

EFFECT OF COBALT ON THE FORMATION OF CRYSTALLINE IRON OXIDES FROM FERRIHYDRITE IN ALKALINE MEDIA

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Abstract—At pH 12 Co-ferrihydrate transformed to either Co-goethite or Co-magnetite, the latter compound appearing at Co additions of >18 mole %. Although Co was readily taken up by the magnetite structure, chemical analysis showed that no more than 7 mole % substitution of Co in goethite was achieved. Hematite formation was not strongly promoted by the presence of Co; with 9 mole % Co in the system, the amount of hematite relative to goethite in the product increased slightly. Co-substituted goethites grew as long, thin crystals. The presence of Co promoted some dendritic twinning of goethite. Cobalt retarded the transformation of ferrihydrate to more crystalline oxides mainly by stabilizing ferrihydrate against dissolution. A comparison of Co with divalent ions previously studied showed that their stabilizing ability decreases in the order Cu > Co > Mn, i.e., they follow the Irving-Williams series for the stability of metal complexes.

Key Words—Cobalt, Crystal growth, Ferrihydrate, Goethite, Spinel, Transmission electron microscopy.

INTRODUCTION

Earlier investigations have shown that foreign ions, such as Al³⁺, Mn²⁺, and Cu²⁺, have a marked influence on the kinetics of the transformation of ferrihydrate into more crystalline products (Lewis and Schwertmann, 1979; Cornell and Giovanoli, 1987, 1988). These ions also influence the composition of the reaction product; Al and Cu lead to an increase in the amount of hematite relative to goethite, and sufficiently high levels of divalent ions promote the formation of a spinel phase. In addition, each ion has its own particular effect on the transformation process, and investigations of these effects have provided further details of the mechanisms by which the reaction proceeds.

These investigations have now been extended to consider the influence of Co²⁺ on the transformation of ferrihydrate. Earlier workers showed that Co²⁺ adsorbs strongly on iron oxides in alkaline media and can also be incorporated in the goethite structure (Music *et al.*, 1979; Borggaard, 1987; Lim-Nunez and Gilkes, 1987). The present work is concerned with the effect of Co on the kinetics and products of the transformation. A further aim is to compare the influence of Co on the reaction with that of previously investigated ions. Co²⁺ has an ionic radius comparable with that of Cu²⁺, but like Mn²⁺ it can be oxidized to the trivalent state at an oxide interface. Its effect on the transformation might, therefore, be expected to show differences from the effects of both the latter ions.

A further reason for studying cobalt is that this element coexists with iron oxides in a variety of systems. On the one hand, it is concentrated in Pacific ferromanganese nodules (Halbach *et al.*, 1982), and on the other hand, Co⁶⁰ appears as an unwanted substituent

in the structure of Fe₃O₄ deposited in the scales of water cooling pipes in nuclear power stations (Ardizzone *et al.*, 1987). In both systems the mechanism of uptake of Co by the iron oxide component is important. Cobalt is also an important trace element which, among other functions, is essential for the healthy growth of cattle; hence, its mobility and availability in soils is of interest. This mobility is governed to a large extent by the balance between Co adsorption on and uptake by soil minerals and its release during dissolution of these minerals.

EXPERIMENTAL METHODS

Transformation studies were carried out using suspensions of ferrihydrate (1 g/liter) with Co/(Co + Fe) mole ratios of between 0.01 and 1.0. Ferrihydrate was precipitated from solutions of ferric nitrate with 1 M KOH. In most experiments Co was coprecipitated with ferrihydrate, but in some, Co(II) nitrate solution was added to already formed ferrihydrate. The final pH of the suspension ranged from 10.5 to 12, although most experiments were carried out at pH 12. The suspensions were held in closed polypropylene bottles at 70°C for as long as 100 hr.

The kinetics of the transformation to Co-goethite were followed by taking subsamples during the reaction and dissolving the unconverted ferrihydrate 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 ferrihydrate) and Fe_t is the total Fe in the system.

After completion of the transformation, the crystalline product was dried at 50°C, and X-ray powder diffraction (XRD) patterns were obtained using a

Table 1. Effect of concentration of Co and order of precipitation on the transformation products at pH 12 and 70°C.

Method of precipitation	Mole % Co added	Product
Co + Fe coprecipitated	0	Co-goethite
	0.9	Co-goethite
	4.5	Co-goethite
	9.0	Co-goethite
	18.0	Co-goethite + some Co-magnetite
	23.0	Co-magnetite
	33.0	Co-magnetite
Co added to ferrihydrite	9.0	Co-goethite
	23.0	Co-goethite + trace Co-magnetite
	33.0	Co-goethite + trace Co-magnetite
	100.0 ¹	Co ₃ O ₄ + CoOOH

¹ Co²⁺ solution alone.

Guinier-Enraf camera (Mk IV) with FeK α_1 radiation. The proportions of goethite and hematite in the products were found with the aid of calibration patterns. To determine the unit-cell dimensions of Co-goethites and Co-magnetites, the 110, 200, 112, and 211 lines of quartz were used as internal spacing standards.

The total amount of Fe and Co in Co-goethite and Co-magnetite was found by dissolving the oxide in 4 M HCl (25°C). Fe and Co were found using atomic absorption spectroscopy. The level of Co incorporation was taken as the difference between the amount of Co adsorbed on the oxide surface or associated with the first few surface layers (i.e., oxalate or acid soluble Co) and the total Co in the oxide. The adsorbed Co was found by oxalate extraction for Co-goethite and by a 30-min extraction with 0.1 M HCl for substituted magnetites; the latter oxide is readily soluble in acid/oxalate solution.

Transmission electron micrographs (TEM) were obtained using a Hitachi H-600-2 electron microscope operating at 100 kV. 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.

Table 2. Mole % Co substitution in Co-goethite.

Mole % Co added initially	Mole % substitution
2.5	1.8
4.5	3.9
9.0	6.7
9.0 ¹	4.7

¹ Co added to ferrihydrite; all other goethites formed from Co-ferrihydrite coprecipitates; pH 12, 70°C.

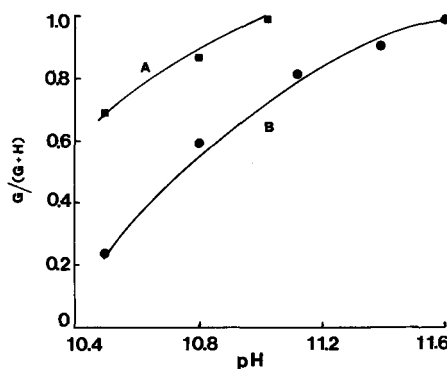


Figure 1. Goethite/(goethite + hematite) ratios in the product vs. final pH. Temperature = 70°C. A = control; B = with 9 mole % Co.

RESULTS

Product mineralogy

At pH 12 Co-ferrihydrite coprecipitates transformed into Co-substituted goethite and/or Co-substituted magnetite (Table 1). Co-magnetite (Co_xFe_{3-x}O₄, 0.10 < x < 1.0) first appeared if the level of Co in the precipitate exceeded 15 mole %. Goethite formation was completely suppressed at Co levels > 23 mole %.

If Co was added to already formed ferrihydrite, higher levels of Co were needed to ensure formation of Co-magnetite; even with 33 mole % Co, the bulk of the product was Co-substituted goethite (Table 1). Seeding a suspension of ferrihydrite (to which 23 mole % Co had been added) with 10% Co-magnetite did not promote the additional formation of the spinel phase.

No hematite formed at pHs > 11.5, but at lower pHs hematite formation was enhanced by the presence of 9 mole % Co (Figure 1). The effect of Co was much less than that of the same level of Cu, which even at pH 12.5 completely suppressed goethite in favor of hematite (Cornell and Giovanoli, 1988). At pH 11, a Co-ferrihydrite coprecipitate containing 23 mole % Co transformed to a mixture of hematite and Co-magnetite.

At pH 12 the initial precipitate from a Co²⁺ solution was a blue-green solid, presumably Co(OH)₂. This material rapidly darkened to light brown and subsequently transformed to a black, compact precipitate which XRD showed to be a mixture of Co₃O₄ and CoOOH.

Degree of substitution

The degree of incorporation of Co in the goethite structure increased with rising level of Co in the system (Table 2). The maximum level of incorporation from a Co-ferrihydrite coprecipitate with 9 mole % Co was, however, only about 6 or 7 mole %. If 9 mole % Co was added to already formed ferrihydrite, the maximum level of substitution in goethite was only 4.7 mole % (Table 2).

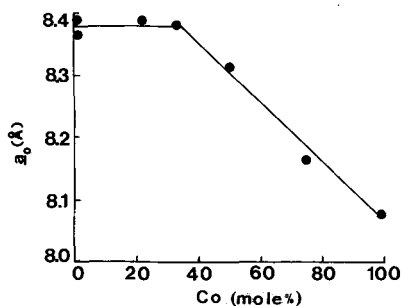


Figure 2. Unit-cell dimensions for the spinel phase vs. Co substitution.

The XRD lines of the Co-goethite containing the highest level of substitution (6.7 mole %) showed a slight, but distinct shift corresponding to a decrease in the dimensions of the unit cell; e.g., b_0 decreased from 9.96 Å (unsubstituted goethite) to 9.93 Å. A smaller unit cell through incorporation of Co in the goethite structure is to be expected because the Co^{3+} ion (radius 0.525 Å) is much smaller than the Fe^{3+} ion (radius 0.64 Å, Shannon and Prewitt, 1969) that it replaces in the goethite structure. A reduction in unit-cell dimensions has also been observed for Al-goethites, presumably owing to the small size of the Al^{3+} ion (radius 0.53 Å) (Schulze, 1984 and references therein).

No measurable Co was found in solution at any stage during the transformation reaction, and no separate, pure Co phase was detectable by XRD. Co that was not incorporated in the goethite structure must, therefore, have been adsorbed on the surface of the crystals of goethite and taken up by the residual ferrihydrite. For Co-goethite containing 6.7 mole % substitution, 30% of the Co originally added to the system was extractable with acid-oxalate solution, whereas only 6% of the total Fe present (i.e., the unconverted ferrihydrite) was extracted by this method.

In systems in which only Co-magnetite formed, chemical analysis indicated that all the Co had been taken up by the magnetite structure. This observation is in accord with the findings of Ardizzone *et al.* (1987), that uptake of Co by magnetite during crystal growth was directly proportional to and numerically almost identical to the level of Co in solution. Over the composition range FeFe_2O_4 – CoFe_2O_4 (Fe^{2+} and Co^{2+} radii are 0.77 Å and 0.74 Å, respectively), the a_0 values of the unit cell fluctuated between 8.39 and 8.38 Å; the fluctuations were erratic and no clear trend was observed. This variability probably reflects different $\text{Me}^{2+} : \text{Fe}^{3+}$ ratios in the samples. In the present experiments, no special precautions were taken to control oxidation. Other authors have reported that a stoichiometric $\text{Fe}^{2+} : \text{Fe}^{3+}$ ratio (0.5) is not obtained for magnetite or substituted magnetite unless oxidation conditions are rigorously controlled (Ardizzone *et al.*, 1983).

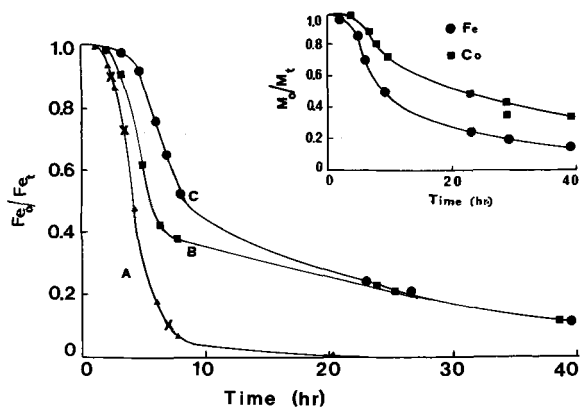


Figure 3. Fe_0/Fe_t as a measure of the degree of transformation of ferrihydrite into goethite and Co-goethite vs. time; pH 12, 70°C. (A) Control (\blacktriangle) and with 0.9 mole % Co (\times); (B) 9 mole % Co added to ferrihydrite; (C) 9 mole % Co coprecipitated with ferrihydrite. Inset: Co_0/Co_t and Fe_0/Fe_t vs. time for the Co-ferrihydrite coprecipitate (B).

As the composition of the spinel phase changed from $\text{Fe}^{3+}\text{Co}^{2+}\text{Fe}^{3+}\text{O}_4$ to $\text{Co}^{2+}\text{Co}_2^{3+}\text{O}_4$, a_0 decreased slightly from 8.38 to 8.08 Å, which reflects the increasing proportion of the smaller Co^{3+} ion in the spinel structure (Figure 2).

Kinetics

Figure 3 shows that at pH 12 the kinetics curves for the transformation were identical for the control system and for a Co-ferrihydrite coprecipitate containing 0.9 mole % Co. Higher levels of Co (e.g., 9 mole %) retarded the transformation to goethite, particularly in the later stages of the reaction (Figure 3). Initially, retardation was more pronounced (i.e., a longer induction period), for a Co-ferrihydrite coprecipitate than for ferrihydrite to which Co had been added. As the reaction proceeded the kinetic curves for the two systems approached each other (Figure 3). Seeding these systems with 6% goethite did not accelerate the overall reaction.

Less Co than Fe was taken up by the growing crystals of goethite (Figure 3, inset). Much of the Co released by dissolution of the ferrihydrite appeared to reabsorb on the remaining ferrihydrite, probably accounting for both the increasing retardation of conversion as the reaction proceeded and the similarity of the kinetics curves in the later stages of the transformation.

Electron microscopy

Co-substituted goethites usually grew under the chosen conditions as long, thin crystals. Those grown from coprecipitated Co-ferrihydrite samples ranged from 3000 to 10,000 Å in length and had an average length:width ratio of 16; unsubstituted goethite crystals grown at pH 12 were as long as 5000 Å and had an average length:width ratio of 5 (cf. Cornell and

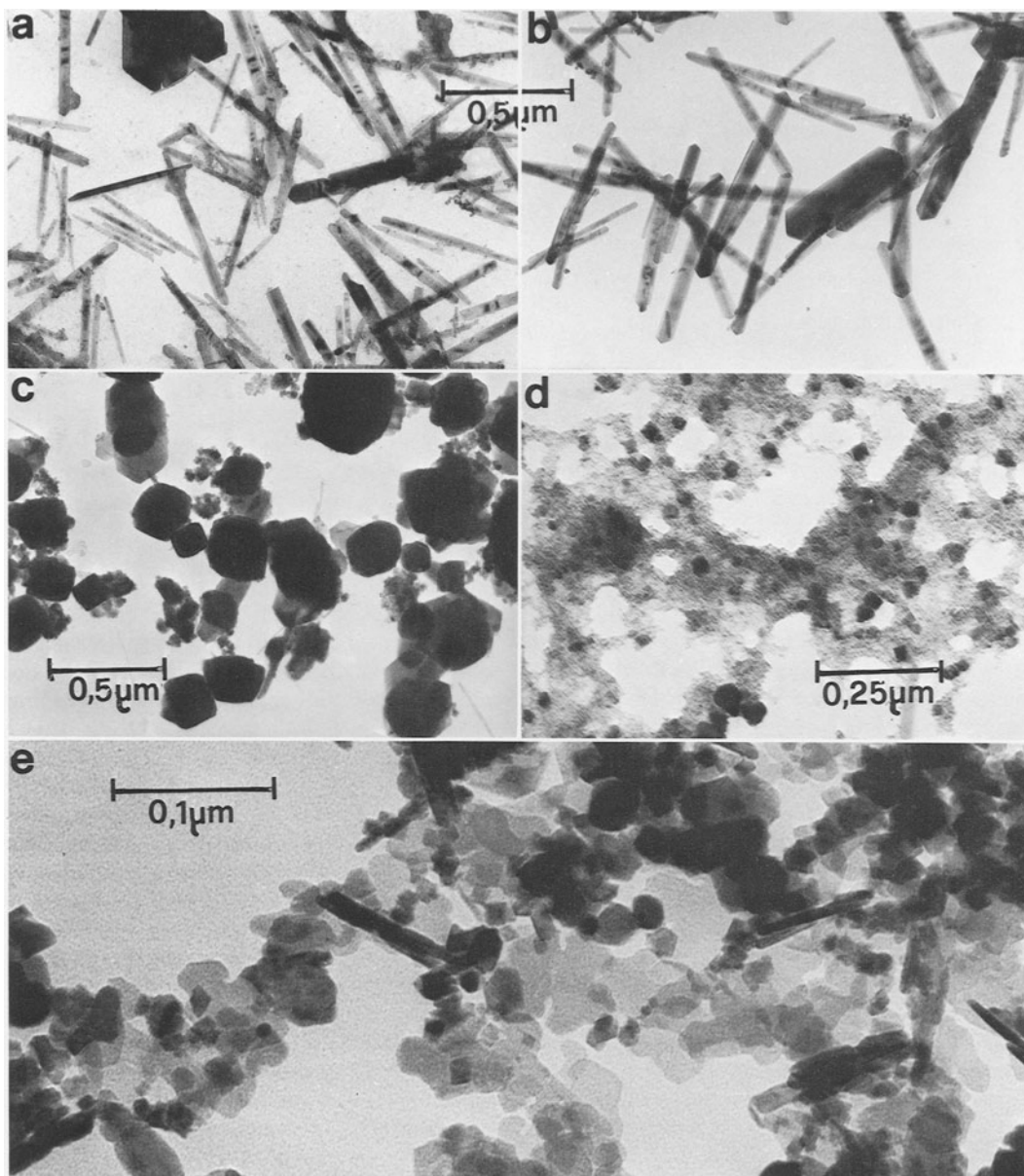


Figure 4. Transmission electron micrographs of the oxides formed in the presence of Co; pH 12, 70°C. (A) Co-goethites (6.7 mole % Co) from Co-ferrihydrate coprecipitates; (B) Co-goethites (4.7 mole % Co) from ferrihydrate to which Co was added; (C) Hematite with goethite outgrowths formed from Co-ferrihydrate coprecipitate; pH 10.5; (D) Co-magnetite together with Co-ferrihydrate; (E) A mixture of Co_3O_4 (cubes) and CoOOH (plates and rods).

Giovanoli, 1985). The Co-goethites were usually single domain and terminated in rounded ends (Figure 4a). Similar Co-goethites containing 2–4 mole % Co have been produced industrially from ferrous systems (Abeck and Hund, 1964).

Co-goethites grown from ferrihydrate to which Co had been added were also single domain, but commonly terminated in well-developed (021) planes (Figure 4b). These crystals (containing slightly smaller amounts of incorporated Co) were not as long or as

thin as those grown from coprecipitates; lengths were $< 6000 \text{ \AA}$; the average length : width ratio was ~ 8 . Although Co-goethites from coprecipitates grew more slowly than those from ferrihydrate to which Co had been added, they were less well-developed at the ends, which suggests that incorporation of Co may have disturbed crystal growth to some extent. Co resembles Mn in its effect on goethite morphology in that the presence of either additive leads to crystals with markedly higher length : width ratios than for crystals grown

at pH 12 in the absence of additives (cf. Cornell and Giovanoli, 1987).

Twinned crystals of goethite seldom form at pHs >12 (Cornell and Giovanoli, 1985). The presence of Co, however, promoted formation of twin pieces and dendritic twins at this pH. These twins were better developed and more numerous for systems in which Co was added to already formed ferrihydrite than for coprecipitates (Figures 4a and 4b). As twinning, particularly dendritic twinning, may be caused by accommodation of impurities during crystal growth (Azaroff, 1960; Maeda and Hirono, 1981), twin formation in these systems was probably the result of adsorption of Co species on the 021 planes of the growing crystals of goethite.

Hematite grown in the presence of Co showed a mixture of square and platy morphologies. The hematite crystals were commonly surrounded by outgrowths of goethite (Figure 4c). Co-magnetites grew as small, cubic or octahedral crystals $\sim 300 \text{ \AA}$ across (Figure 4d). Contact recrystallization to larger crystals of the sort reported by Sugimoto (1987) was not noted.

The mixed $\text{Co}_3\text{O}_4/\text{CoOOH}$ precipitate appeared to consist of cubic crystals (Co_3O_4) and a mixture of plates and rods (Figure 4e).

DISCUSSION

The presence of Co retarded the transformation of ferrihydrite into more crystalline products and, depending on the pH and the concentration of Co, suppressed goethite in favor of magnetite or hematite. Goethite precipitates in solution from soluble ferric species released by dissolution of ferrihydrite (Feitknecht and Michaelis, 1962; Schwertmann and Fischer, 1966). Foreign species can retard goethite formation by interference at two stages of its formation: (1) by retarding dissolution of ferrihydrite and (2) by hindering nucleation and growth in solution. Co-ferrihydrite coprecipitates transformed to goethite more slowly than ferrihydrite to which an equivalent level of Co had been added, suggesting that Co acted mainly by stabilizing ferrihydrite against dissolution (cf. Cornell, 1987).

Whether goethite or hematite forms appears to depend on the degree of retardation at the beginning of the transformation. At pH 12, 9 mole % Co led to 100% goethite, whereas 9 mole % Cu, which also stabilizes ferrihydrite against dissolution, leads to 100% hematite; Cu strongly retards the reaction from the start (Cornell and Giovanoli, 1988), whereas the effect of Co became increasingly noticeable after 60–70% reaction. The comparison of the effects of the two ions suggests that for hematite formation to be competitive with that of goethite, ferrihydrite must be strongly stabilized against dissolution in the earliest stage of the transformation. This conclusion is in line with the hypothesis that nucleation of hematite is confined to the

initial stage of the transformation (Cornell and Giovanoli, 1985); if ferrihydrite dissolved rapidly enough for goethite to nucleate readily, hematite did not form despite subsequent stabilization of ferrihydrite.

The transition metals studied to date stabilize ferrihydrite against transformation to more crystalline oxides in the order:



This order corresponds to the Irving-Williams series (1953) for the strength of interaction of divalent transition metals with ligands; in the present system the ligands are the $\text{O}^{2-}/\text{OH}^-$ groups of ferrihydrite.

Dissolution of Co-ferrihydrite released both ferric and cobaltous species. Although Co^{2+} is not readily oxidized in solution, oxidation occurs quite readily at oxide interfaces, particularly those containing small, highly charged ions such as Fe^{3+} (Halbach *et al.*, 1982). Some Co associated with ferrihydrite was probably already oxidized, but the formation of the spinel phase indicates that much Co remained in the divalent form. Most probably the kinetics of oxidation depend to some extent on the Co:Fe ratio at the oxide surface, with oxidation proceeding more rapidly at low Co:Fe ratios. The kinetic study showed that a proportion of Co^{2+} released into solution was taken up by the growing crystals of goethite; adsorption at the surface was followed by oxidation to the trivalent state and incorporation into the structure. Co^{3+} is a d^6 ion, and because of its high charge it exerts a strong crystal field. In nearly all Co^{3+} complexes and compounds, therefore, the ion is in the low-spin configuration, in which case the ionic radius is 0.53 \AA .

In contrast to Mn (Stiers and Schwertmann, 1985), incorporation of high levels of Co in goethite was not readily achieved. Although as much as 10 mole % substitution has been reported for Co-goethites formed from ferrous systems, no more than 7 mole % substitution has been achieved for Co-goethites grown from ferrihydrite (see Abeck and Hund, 1964). The chief reason may be that as low spin Co^{3+} is so much smaller than Fe^{3+} , with a 17% difference in ionic radii, it does not occupy the available structure sites with the same ease as Fe^{3+} . The actual level of incorporation may be governed by the rate of release of Co from ferrihydrite with slow release favoring higher uptake.

Like other divalent ions, Co^{2+} interacted with ferrihydrite to give a spinel phase. Sidhu *et al.* (1978) showed that in aqueous systems, magnetite appeared to precipitate directly from solution. Formation of magnetite by interaction of Fe^{2+} ions with $\gamma\text{-FeOOH}$ and by the oxidation of $\text{Fe}(\text{OH})_2$ also appears to involve dissolution of the initial solid phase (Schwertmann and Taylor, 1972; Tamaura *et al.*, 1981). TEM studies of Sugimoto and Matijevic (1979), however, indicated that magnetite nucleated on or near the surfaces of the $\text{Fe}(\text{OH})_2$ platelets. Other authors have sug-

gested that nucleation of spinels takes place in the water layer adsorbed on the surface of the solid precursor (Giovanoli, 1976; Cornell and Giovanoli, 1987). In the present work some evidence that the spinel does not nucleate in the bulk solution comes from the finding that addition of spinel seed crystals did not promote spinel formation. Furthermore, ferrihydrite to which 23 mole % Co was added transformed almost entirely to goethite; here, comparatively high levels of Co were released into solution by dissolution of ferrihydrite and so, if precipitation in the bulk solution were important, the formation of the spinel should have been favored. Goethite may have formed preferentially in this situation because dissolution of ferrihydrite was retarded to a lesser extent than for a coprecipitated system.

At pH 11 coprecipitates containing 23 mole % Co transformed to a mixture of hematite and Co-magnetite. Hematite, which forms within the solid (Feitknecht and Michaelis, 1962), was promoted at lower pH because the dissolution of ferrihydrite fell with decreasing pH; hence, this result may be considered as further support for the concept that the formation of a spinel phase involved a dissolution step.

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