition to the more common one via recrystallization of hausmannite.

A feature of the akaganéite-Mn system was the separate precipitation of Mn and Fe phases; no Mn was incorporated in the goethite structure, and the Fe/Mn spinel, jacobsite, did not form, probably because of the low level of soluble divalent Mn species in the system. Incorporation of Mn in the goethite structure depends on the charge, valence, and ionic radius of the replacing ion (Goldschmidt, 1937). Although Mn is incorporated in the goethite structure as the trivalent ion (Stiers and Schwertmann, 1985), an essential preliminary step in the present reactions was apparently the adsorption of the divalent species, which was then oxidized at the surface of the goethite crystal. Cornell and Giovanoli (1987) showed that incorporation of Mn in the structure of goethite formed from ferrihydrite is greatly reduced if Mn is added to the system in the trivalent form. In the present investigation, the akaganéite surface provided a sink for soluble Mn released by the dissolution of the Mn phases, and adsorbed Mn(II) was rapidly oxidized to Mn(III).

The formation of jacobsite ($Mn(II)Fe(III)_2O_4$) also appears to require a certain threshold level of Mn^{2+} (Cornell and Giovanoli, 1987). This requirement was not met in the present investigation, presumably because Mn^{2+} was removed from the system by rapid oxidation at the surfaces of the solid phases. A similar situation occurs with ferrihydrite to which Mn^{2+} solution was added (Cornell and Giovanoli, 1987); jacobsite formation is greatly reduced, probably because much of the added Mn(II) was oxidized at the ferrihydrite surface. On the other hand, jacobsite formed from ferrihydrite-Mn coprecipitates. Although some Mn(II) was again oxidized, the proportion was probably lower because some Mn was located within the particles of ferrihydrite and, hence, was less accessible to oxidation.

SUMMARY AND CONCLUSIONS

In the akaganéite-Mn system, akaganéite recrystallized to goethite and hematite, whereas Mn formed hausmannite and birnessite at high pH and manganite in neutral to slightly alkaline media. The presence of Mn did not suppress formation of hematite. Mn appeared to influence hematite formation only indirectly through its effect on the rate of dissolution of the Fe precursor. The main effect of Mn was on the kinetics of the transformation of akaganéite; dissolution was retarded. Akaganéite, on the other hand, promoted the formation of birnessite by catalyzing the oxidation of Mn^{2+}.

Interactions between Mn and Fe oxides depended mainly on the rates of dissolution of the solid phases and on the surface properties of the oxides, i.e., whether adsorption of ions of the other element could take place. Mixed Mn-Fe phases formed from the ferrihydrite-Mn coprecipitates, but not in the akaganéite-Mn system. The formation of mixed phases required an $Mn^{2+}:Fe_{total}$ ratio in the system of >0.2, and this was not achieved because the akaganéite surface promoted the oxidation

of Mn^{2+}. If separate Mn(II) and Fe(III) phases recrystallize simultaneously, these two elements are apparently also separated in the reaction products.

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