

## INFLUENCE OF MANGANESE OXIDE MINERALS ON THE FORMATION OF IRON OXIDES<sup>1</sup>

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**Abstract**—The influence of manganese oxide minerals (cryptomelane, hausmannite, and pyrolusite) on the formation of iron oxides was studied in the  $\text{FeCl}_2\text{-NH}_4\text{OH}$  system at different Mn/Fe molar ratios (0, 0.01, 0.1, and 1.0) and pHs (3.0, 4.0, 5.0, and 6.0) by X-ray powder diffraction, infrared absorption, transmission electron microscopic, and chemical analyses. In the absence of Mn minerals, lepidocrocite ( $\gamma\text{-FeOOH}$ ) precipitated at pHs 5.0 and 6.0; however, no precipitate formed at lower pHs. All the Mn minerals studied promoted the precipitation of iron oxides and oxyhydroxides. In the presence of Mn oxides,  $\text{Fe}^{2+}$  was oxidized to  $\text{Fe}^{3+}$ , which hydrolyzed and precipitated as noncrystalline and/or different crystalline iron oxides and oxyhydroxides, depending on the nature of the Mn oxides present in the system. Simultaneously,  $\text{Mn}^{2+}$  was detected in solution after the reaction by electron spin resonance spectroscopy. The presence of cryptomelane and hausmannite resulted in the formation of akaganeite ( $\beta\text{-FeOOH}$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ), respectively. Thus, the effect of Mn oxides on the formation of Fe oxide minerals in the weathering zone merits attention.

**Key Words**—Akaganeite, Cryptomelane, Feroxyhyte, Hausmannite, Iron oxides, Manganese, Oxidation-reduction, Pyrolusite, Synthesis.

### INTRODUCTION

The nature of Fe oxide minerals in soils is of interest from the viewpoints of both pedogenesis and soil behavior. Six different crystalline Fe oxides<sup>2</sup> have been identified in soils (Schwertmann and Taylor, 1977; Murray, 1975), along with significant amounts of short-range ordered Fe oxides. Although these Fe oxides have rather simple chemical compositions, they differ considerably in their crystal structure and surface reactivity. They play a significant role in the pedogenesis and dynamics of soils and in the fate of nutrients and pollutants in soil systems. The effect of pedogenic environments on the formation and transformation of the crystalline Fe oxides was thoroughly reviewed by Schwertmann (1985). The presence of short-range ordered Fe oxides in soils reflects the influence of perturbing ions, such as citrate, phosphate, and silicate, on the crystallization processes of Fe oxides (e.g., see Schwertmann *et al.*, 1986).

The chemical similarity between Mn and Fe is reflected geologically in their common association in rocks of all kinds. The oxides of Mn are widely distributed in soils and sediments (Jenne, 1968). Birnessite, one of the most common Mn oxides in soils (McKenzie, 1972), promotes the formation of organic nitrogen complexes and humic substances (Shindo and Huang, 1982, 1984) and the oxidation of arsenite (Oscarson *et al.*, 1981). Oscarson *et al.* (1983) explained the differ-

ences in kinetics of oxidation of arsenite by three forms of  $\text{MnO}_2$  minerals on the basis of differences in their crystallinity and surface areas. Postma (1985) reported that the surface of birnessite and possibly other Mn(IV) oxides can limit the rate of the solution  $\text{Fe}^{2+}$ -Mn(IV) oxide interactions. Krishnamurti and Huang (1987) reported that the presence of birnessite perturbed the crystallization of lepidocrocite ( $\gamma\text{-FeOOH}$ ), leading to the formation of noncrystalline Fe oxides, in Fe(II) systems in the pH range 4–6. The influence of other Mn oxides, having different structural and surface properties, on the crystallization processes of Fe oxides still remains obscure.

The objective of the present study was to compare the influence of three Mn oxide minerals of widely different crystalline and surface properties, i.e., cryptomelane ( $\alpha\text{-MnO}_2$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), and pyrolusite ( $\beta\text{-MnO}_2$ ) on the formation of iron oxide precipitates.

### EXPERIMENTAL

#### *Preparation and characterization of Mn oxide minerals*

The Mn oxide minerals were prepared following the methods outlined by McKenzie (1971). The X-ray powder diffraction (XRD) patterns of the synthesized minerals were obtained using  $\text{FeK}\alpha$  radiation on a Philips X-ray diffractometer (Model PW 1310). The infrared (IR) spectra of the synthetic products were taken on a Perkin Elmer 983 infrared spectrophotometer. The products were also examined using a Philips EM 400 transmission electron microscope (TEM). The Mn oxides were also characterized for surface area follow-

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<sup>2</sup> For brevity, this term is used as a group name for Fe oxides and oxyhydroxides.

ing the ethylene glycol monoethylether method of Eltantawy and Arnold (1973). Their cation-exchange capacities (at pH 7.0) were measured using the weighing-in-excess-salt method (Jackson, 1979). The Mn content of the minerals was determined after the samples were dissolved by 0.125 M hydroxylamine hydrochloride in 3 M HCl (10 mg of mineral sample in 50 ml of solution) at 80°C, by atomic absorption spectrophotometry.

#### Iron oxide precipitates

To 100 ml of an aqueous solution of 0.1 M  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in a 250-ml beaker, suitable quantities of a Mn oxide mineral were added to obtain desired Mn/Fe molar ratios (0, 0.01, 0.1, and 1.0). The Mn/Fe molar ratios in this study refer to the initial molar ratios of  $\text{Mn}_{\text{solid}}/\text{Fe}_{\text{solution}}$ . The pH and Eh of the suspension were measured with a Fisher Acumet pH meter (Model 825 MP) using a pH combination electrode and a platinum combination electrode, respectively. A 0.1 M  $\text{NH}_4\text{OH}$  solution was then added to the suspensions drop-wise, maintaining a flow-rate of 2 ml/min, with constant stirring using a magnetic stirrer. The suspension was held at final pHs of 3.0, 4.0, 5.0, and 6.0 for cryptomelane, 4.0, 5.0, and 6.0 for hausmannite, and 5.0 and 6.0 for pyrolusite with 0.1 M  $\text{NH}_4\text{OH}/0.1$  M HCl for 1 hr. Air had free access to the system. The final Eh of the suspensions was also measured. The precipitates formed were repeatedly washed with 50% acetone by centrifugation at 1750 g for 20 min until they were free of the electrolytes and then dried in vacuum.

The Fe and Mn contents of the precipitates were determined by atomic absorption spectrophotometry after complete dissolution of the precipitates in 0.125 M hydroxylamine hydrochloride in 3 M HCl at 80°C. The Fe content of the noncrystalline precipitates was estimated using the hydroxylamine hydrochloride extraction method of Chao and Zhou (1983).

The XRD patterns of the precipitates were taken using  $\text{FeK}\alpha$  radiation. The differential infrared spectra of the Fe-bearing precipitation products were taken in the range 300–1900  $\text{cm}^{-1}$  using the KBr pellet technique (1 mg of sample mixed with 300 mg of KBr, pressed at 15,000 psi pressure), with the respective proportion of the Mn oxide mineral + KBr in the reference beam. For TEM examination, a drop of a sample suspension was deposited on carbon-coated Formvar film on a copper grid. The electron spin resonance (ESR) spectra of the filtrates after the reaction were taken on a Bruker Physik B-ER 418S EPR spectrometer in X-band mode.

## RESULTS

#### Characterization of Mn oxide minerals

Manganese oxide minerals are often referred to by both mineral and chemical names. Synthetic products,

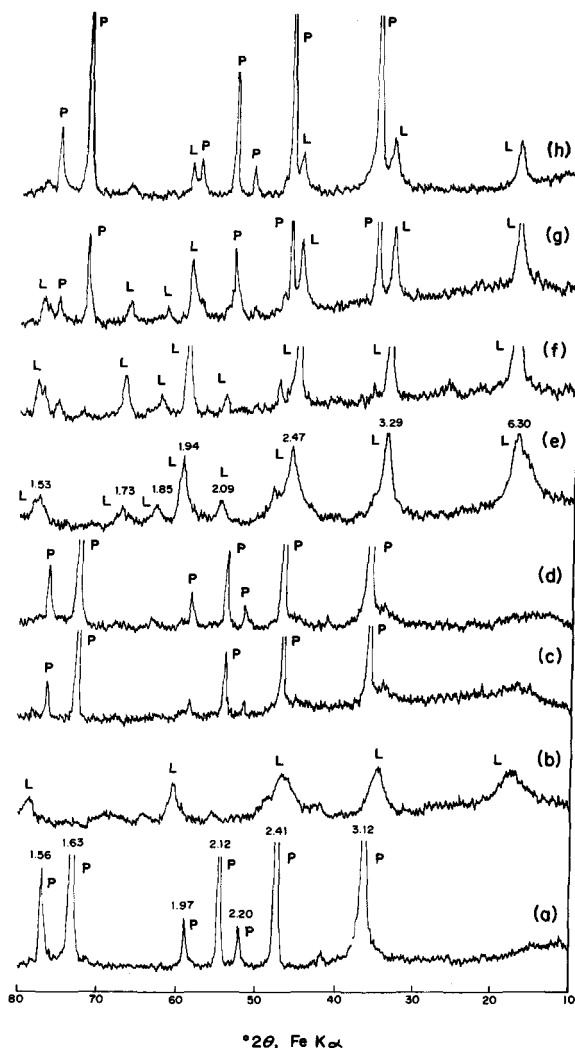


Figure 1. X-ray powder diffractograms of pyrolusite and iron oxide precipitates formed in the presence of pyrolusite. (a) pyrolusite; at pH 5.0 and Mn/Fe molar ratios of (b) 0, (c) 0.1, and (d) 1.0, respectively; at pH 6.0 and Mn/Fe molar ratios of (e) 0, (f) 0.01, (g) 0.1, and (h) 1.0, respectively. d-values are in Å. L = lepidocrocite; P = pyrolusite.

although they may be identical to those occurring in nature, are usually given different names. To avoid confusion, only mineral names are used in this report.

The XRD peaks of the synthetic Mn oxides match well the standard data of pyrolusite (Figure 1a, JCPDS 24-735), cryptomelane (Figure 2a, JCPDS 20-908), and hausmannite (Figure 3a, JCPDS 24-734). The IR absorption bands also match well the data reported by Potter and Rossman (1979) for these minerals. The Mn content, specific surface, and CEC (at pH 7.0) were 51.4%, 39  $\text{m}^2/\text{g}$ , and 2.0 meq/100 g, respectively, for pyrolusite; 47.4%, 475  $\text{m}^2/\text{g}$ , and 11.9 meq/100 g, respectively, for cryptomelane; and 48.9%, 143  $\text{m}^2/\text{g}$ , and 4.0 meq/100 g, respectively, for hausmannite. The

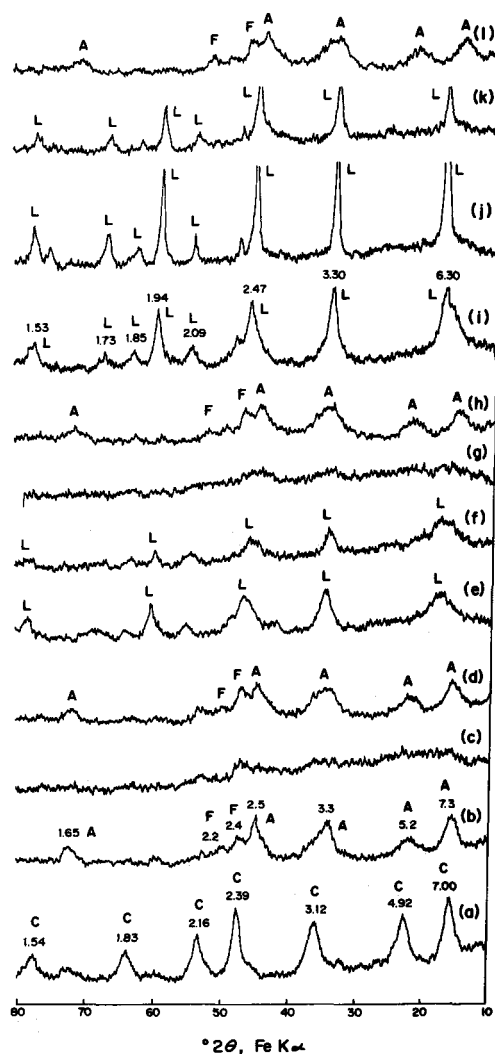


Figure 2. X-ray powder diffractograms of cryptomelane and iron oxide precipitates formed in the presence of cryptomelane. (a) cryptomelane; (b) at pH 3.0 and a Mn/Fe molar ratio of 1.0; at pH 4.0 and Mn/Fe molar ratios of (c) 0.1 and (d) 1.0, respectively; at pH 5.0 and Mn/Fe molar ratios of (e) 0, (f) 0.01, (g) 0.1, and (h) 1.0, respectively; at pH 6.0 and Mn/Fe molar ratios of (i) 0, (j) 0.01, (k) 0.1, and (l) 1.0, respectively. d-values are in Å. L = lepidocrocite, C = cryptomelane, A = åkaganeite, F = feroxyhyte.

electron micrographs of the synthetic Mn oxides are shown in Figures 4a, 4c, and 4f.

#### *Influence of Mn oxide minerals on the nature of the iron oxide precipitates*

Chemical data on the precipitates formed in the  $\text{FeCl}_2\text{-NH}_4\text{OH}$  system at different pHs and Mn/Fe molar ratios are given in Table 1. The precipitation of iron increased with increasing amounts of Mn oxides present. The increase was more pronounced at a Mn/Fe molar ratio of 1.0, as has been shown for birnessite (Krishnamurti and Huang, 1987). At a Mn/Fe molar

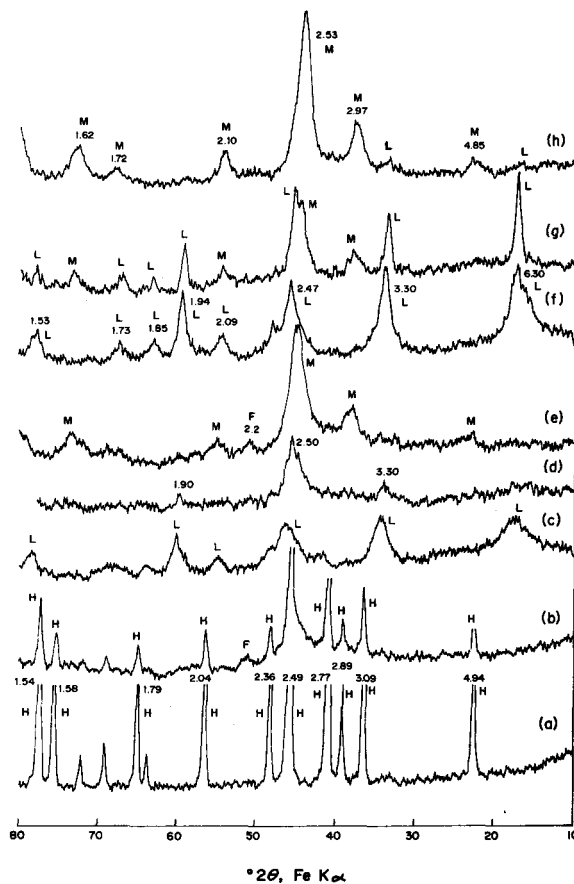


Figure 3. X-ray powder diffractograms of hausmannite and iron oxide precipitates formed in the presence of hausmannite. (a) hausmannite; (b) at pH 4.0 and Mn/Fe molar ratios of 1.0; at pH 5.0, and Mn/Fe molar ratios of (c) 0, (d) 0.1, and (e) 1.0, respectively; at pH 6.0 and a Mn/Fe molar ratio of (f) 0, (g) 0.1 and (h) 1.0, respectively. d-values in Å. L = lepidocrocite, M = magnetite, F = feroxyhyte, H = hausmannite.

ratio of 1.0 in the presence of cryptomelane, nearly 100% of the Fe in solution precipitated at all pHs; 19.4, 58.9, and 67.9% at pHs of 4.0, 5.0, and 6.0, respectively, in the presence of hausmannite; and 12.6 and 28.0% at pHs of 5.0 and 6.0, respectively, in the presence of pyrolusite (Table 1).

In the absence of Mn oxide minerals, the iron oxide precipitates formed at pHs of 5.0 and 6.0 were identified as lepidocrocite (no precipitate was observed at pHs of 3.0 and 4.0) on the basis of XRD peaks at 6.30, 3.30, 2.47, 1.94, 1.73, and 1.53 Å (JCPDS 8-98) and IR absorption bands at 1156, 1022, 743, 476, and 354  $\text{cm}^{-1}$  (Gadsden, 1975). The results on the influence of specific Mn oxide minerals on the nature of the iron oxide precipitates formed are presented below:

**Pyrolusite.** The XRD patterns of the Fe oxides formed in the presence of pyrolusite are presented in Figure 1. No precipitate was observed at pHs of 3.0 and 4.0.

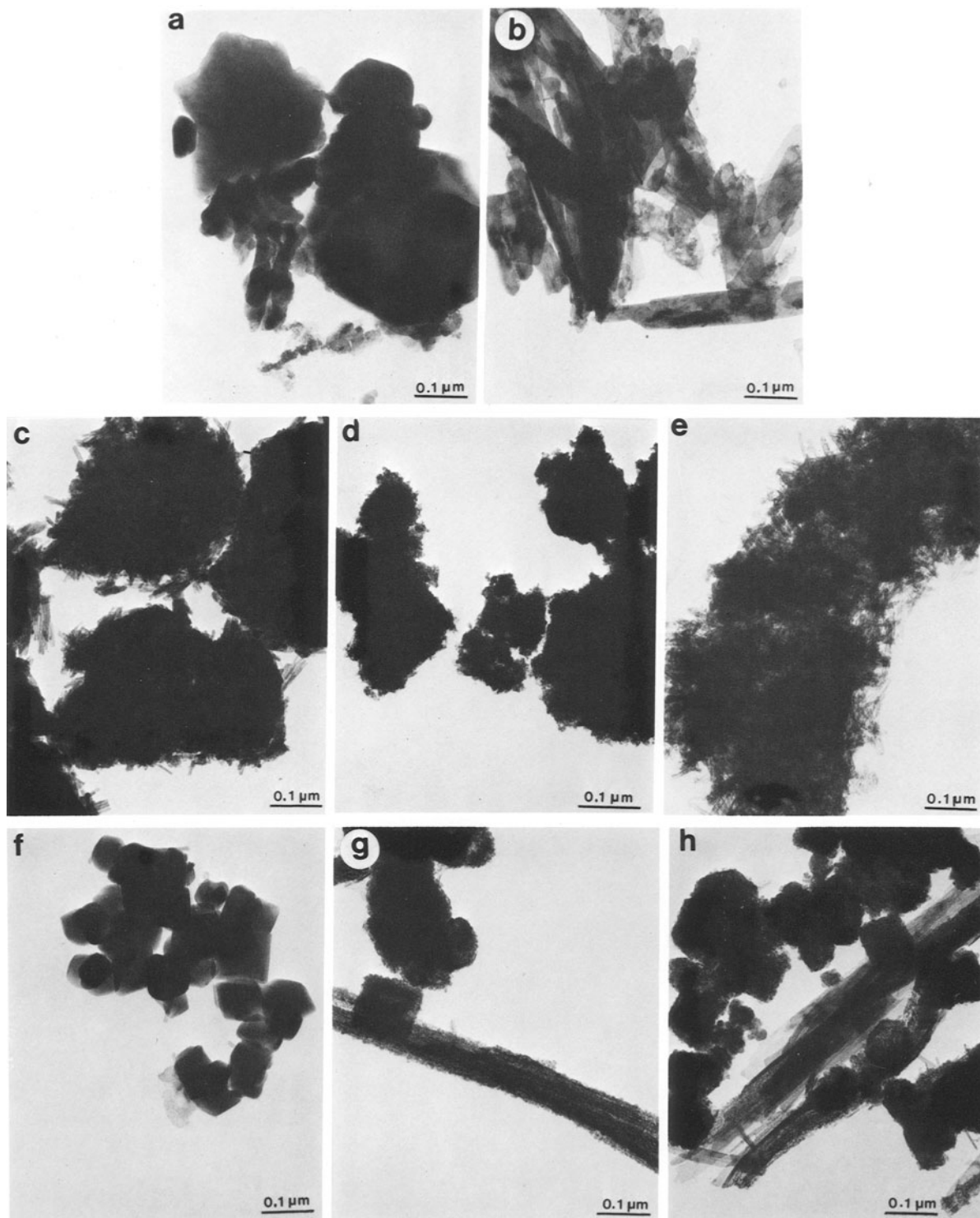


Figure 4. Transmission electron micrographs of the Mn oxide minerals and precipitates formed in the Mn oxide-FeCl<sub>2</sub>-NH<sub>4</sub>OH system. (a) pyrolusite; (b) precipitate formed in the presence of pyrolusite at pH 6.0 and a Mn/Fe molar ratio of 1.0; (c) cryptomelane; (d) and (e) precipitate formed in the presence of cryptomelane with a Mn/Fe molar ratio of 1.0, at pHs of 4.0 and 6.0, respectively; (f) hausmannite; (g) and (h) precipitates formed in the presence of hausmannite with a Mn/Fe molar ratio of 1.0, and at pHs of 4.0 and 6.0, respectively.

Table 1. Precipitates formed in the FeCl<sub>2</sub>-NH<sub>4</sub>OH systems in the presence and absence of Mn oxide.

pH <sup>1</sup>	Mn/Fe molar ratio	Eh (mV)	Fraction of Fe precipitated from solution (%)	Chemical composition of the precipitate (%)	
				Fe	Mn
<b>Pyrolusite</b>					
5.0	0	+140	1.4	40.0	0
	0.1	+180	5.3	21.4	34.3
	1.0	+190	12.6	11.9	42.4
6.0	0	0	8.0	45.0	0
	0.1	-30	8.9	29.4	28.2
	1.0	-30	28.0	12.9	42.1
<b>Cryptomelane</b>					
3.0	0	+420	0	na <sup>2</sup>	na
	1.0	+635	100	40.9	15.7
4.0	0	+340	0	na	na
	0.1	+400	9.7	37.2	17.9
5.0	1.0	+495	99.5	38.3	15.5
	0	+140	1.4	40.0	0
	0.01	+190	4.5	50.0	6.0
6.0	0.1	+230	14.9	46.1	13.9
	1.0	+485	99.5	37.6	15.9
	0	0	8.0	45.0	0
	0.01	-50	12.8	58.3	1.7
	0.1	-30	22.6	54.8	9.5
1.0	+525	100	36.6	17.0	
<b>Hausmannite</b>					
4.0	0	+340	0	na	na
	1.0	+405	19.4	15.9	22.5
5.0	0	+140	1.4	40.0	0
	0.1	+160	5.7	32.0	3.0
	1.0	+230	58.9	48.5	2.3
6.0	0	0	8.0	45.0	0
	0.1	-50	8.4	39.2	0.8
	1.0	+20	67.9	47.5	1.5

<sup>1</sup> pH was maintained for 1 hr with 0.1 M NH<sub>4</sub>OH/0.1 M HCl.

<sup>2</sup> Not applicable.

Some patterns (Figures 1c, 1d, 1g, and 1h) contained intense peaks of pyrolusite. Between 48.7 and 98.3% of the Mn initially added to the solution was found to be present in the precipitate. At Mn/Fe molar ratios of 0.1 and 1.0, the iron oxide precipitates formed at pH 5.0 were X-ray amorphous (Figures 1c and 1d), whereas the crystalline component of the precipitation products formed at pH 6.0 at all Mn/Fe molar ratios studied (0.01, 0.1, and 1.0) was lepidocrocite (Figures 1f, 1g, and 1h). The differential IR data (Table 2) corroborate the XRD findings. The Fe extractable in hydroxylamine hydrochloride, which reflects the amounts of noncrystalline Fe oxides present (Chao and Zhou, 1983), was 100 and 85% of the precipitate formed at pHs 5.0 and 6.0, respectively, at a Mn/Fe molar ratio of 1.0 (Table 2). TEMs of the Fe oxide formed at pH 6.0 (Figure 4b) show the typical lath-shaped morphology of lepidocrocite (Schwertmann and Taylor, 1979), together with particles of indefinite morphology.

**Cryptomelane.** The broad XRD peaks at about 7.3, 5.2, 3.3, 2.5, and 1.65 Å (Figures 2b, 2d, 2h, and 2l)

Table 2. X-ray powder diffraction identification, differential infrared properties, and noncrystalline Fe content of iron oxide precipitates formed in the FeCl<sub>2</sub>-NH<sub>4</sub>OH system in presence of different Mn oxide minerals.<sup>1</sup>

pH <sup>2</sup>	Extractable Fe <sup>3</sup> (%)	Minerals present <sup>4</sup>	Differential infrared spectra <sup>5</sup> (cm <sup>-1</sup> )				
			369	483	744	1020	1146
<b>Pyrolusite</b>							
5.0	100	PCL	369	483	744	1020	1146
6.0	85	L	354	476	743	1022	1156
<b>Cryptomelane</b>							
3.0	100	A, F	445	675	1115	1400	1556 1636
4.0	100	A, F	458	672	1123	1402	1556 1630
5.0	100	A, F	447	679	1115	1402	1555 1634
6.0	100	A, F	442	672	1117		1556 1630
<b>Hausmannite</b>							
4.0	91	NC, F	495	607	1624		
5.0	41	M, F	442	585	1626	3422	
6.0	32	M	441	584	1626	3416	

<sup>1</sup> Mn/Fe molar ratio of 1.0.

<sup>2</sup> pH of synthesis; pH was maintained for 1 hr with 0.1 M NH<sub>4</sub>OH/0.1 M HCl.

<sup>3</sup> Extractable in hydroxylamine hydrochloride.

<sup>4</sup> Dominant constituent of the iron oxide precipitate. PCL = poorly crystalline lepidocrocite; L = lepidocrocite; A = åkaganeite; F = feroxyhyte; M = magnetite.

<sup>5</sup> Spectra for the iron oxide precipitate formed at pHs of 5.0 and 6.0 in the presence of hausmannite are infrared spectra; differential infrared spectra were not attempted because the amount of Mn in the precipitates was only 1.5–2.3%.

match well the data for synthetic åkaganeite (JCPDS 13-157), indicating that the Fe oxide formed at all pHs and at a Mn/Fe molar ratio of 1.0 was åkaganeite ( $\beta$ -FeOOH). The precipitate that formed at pHs of 4.0 and 5.0 and at a Mn/Fe molar ratio of 0.1 was found to be X-ray amorphous (Figures 2c and 2g). Lepidocrocite was identified as the precipitate formed at pH 5.0 and a Mn/Fe molar ratio of 0.01 (Figure 2f) and at pH 6.0 and at Mn/Fe molar ratios of 0.01 and 0.1 (Figures 2j and 2k). The Fe oxides formed at all pHs and at a Mn/Fe molar ratio of 1.0 were completely extractable by hydroxylamine hydrochloride (Table 2). The reactivity of åkaganeite towards the reducing agent (NH<sub>2</sub>OH·HCl) (Table 2) may be due to its poorly crystalline nature (Figures 2b, 2d, 2h, and 2l) and/or its tunnel structure (Holm, 1985).

The TEMs of Fe oxides formed at pHs of 4.0 and 6.0 and at a Mn/Fe molar ratio of 1.0 (Figures 4d and 4e) show aggregates of needle-shaped and shapeless particles. Marshall and Rutherford (1971) reported that the TEMs of åkaganeite show spindle-shaped particles which tend to align in clusters. According to McKenzie (1977), the TEMs of cryptomelane show needle-shaped particles.

**Hausmannite.** The XRD patterns of the precipitates formed at pH 4.0 and a Mn/Fe molar ratio of 1.0 show the presence of hausmannite only (Figure 3b), indi-

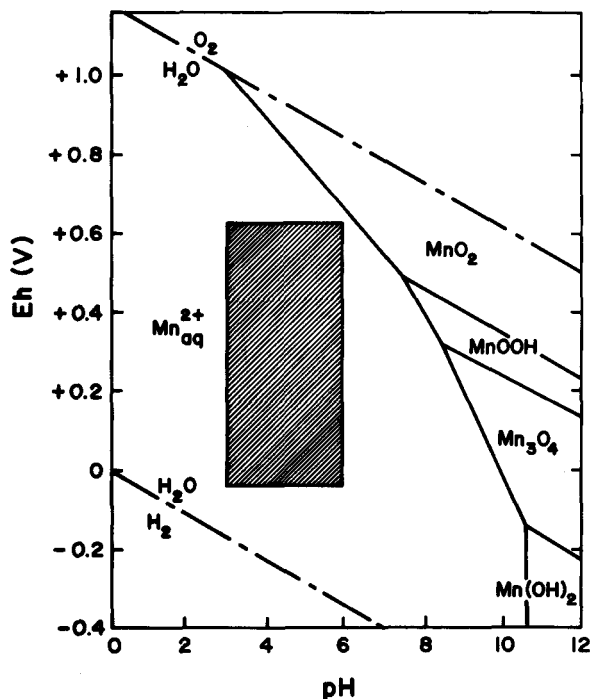
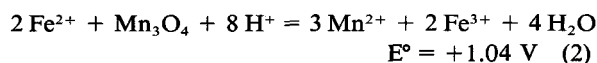
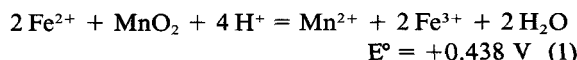


Figure 5. Stability relations of different species of Mn at 25°C, 0.101 MPa, and  $a_{\text{Mn}^{2+}} = 10^{-6}$  (Bricker, 1965). The Eh and pH ranges of the systems during the formation of iron oxide precipitates in the presence of Mn oxides in the present study are shown as shaded region.

cating that the Fe oxide formed was X-ray amorphous. On the other hand, the Fe oxide formed at pHs of 5.0 and 6.0 and at a Mn/Fe molar ratio of 1.0 (Figures 3e and 3h) contained XRD peaks at 4.85, 2.97, 2.53, 2.10, and 1.62 Å. The Fe extractable by hydroxylamine hydrochloride in the Fe oxides formed at pHs of 4.0, 5.0, and 6.0 and at Mn/Fe molar ratio of 1.0 was 91, 41, and 32%, respectively (Table 2). The IR spectra of the Fe oxides formed in the presence of hausmannite at pHs of 5.0 and 6.0 and at a Mn/Fe molar ratio of 1.0 (Table 2) show bands at about 3420, 1626, 584, and 442  $\text{cm}^{-1}$ .

## DISCUSSION

The standard electrode potentials ( $E^\circ$ ) of the redox pairs  $\text{Fe}^{2+}$ - $\text{MnO}_2$  and  $\text{Fe}^{2+}$ - $\text{Mn}_3\text{O}_4$  can be represented by the following equations (Bricker, 1965):



These  $E^\circ$  values indicate that oxidation of  $\text{Fe}^{2+}$  by Mn oxides is thermodynamically feasible. The Eh-pH diagram (Figure 5) indicates the feasibility of the reduction of  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  in the Mn oxides to  $\text{Mn}^{2+}$  in the Eh-pH ranges of the systems during the formation of

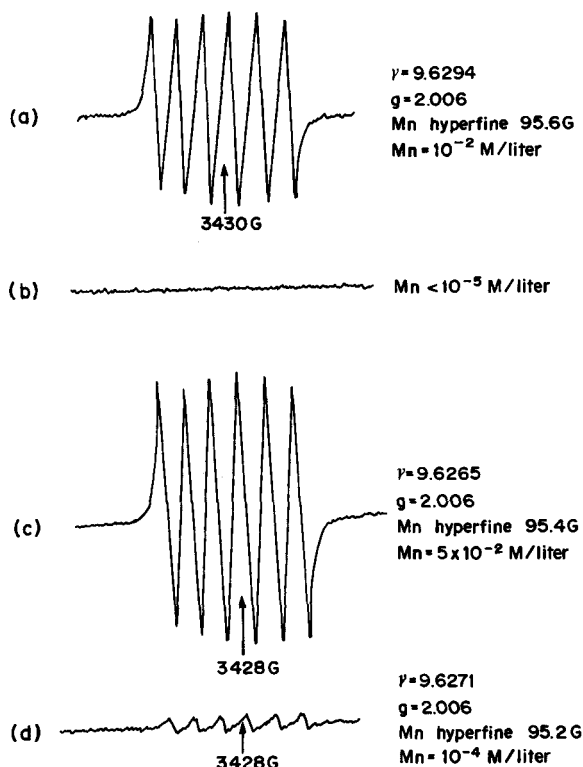


Figure 6. Electron spin resonance spectra of Mn(II) in the filtrates after reaction at pH 5.0. (a) cryptomelane- $\text{FeCl}_2$ - $\text{NH}_4\text{OH}$  system, Mn/Fe molar ratio = 1, (b) cryptomelane- $\text{H}_2\text{O}$ - $\text{NH}_4\text{OH}$  system, (c) Hausmannite- $\text{FeCl}_2$ -HCl system, Mn/Fe molar ratio = 1, and (d) Hausmannite- $\text{H}_2\text{O}$ -HCl system.

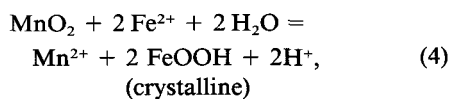
Fe oxides. Furthermore, the ESR spectra of the filtrates (Figures 6a and 6c) after the reaction show significant amounts of  $\text{Mn}^{2+}$  in the filtrates. The reaction time of 1 hr was not sufficient to disproportionate  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  of the Mn oxides (Figures 6b and 6d) to the large amounts of  $\text{Mn}^{2+}$  observed in the filtrates (Figures 6a and 6c). The g and Mn-hyperfine G values of  $\text{Mn}^{2+}$  in the filtrates (given in the respective figures) compare well with standard data (2.007 and 95.2 G) for  $\text{Mn}^{2+}$  species in solution (Bielski and Gebicke, 1967). The data (Table 1) indicate that  $\text{Mn}^{4+}$  or  $\text{Mn}^{3+}$  of the Mn oxides were partly dissolved by reduction to  $\text{Mn}^{2+}$ . Simultaneously, the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by Mn oxides led to subsequent hydrolysis of  $\text{Fe}^{3+}$  to form the precipitation products of Fe.

Murray (1975) reported that the affinity of  $\text{Mn}^{2+}$  to the hydrous  $\text{MnO}_2$  surface was the greatest amongst all the divalent ions studied by them. The sorption of  $\text{Mn}^{2+}$  was attributed by Murray (1975) to the separation of a proton from the OH groups at the surface and the association of solution  $\text{Mn}^{2+}$  with this site:

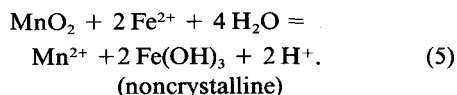


Consistent with the above mechanism, a decrease in

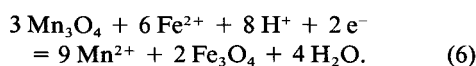
pH of the suspension from 3.70 to 2.40 and 3.50 was observed in the presence of cryptomelane and pyrolusite, respectively, before the addition of  $\text{NH}_4\text{OH}$  to maintain the constant pHs of the systems (not shown). The decrease in pH may also have been partly caused by the reduction of  $\text{Mn}^{4+}$  and the subsequent oxidation of  $\text{Fe}^{2+}$  and the hydrolysis of  $\text{Fe}^{3+}$ :



and



In the presence of hausmannite, however, a Mn oxide mineral which contains Mn in different valencies, slow increase in pH from 3.70 was observed, and 0.1 M HCl was added to maintain the constant pHs of the systems (not shown). This increase in pH indicates proton consumption during the almost complete reduction in the presence of hausmannite (at pHs of 5.0 and 6.0, where 2.0–6.1% Mn remained in the precipitates) by  $\text{Mn}^{3+}$  and the oxidation of  $\text{Fe}^{2+}$  as follows:



The iron oxide precipitate formed in the presence of pyrolusite at pH 5.0 and a Mn/Fe molar ratio of 1.0 showed very weak XRD peaks at 3.30 and 1.80 Å (Figure 1d), probably due to the presence of poorly ordered lepidocrocite. Poorly ordered lepidocrocite typically does not show the strong peak at 6.26 Å (Schwertmann and Taylor, 1979). Thus, the rate of oxidation of  $\text{Fe}^{2+}$  was apparently modified, and the crystallization of lepidocrocite was retarded in the presence of pyrolusite at pH 5.0, even though similar bonding of Fe, O, and OH ions is indicated by the IR spectra.

The XRD patterns of the precipitate formed in the presence of cryptomelane at all pHs and a Mn/Fe molar ratio of 1.0 showed broad peaks of åkaganeite (Figures 2b, 2d, 2h, and 2l). According to Watson *et al.* (1962), åkaganeite gives broad XRD peaks, because the crystals grow 14 times faster along the *c*-axis than along the *a* and *b* directions. This disparate growth apparently accounts for the broadening of the åkaganeite peaks (Figures 2b, 2d, 2h, and 2l). Mn substitution in åkaganeite could also result in the broadening of the peaks (% Mn in the precipitates was 15.5–17.0). The additional broad peaks at 2.4 and 2.2 Å (Figures 2d, 2h, and 2l) are probably due to the presence of ferroxhyte ( $\delta'$ -FeOOH), a Fe oxide mineral which has been reported in iron-manganese nodules collected from the ocean bottom (Chukhrov *et al.*, 1977). Possibly, the presence of cryptomelane favored the formation of ferroxhyte. The XRD peaks at 2.4 and 2.2 Å could also be attributed to ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ); however,

the presence of ferrihydrite is uncertain because of the absence of its other characteristic XRD peaks at 1.98, 1.73, and 1.51 Å (Chukhrov *et al.*, 1973; Karim, 1984). Further, the formation of ferrihydrite from  $\text{FeCl}_2$  solutions is particularly favored by the presence of Si in the system (Schwertmann and Thalmann, 1976; Karim, 1977). In the system studied here, Si was not present. The differential IR spectra of the iron oxide precipitates show absorption bands at about 1630, 1555, 1400, 675, and 450  $\text{cm}^{-1}$  (Table 2), characteristic of åkaganeite (Gadsden, 1975). Åkaganeite was also identified in the XRD patterns of the precipitates (Figures 2b, 2d, 2h, and 2l). Åkaganeite is distinguished from other forms of FeOOH by the presence of the  $\delta$ -OH band at 680  $\text{cm}^{-1}$  (Marshall and Rutherford, 1971).

The precipitate formed at pH 5.0 and a Mn/Fe molar ratio of 0.1, in the presence of hausmannite, gave broad XRD peaks at about 3.3, 2.5, and 1.9 Å (Figure 3d), which may be assigned to poorly ordered lepidocrocite. Poorly ordered lepidocrocite typically does not show the strong peak at 6.26 Å (Schwertmann and Taylor, 1979). On the other hand, the precipitate formed at the same pH but at a Mn/Fe molar ratio of 1.0 (Figure 3e) was magnetite, as indicated by XRD. The characteristic XRD peak observed at  $2.526 \pm 0.003$  Å (scanning speed of  $1/4^\circ 2\theta/\text{min}$ ) strongly suggests the presence of magnetite (JCPDS 19-629) and appears to distinguish magnetite from maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), which has a strong peak at 2.51 Å (JCPDS 25-1402). Further, Schwertmann and Thalmann (1976) reported that maghemite will not form at  $\text{pH} < 6$ . The IR spectra of the iron oxide precipitates formed at pHs of 5.0 and 6.0 and at a Mn/Fe molar ratio of 1.0 show intense broad bands at 584 and 442  $\text{cm}^{-1}$  (Table 2). Both natural and synthetic magnetite have been reported to give two broad bands at about 400 and 590  $\text{cm}^{-1}$  (Afremow and Vandenberg, 1966; Liese, 1967; Farrell, 1972; Gadsden, 1975; van der Marel and Beutelspacher, 1976). Maghemite has been reported to give a series of absorption bands in the region 300–800  $\text{cm}^{-1}$  (Farrell, 1972; Taylor and Schwertmann, 1974; van der Marel and Beutelspacher, 1976). The IR absorption bands observed at 3420 and 1626  $\text{cm}^{-1}$  can be assigned to OH-stretching and HOH-bending vibrations of structural water (Nakamoto, 1970). These bands persisted even in the spectra of the precipitates preheated to 200°C for 24 hr and equilibrated over  $\text{P}_2\text{O}_5$  for 24 hr. The weak band at 1020  $\text{cm}^{-1}$  (not included in Table 2) in all the spectra is due to the presence of trace amounts of lepidocrocite. The XRD patterns of the iron oxide precipitates formed at pH 6.0 and Mn/Fe molar ratios of 0.1 and 1.0 (Figures 3g and 3h) indicate magnetite as the dominant crystalline constituent. The TEMs of the precipitates (Figures 4g and 4h) show cubes and a few laths, characteristic of magnetite and lepidocrocite, respectively (Schwertmann and Taylor, 1977).

Even though goethite and hematite are the most stable Fe oxide minerals, åkaganeite and magnetite are common in most Fe-Mn nodules and in concretions in soils and sediments (Murray, 1979). The results of the present investigation clearly indicate the influence of Mn oxides on the crystallization processes of Fe oxides and suggest the possible reasons for the presence of åkaganeite and magnetite in the Fe-Mn nodules in nature.

### SUMMARY AND CONCLUSIONS

Lepidocrocite ( $\gamma$ -FeOOH) was a commonly formed iron oxyhydroxide in the FeCl<sub>2</sub> system at pHs of 5.0 and 6.0 in the absence of Mn oxides. The Mn oxides differed in their ability to promote the precipitation of Fe oxides from FeCl<sub>2</sub> solutions in the pH range studied (Table 1) through redox mechanism, as confirmed by the presence of Mn<sup>2+</sup> in the ESR spectra of the filtrates after the reaction (Figure 6). The oxidation of Fe<sup>2+</sup> by the Mn oxides and the simultaneous reduction of Mn<sup>4+</sup> or Mn<sup>3+</sup> of the Mn oxides to Mn<sup>2+</sup> is thermodynamically feasible in the Eh-pH ranges of the systems studied (Figure 5). At a Mn/Fe molar ratio of 1.0, the precipitation of Fe was nearly 100% in the presence of cryptomelane (in the pH range 3.0–6.0), 19.4 to 67.9% in the presence of hausmannite (in the pH range 4.0–6.0), and 12.6 to 28.0% in the presence of pyrolusite (in the pH range 5.0–6.0) (Table 1). The highly reactive Mn oxides modified the crystallization process of the iron oxide precipitates, resulting in the formation of X-ray amorphous and/or different crystalline iron oxide precipitates, such as åkaganeite ( $\beta$ -FeOOH), magnetite (Fe<sub>3</sub>O<sub>4</sub>), and feroxyhyte ( $\delta'$ -FeOOH) (Table 2). Åkaganeite formed in the presence of cryptomelane (Figure 2), and magnetite formed in the presence of hausmannite (Figure 3) at a Mn/Fe molar ratio of 1.0. Such products did not form in the presence of pyrolusite (Figure 1), due to the high crystallinity, low specific surface, and slow dissolution properties of the Mn mineral. The TEM (Figure 4) and IR data (Table 2) of the iron oxide precipitates substantiate the XRD data (Figures 1–3). The role of the Mn oxides in the natural formation of Fe oxides, thus, merits close attention.

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