

EFFECT OF PHOSPHATE ON THE CRYSTALLIZATION OF HEMATITE, GOETHITE, AND LEPIDOCROCITE FROM FERRIHYDRITE

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Abstract—We investigated the crystallization of ferrihydrite prepared by hydrolysis of $\text{Fe}(\text{NO}_3)_3$ solutions containing phosphate. Crystallization was studied at different pH (3–9), temperatures (298, 323, and 373 K), and initial P/Fe atomic ratios for periods to 730 d. Generally, crystallization was inhibited or only poorly crystallized lepidocrocite was formed at $\text{P/Fe} > 2.5\%$. Phosphate favored the formation of hematite over goethite at all temperatures for most of the pH and P/Fe ranges investigated. This result is consistent with a model in which phosphate acts as a template for hematite formation, in analogy with other anions, such as oxalate. However, goethite was preferentially formed at alkaline pH and $\text{P/Fe} > 1\%$, probably because high phosphate concentration resulted in a large increase in the negative charge of the ferrihydrite particles. This resulted in turn in less aggregation, a process that is known to precede dehydration to hematite. Phosphate greatly influenced the morphology of hematite and goethite. Hematite was often ellipsoidal or spindle-shaped. Twinned goethite crystals with a hematite core were formed at alkaline pH at $\text{P/Fe} > 1\%$. Both hematite and goethite particles incorporated phosphate in an occluded form not desorbable by repeated alkali treatments.

Key Words—Crystallization, Ferrihydrite, Goethite, Hematite, Lepidocrocite, Phosphate.

INTRODUCTION

The mechanisms governing the formation of crystalline Fe oxides from ferrihydrite were extensively studied. Cornell and Schwertmann (1996) discussed the competing pathways in which different Fe oxides are formed. For example, temperature, pH, Fe(III) concentration, nature of the accompanying anion, and additives affect, among other factors, the hematite/goethite ratio of the resulting products.

Phosphate, a ubiquitous anion in natural environments, interacts strongly with Fe oxides, particularly via specific adsorption (ligand exchange) with surface OH groups. Therefore, the degree and type of transformation of ferrihydrite or other Fe oxides produced by mineral weathering should be affected by adsorbed phosphate. Experiments with synthetic systems support this. Schwertmann (1969) and Barton (1990) observed lack of transformation of ferrihydrite in the presence of phosphate.

The shape of the hematite particles formed in FeCl_3 systems with akaganéite as the precursor was determined by the concentration of phosphate (Reeves and Mann, 1991; Kadori *et al.*, 1992; Morales *et al.*, 1992; Matijevic, 1993; Sugimoto *et al.*, 1993; Ocaña *et al.*, 1995). Paige *et al.* (1997) studied the effect of phosphate on the transformation of ferrihydrite at pH 12 and reported the formation of an unusual Fe(III) oxide, $\eta\text{-Fe}_2\text{O}_3$. Barrón *et al.* (1997) recently reported that small amounts of phosphate (i) retard the crystallization of ferrihydrite at alkaline pH, (ii) favor the formation of hematite crystals that form nuclei for the epitaxial growth of goethite, and (iii) reduce the growth of goethite crystals in the [001] direction.

Research on the transformation of ferrihydrite to crystalline Fe oxides in the presence of phosphate is limited. Also, the fate of phosphate during crystallization of Fe oxides has received little attention, although natural Fe oxides generally contain phosphate in non-desorbable, “occluded” forms, which are of both pedogenic and environmental significance (Torrent, 1997). In this study, we show and discuss the effect of phosphate concentration on the degree of crystallization of ferrihydrite in aqueous suspensions at different pH values and temperatures, as well as the nature, morphological properties, and phosphate content of the resulting crystalline products.

EXPERIMENTAL

Suspensions of two-line ferrihydrite were prepared by precipitating 0.02 M $\text{Fe}(\text{NO}_3)_3$ with 1 M KOH, in 5–10 steps. Phosphate was previously added to the $\text{Fe}(\text{NO}_3)_3$ solutions to obtain values of the P/Fe atomic ratio in the 0–3% range. The final pH ranged from 3 to 9. No buffers were used to avoid other foreign ions; therefore, the pH was periodically readjusted to the target value with 1 M KOH. The suspensions (three series) were stored in closed polypropylene bottles at 298, 323, and 373 K for 2 y, 2 mo, and 2 wk, respectively. Then, the products were washed free of salts by centrifuging at an acceleration of $1.5 \times 10^4 \text{ m s}^{-2}$ and decanting the suspension and, finally, by dialysis in deionized water until the electrical conductivity of the equilibrium solution was $< 1 \text{ S m}^{-1}$.

Oxalate-soluble material in the products was determined by dissolving them in pH 3, 0.2 M NH_4 -oxalate for 2 h in the dark (Schwertmann, 1964). Total Fe and P (Fe_t , P_t) in the products were determined after dis-

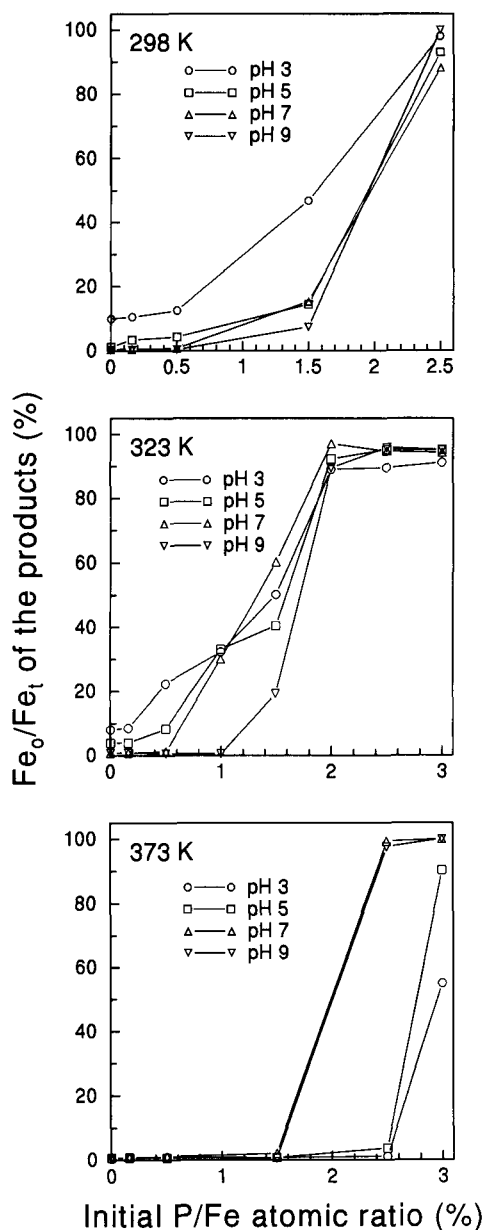


Figure 1. Oxalate-extractable/Total Fe (Fe_0/Fe_t) ratio of the products synthesized at 298, 323, and 373 K as a function of the P/Fe atomic ratio of the initial solution.

solution with cold 11 M HCl. To determine KOH-extractable P, four successive extractions with 0.1 M KOH in 0.5 M KCl were performed in a reciprocating shaker (2.5 Hz, 16 h, 298 K). In all extracts, Fe was determined by the *o*-phenanthroline method (Olson and Ellis, 1982), and P by the molybdenum blue method of Murphy and Riley (1962).

Subsamples of the dialyzed products were freeze-dried and X-ray powder diffraction (XRD) patterns were obtained using a Siemens D5000 diffractometer

with monochromatized $CoK\alpha$ radiation. The proportions of goethite and hematite were estimated using the 012 and 110 peaks of hematite, and the 110 and 111 peaks of goethite, by comparison with mixtures of standard hematites and goethites synthesized in conditions similar to those of the present experiments. Transmission electron micrographs were obtained using a JEOL JEM-200 CX microscope operating at 120 kV. Samples were dispersed in acetone by ultrasonic treatment and a drop of suspension was dried on a carbon-coated copper grid. The specific surface area of selected samples was determined in a Micromeritics ASAP 2010 equipment with the BET method using N_2 as adsorbate.

RESULTS

Effect of phosphate on the crystallization of ferrihydrite

The ratio of oxalate-extractable to total Fe (Fe_0/Fe_t) is normally used to estimate the proportion of the poorly crystalline material in a mixture of Fe oxides; this material includes mainly ferrihydrite and a fraction of the crystalline oxides having large specific surface area. The Fe_0/Fe_t of the final products depended on pH, temperature, and initial P/Fe (Figure 1). The aging periods (730 d at 298 K, 60 d at 323 K, and 14 d at 373 K) were sufficient for nearly complete transformation of ferrihydrite in the absence of phosphate, *i.e.*, Fe_0/Fe_t was close to 0 when the P/Fe was 0 (Figure 1). With increasing P/Fe, the degree of transformation of ferrihydrite to highly crystalline products decreased, *i.e.*, Fe_0/Fe_t increased, so Fe_0/Fe_t was near to 1 for P/Fe > 1.5% in many cases.

The degree of transformation of ferrihydrite increased with increasing pH at the two lower temperatures (298 and 323 K) for small P/Fe values, as observed by Schwertmann and Murad (1983) in P-free systems. However, the opposite trend was observed at these temperatures for P/Fe values greater than ~2% and at 373 K for all the P/Fe range. The negative effect of increasing pH on the apparent ferrihydrite transformation at high P/Fe values was particularly marked at 373 K.

Nature and morphology of the crystalline products

Where $Fe_0/Fe_t < 0.8$ only goethite and hematite were identified as crystalline products; the only exception was a mixture of ferrihydrite, hematite, and lepidocrocite, which formed at pH 3 and 373 K (Figure 2). Where phosphate was absent, the hematite/goethite ratios (Figure 3) agreed reasonably well with previous studies for similar synthesis conditions (Cornell and Schwertmann, 1996, and references therein). Maximum goethite formation occurred at moderately acidic pH values, and increasing temperature favored hematite formation over goethite.

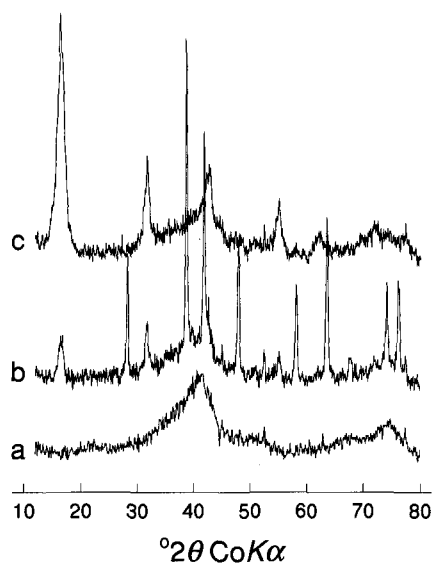


Figure 2. Diffractograms of (a) two-line ferrihydrite (aging time = 15 d; T = 373 K; pH = 9; P/Fe = 3%); (b) mixture of ferrihydrite, lepidocrocite, and hematite (aging time = 15 d; T = 373 K; pH = 3; P/Fe = 3%), and (c) mixture of ferrihydrite and lepidocrocite (aging time = 720 d; T = 298 K; pH = 3; P/Fe = 2.5%).

The effect of phosphate on the hematite/goethite ratio depended on pH, especially at 298 K and 323 K. In acidic solutions, larger initial P/Fe ratios favored hematite formation (trend to darker gray zones, Figure 3). This effect was greater at pH 3–4 than it was at pH 5–6. Thus, a large initial phosphate concentration was needed to promote hematite formation at pH ~5, where goethite was predominant in the absence of phosphate. Goethites formed at these acidic pH values exhibited the acicular or lath habits common in that mineral. The hematites produced in the presence of phosphate in acidic to neutral media were lenticular with an occasional grainy appearance (Figure 4a).

The effects of pH and P/Fe on the hematite/goethite ratio at 373 K were less marked, although the trends were similar to those observed at lower temperatures. In essence, the pro-hematitic effect of the high temperatures dampened differences due to these two factors.

In neutral and alkaline media (pH 7–9), the hematite/goethite ratio increased with the P content to a P/Fe of ~0.5, with the exception of the products formed at 373 K (where no clear trend was observed). With further increases in P/Fe, the proportion of hematite decreased, so only goethite was detected by XRD for P/Fe = 1.5% (Figure 3). This occurred even at 373 K, a temperature that strongly favors hematite formation in P-free systems (Cornell and Schwertmann, 1996).

The morphologies of hematite and goethite were sensitive to the P/Fe, *e.g.*, the morphology of hematites formed at pH 9 changed from rounded platy crystals

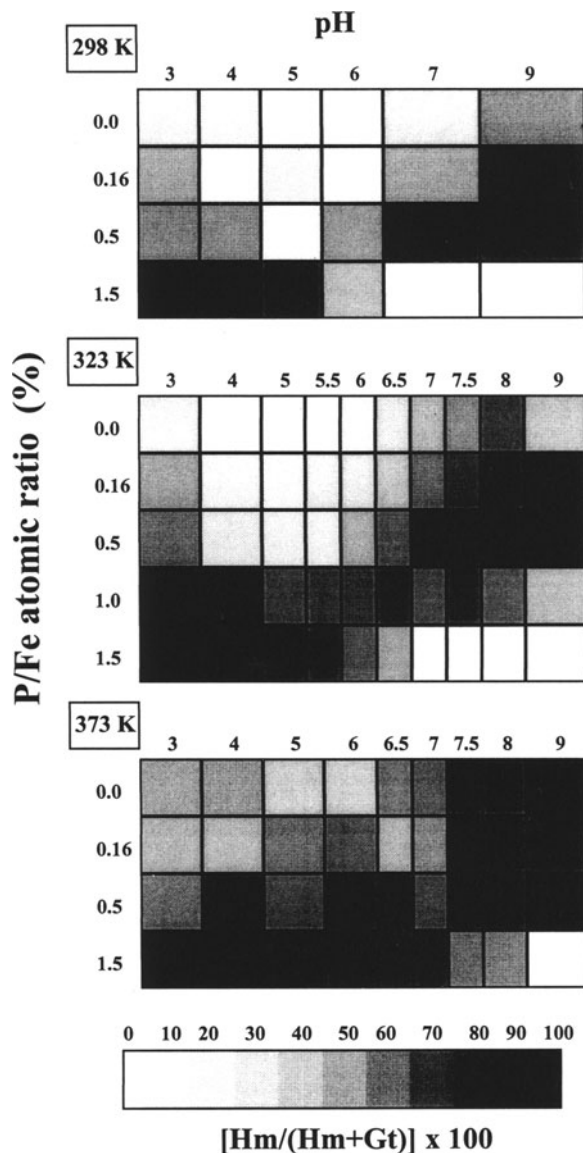


Figure 3. The Hematite/(Hematite + Goethite) [Hm/(Hm + Gt)] ratio of the crystalline products as a function of synthesis temperature, pH and P/Fe atomic ratio.

at P/Fe = 0.16% (Figure 4b) to grainy ellipsoids or spindles at P/Fe = 0.5% (Figure 4c). These ellipsoids or spindles were elongated in the [001] direction, as indicated by the increase in the 110/104 peak intensity ratio in the oriented mineral aggregates with respect to the random mineral powder samples (results not shown). The latter morphologies were somewhat similar to those reported for hematite prepared by hydrolysis of FeCl₃ (Ozaki *et al.*, 1984; Reeves and Mann, 1991; Morales *et al.*, 1992). However, in the latter case, ferrihydrite crystallized first as akaganéite, which was then transformed to hematite.

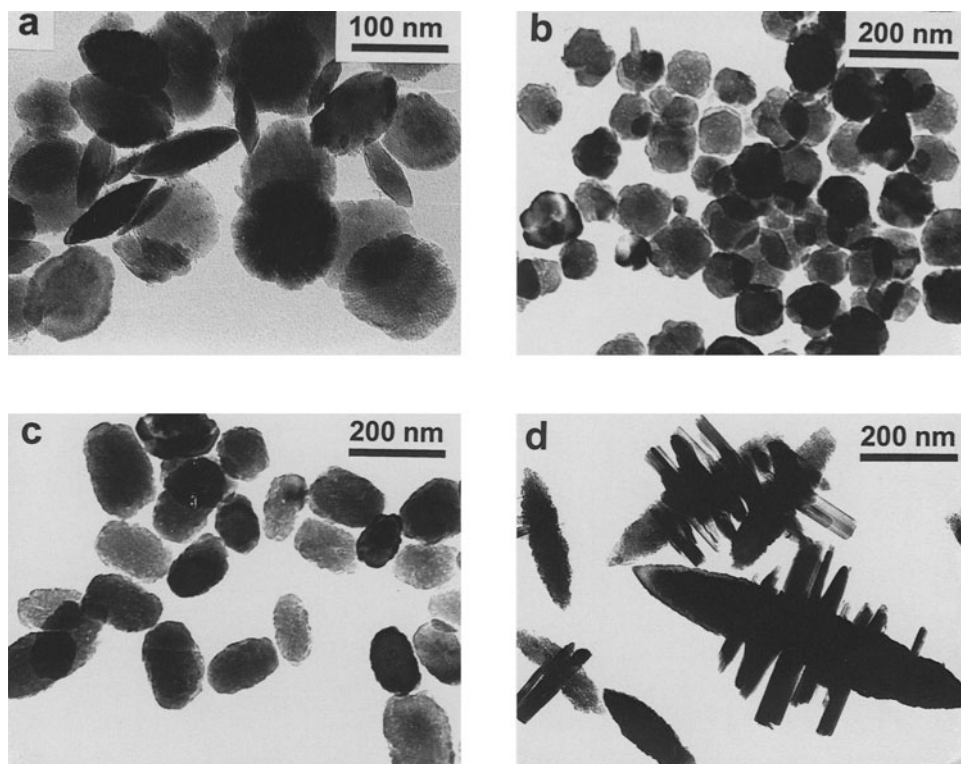


Figure 4. (a) Transmission electron micrographs of hematite produced at pH 7, 373 K, and $P/Fe = 2\%$ showing lenticular shape and grainy appearance. (b) Rounded platy crystals of hematite produced at pH 9, 323 K, and $P/Fe = 0.16\%$. (c) Grainy hematite ellipsoidal particles elongated in the $[001]$ direction produced at pH 9, 323 K, and $P/Fe = 0.5\%$. (d) Samples synthesized at pH 9, 323 K, and $P/Fe = 1\%$ consist of acicular goethite particles that appear to have grown on, and are set perpendicular to larger spindle-shaped hematites.

The samples synthesized at 323 K and $P/Fe = 1\%$, showed acicular goethite particles apparently grown on, and perpendicular to, larger spindle-shaped hematites (Figure 4d). At higher P/Fe values goethite twins with a hematite core (not detected by XRD, but detected by selected area electron diffraction) were

produced, as described elsewhere (Barrón *et al.*, 1997).

Based on the XRD patterns, the products with $Fe_o/Fe_t > 0.8$ contained two-line ferrihydrite, either alone or mixed with poorly crystalline lepidocrocite (Figure 2), which occurred as thin, fibrous laths in the transmission electron microscope (TEM) (Figure 5). The high oxalate solubility of products that, according to TEM and XRD, contained a large proportion of lepidocrocite was probably caused by the large specific surface area of this mineral. Indeed, samples rich in lepidocrocite have specific surface area values of $>250 \text{ m}^2 \text{ g}^{-1}$ (results not shown) and the XRD patterns of this mineral were broad (full-width at half-maximum $>1^\circ 2\theta$). The proportion of lepidocrocite in the samples with $Fe_o/Fe_t > 0.8$, as estimated by XRD, seemed to increase with decreasing temperature and with decreasing pH, so little lepidocrocite was formed at 373 K.

Forms of phosphate associated to the final products

Nearly all the phosphate initially present in the $Fe(NO_3)_3$ solution was generally associated with the solid phases. This is supported by the fact that the P/Fe of the solid phase was similar to the P/Fe of the

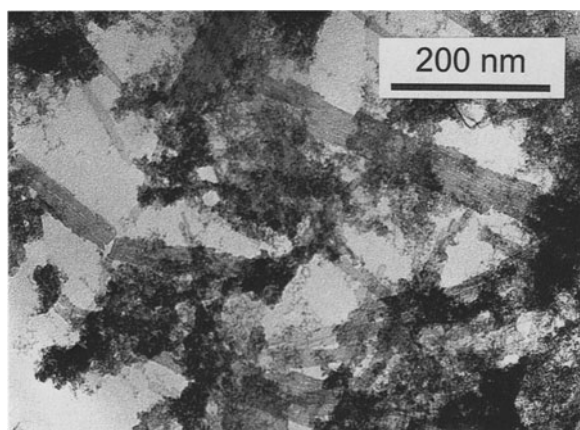


Figure 5. Transmission electron micrograph of a mixture of ferrihydrite and lepidocrocite (aging time = 720 d; $T = 298 \text{ K}$; $pH = 3$; $P/Fe = 2.5\%$).

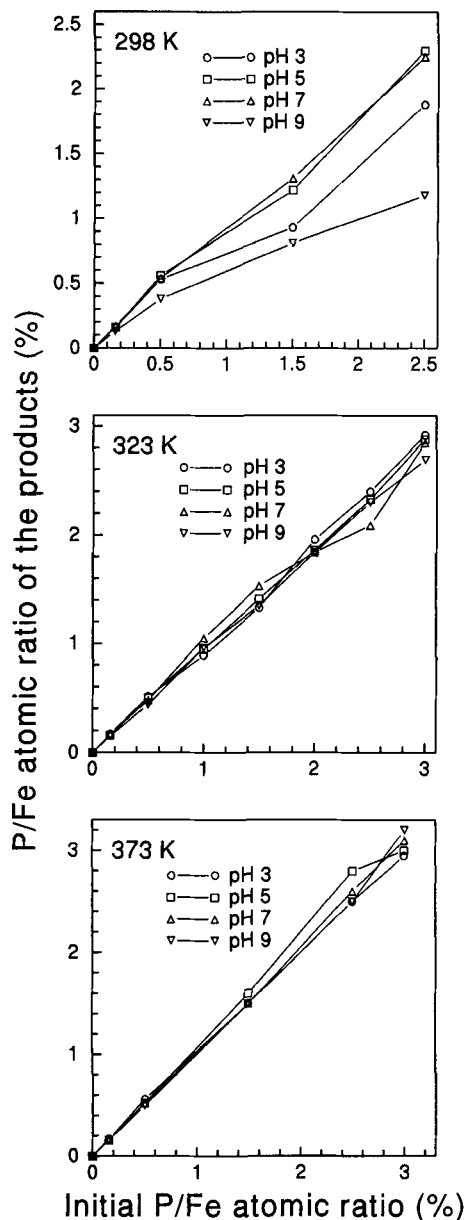


Figure 6. Relationship between the P/Fe in the solid products and the P/Fe atomic ratio in the initial solution.

corresponding initial phosphated Fe(III) solution (Figure 6). Only in some products prepared at 298 K at pH 9 (Figure 6) and pH 12 (data not shown) was that ratio significantly <1 , probably because Fe oxides adsorb little phosphate at such pH values.

The phosphate in the solid phases extractable by KOH (P_{KOH}) was considered as the phosphate adsorbed on the surface of the Fe oxides. The ratio between P_{KOH} and the total amount of P in the solid phases (P_t) varied with the synthesis pH and temperature, and the initial P/Fe. The plots of P_{KOH}/P_t against the initial P/

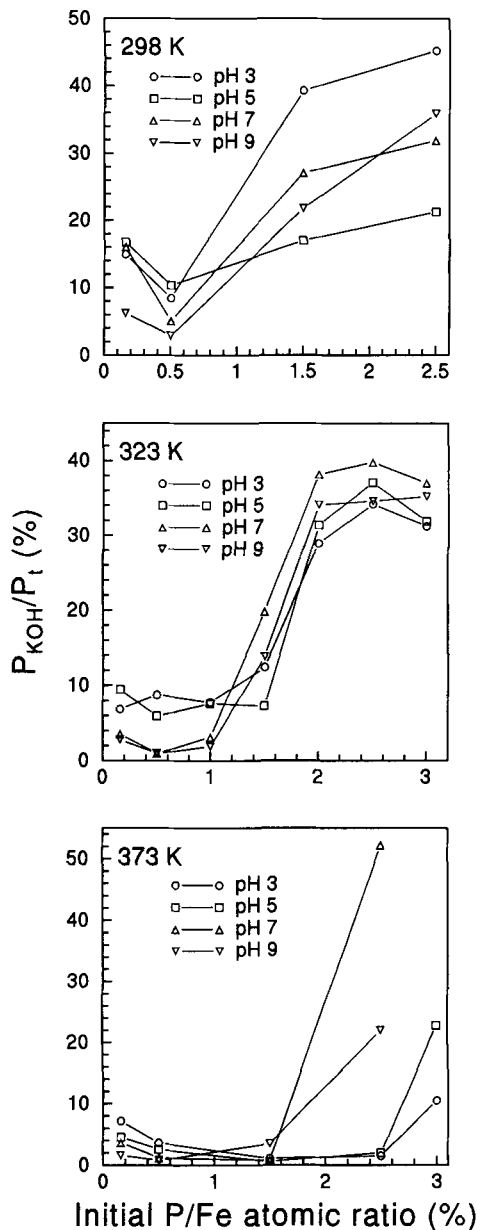


Figure 7. The ratio of KOH-extractable P to total P (P_{KOH}/P_t) in the solid products as a function of the P/Fe atomic ratio in the initial solution.

Fe (Figure 7) are similar in shape to those of Fe_o/Fe_t against P/Fe (Figure 1). This indicates that the fraction of the initial phosphate that remains desorbable increases as the amount of residual poorly crystalline material increases. Thus, the crystalline products were more efficient than ferrihydrite (and, occasionally, lepidocrocite) in retaining significant amounts of phosphate in non-desorbable, occluded forms. In fact, a good correlation was found between P_{KOH}/P_t and Fe_o/Fe_t (Figure 8). Generally, $<10\%$ of P_t was extractable

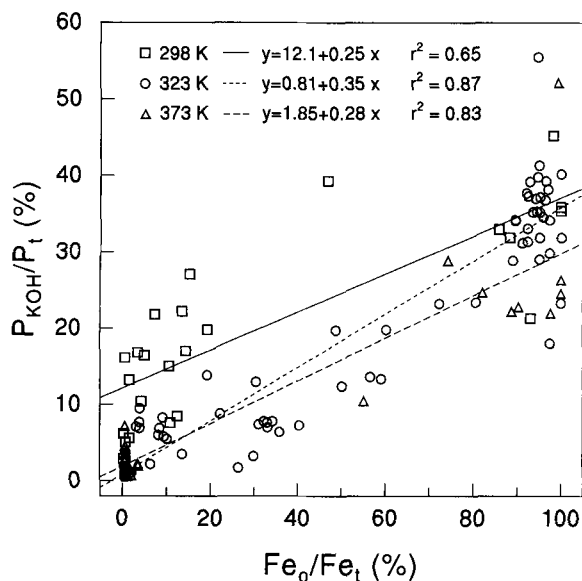


Figure 8. Relationship between P_{KOH}/P_t and Fe_o/Fe_t for all the products synthesized.

with KOH if the products were crystalline and $\sim 40\%$ if ferrihydrite was the predominant Fe oxide. Note that the capacity of ferrihydrite to retain significant amounts of non-desorbable phosphate after aging contrasts with the poor phosphate retention capacity for the fresh P-ferrihydrite precipitates, for which $>75\%$ of the P added was readily extracted with KOH.

DISCUSSION

In phosphate-free systems, the present experiments yield results similar to those of previous studies (Cornell and Schwertmann, 1996, and references therein), *e.g.*, (i) the hematite/goethite ratio shows a maximum in the slightly alkaline pH range and a minimum in the moderately acidic pH range, and (ii) increasing temperature results in more rapid transformation of ferrihydrite and in an increase in the hematite/goethite ratio (Figure 3).

These experiments show that phosphate hinders the transformation of ferrihydrite and affects the hematite/goethite ratio of the final products. Moreover, the latter effect also depends on the pH. In the moderately acidic pH, phosphate favors the formation of hematite over goethite (Figure 3), probably by the mechanism discussed by Cornell and Schwertmann (1996), *i.e.*, a phosphate ion adsorbed on ferrihydrite or on a small hematite nucleus acts as a template, in a way similar to oxalate and carboxylic and hydroxy-carboxylic acids that form binuclear surface complexes (Fischer and Schwertmann, 1975; Cornell and Schwertmann, 1979). Thus, the spindle-shaped and granular ellipsoidal hematite crystals produced in our experiments are similar to those synthesized, for example, in oxalate media (Fischer and Schwertmann, 1975).

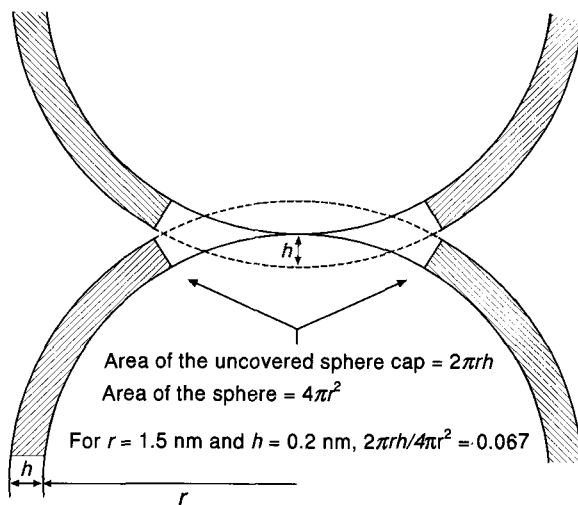


Figure 9. Ideal section representation of the areas covered and not covered by a 0.2 nm-thick layer of phosphate adsorbed on two contacting ferrihydrite particles of 1.5 nm radius.

The sharp decrease in the transformation of ferrihydrite to hematite at all pH values as the P/Fe approaches 2% can be partly explained by the adsorption and size properties of ferrihydrite, as follows: First, in the fresh P-ferrihydrites, most of the phosphate appears adsorbed on the surface of the ferrihydrite (as suggested by the high proportion of phosphate desorbed by KOH). Second, a typical two-line ferrihydrite consists of spherical particles with an average diameter of ~ 3 nm and a density of 4 g cm^{-3} , which gives a calculated specific surface area of $\sim 500 \text{ m}^2 \text{ g}^{-1}$. This value, combined with a phosphate adsorption capacity of $2.5 \times 10^{-3} \text{ mmol P m}^{-2}$ (Torrent, 1997) and a Fe content of 10.4 mmol g^{-1} (for the ideal $\text{Fe}_3\text{HO}_8 \cdot 4\text{H}_2\text{O}$ formula) results in a P/Fe of 12% if the ferrihydrite surface is saturated with a monolayer of phosphate ions. Consequently, a P/Fe of only 2% corresponds at the most to ferrihydrite with only 17% of its surface covered with phosphate. It is difficult then to understand how this small coverage can inhibit ferrihydrite aggregation and internal dehydration to hematite.

However, in hexagonal close-packing of contacting ferrihydrite spheres, each sphere is surrounded by twelve other spheres. By taking the thickness of the phosphate ion adsorbed in the form of a bidentate complex as ~ 0.2 nm (Figure 9), each sphere has twelve sphere caps free of phosphate. The area of one sphere cap is $2\pi rh$, r being the radius of the sphere and h the thickness of the adsorbate layer. This calculation yields an area equivalent to the 6.7% of the total sphere surface per cap (Figure 9), or 80% for the twelve caps. Thus, only 20% of the sphere surface can accommodate phosphate ions, a figure similar in mag-

nitude to the aforementioned 17% coverage for a P/Fe of 2%.

Higher phosphate coverage would probably result in fewer chances for phosphate-coated ferrihydrite spheres to enter in intimate contact with each other and undergo further transformation into hematite. Since some P seems to be occluded in the freshly precipitated ferrihydrite, an additional explanation for the effect of P is the possible interference of the P coprecipitated with Fe in the nucleation of hematite within the ferrihydrite spheres.

In the 7–9 pH range, pure ferrihydrites in equilibrium with atmospheric CO₂ are close to their point of zero charge and the van der Waals forces promote aggregation and further crystallization of ferrihydrite. In contrast, growth of goethite is hindered by the low concentration of the precursor monomeric species (Schwertmann and Murad, 1983), thus hematite usually predominated in the crystallization products. Phosphate tended to further favor hematite formation but only to a P/Fe of ~0.5%. Higher P/Fe values resulted in marked reduction in the hematite content of the products.

The contrasting effect of phosphate at different concentrations is probably caused by the twofold effect of this anion. Not only does it act as a template for hematite formation, but also phosphate adsorption at alkaline pH increases the negative surface charge of ferrihydrite. Thus, the electrostatic repulsion between particles increases, which in turn retards aggregation and further transformation to hematite. Whether one or the other effect predominates depends on the amount of phosphate adsorbed.

Note that adsorbed phosphate hinders ferrihydrite dissolution (Biber *et al.*, 1994) and hence the concentration in solution of species usually considered as precursors for goethite nucleation and growth. This effect, however, seems subordinate to the “antihematitic” effect of phosphate in alkaline media in the 0.5–2% P/Fe range. The likely reduction in the number of the goethite nuclei formed under these conditions made goethite grow epitaxially on spindle-shaped hematite crystals at P/Fe values of ~1% (Figure 4d). At higher P/Fe values, the more pronounced scarcity of nuclei resulted in the formation of large star-shaped goethite crystals growing on a hematite core, the size of which decreases with increasing P/Fe, as expected from the former considerations. The arms of these star-shaped crystals were very short with well developed {021} faces because phosphate adsorbs on this face (Barrón *et al.*, 1997).

The formation of lepidocrocite in the presence of inorganic phosphate was not previously reported. Reeves and Mann (1991) observed that some phosphate-based organic additives (*e.g.*, methyl-dihydrogen phosphate) induced lepidocrocite formation. These authors used the partial-charge model of Livage *et al.*

(1988) to explain that these additives favored olation (FeOOH formation), whereas inorganic phosphate tended to favor oxolation (hematite formation). This hypothesis does not seem to apply to our results. The reason why lepidocrocite, instead of goethite, formed at low pH and high P is obscure. One factor may be the nature of the low molecular weight oligomers produced by the dissolution of ferrihydrite, as well as the nature of the association of these oligomers with the phosphate ions.

The occluded P/total Fe ratio can approach 1.5% in goethite (pH 9, 373 K samples) and 2.5% in hematite (pH 3, 373 K samples). Such values were not previously reported in synthetic oxides, but are not unusual in soil hematites and goethites (Torrent, 1997). Significant structural incorporation of P in goethites is probably not a factor (Cornell and Schwertmann, 1996). Similarly, Si occluded in goethite occurred in apparently isolated clusters rather than in structural form (Glasauer, 1995). Yet, we observed congruent acid dissolution of P and Fe in all the hematites and goethites that contained significant amounts of occluded P (results not shown). This suggests either that structural P is present, or that phosphate ions are homogeneously distributed in the crystal as phosphate adsorbed on internal pores or trapped in interdomain spaces.

Ferrihydrite coprecipitated with phosphate still retained >50% of its total phosphate in occluded form after several weeks or months of contact, depending on the temperature. However, in contrast to hematite or goethite, we did not observe congruent acid dissolution of P and Fe. Thus, occluded P may be phosphate adsorbed on micropores not readily accessible from the external solution. This is consistent with the results of Gruenhagen *et al.* (1996), who, based on infrared spectra, concluded that coprecipitated P was bonded to ferrihydrite in a manner similar to adsorbed phosphate. Occlusion of P in micropores is not observed when phosphate is reacted with ferrihydrite prepared from pure Fe(III) solutions (Willett *et al.*, 1988).

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REFERENCES

- Barrón, V., Gálvez, N., Hochella, M.F., Jr., and Torrent, J. (1997) Epitaxial overgrowth of goethite on hematite synthesized in phosphate media: A scanning force and transmission electron microscopy study. *American Mineralogist*, **82**, 1091–1100.
- Barton, T.F. (1990) The effect of surface modification on the crystal growth of iron oxides. Ph.D. thesis, Virginia Tech., Blacksburg, Virginia, 167 pp.
- Biber, M.V., Alfonso, M.S., and Stumm, W. (1994) The coordination chemistry of weathering: IV. Inhibition of the

- dissolution of oxide minerals. *Geochimica et Cosmochimica Acta*, **58**, 1999–2010.
- Cornell, R.M. and Schwertmann, U. (1979) Influence of organic anions on the crystallization of ferrihydrite. *Clays and Clay Minerals*, **27**, 402–410.
- Cornell, R.M. and Schwertmann, U. (1996) *The Iron Oxides*. VCH, Weinheim. 573 pp.
- Fischer, W.R., and Schwertmann, U. (1975) The formation of hematite from amorphous iron (III) hydroxide. *Clays and Clay Minerals*, **23**, 33–37.
- Glasauer, S.M. (1995) Silicate associated with Fe(hydr)oxides. Ph.D. thesis, Technische Univ. München-Weihenstephan, München, Germany, 133 pp.
- Gruenhagen, S.E., Schulze, D.G., and Johnston, C.T. (1996) Phosphate adsorbed on and occluded in ferrihydrite. *Agronomy Abstracts*, ASA, CSSA, SSSA, 323.
- Kandori, K., Uchida, S., Kataoka, S., and Ishikawa, T. (1992) Effects of silicate and phosphate ions on the formation of ferric oxide hydroxide particles. *Journal of Materials Science*, **27**, 719–728.
- Livage, J., Henry, M., and Sanchez, C. (1988) Sol-gel chemistry of transition metal oxides. *Progress in Solid State Chemistry*, **18**, 259–341.
- Matijevic, E. (1993) Preparation and properties of uniform size colloids. *Chemistry of Materials*, **5**, 412–426.
- Morales, M.P., González-Carreño, T., and Serna, C.J. (1992) The formation of α -Fe₂O₃ monodispersed particles in solution. *Journal of Materials Research*, **7**, 2539–2444.
- Murphy, J. and Riley, J.P. (1962) A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, **27**, 31–36.
- Ocaña, M., Morales, M.P., and Serna, C.J. (1995) The growth mechanism of α -Fe₂O₃ ellipsoidal particles in solution. *Journal of Colloid and Interface Science*, **171**, 85–91.
- Olson, R.V. and Ellis, R., Jr. (1982) Iron. In *Methods of Soil Analysis, Part 2, 2nd edition*, A.L. Page, R.H. Miller, and D.R. Keeney, eds., American Society of Agronomy and Soil Science Society of America, Madison, Wisconsin, 301–312.
- Ozaki, M., Krathovil, S., and Matijevic, E. (1984) Formation of monodispersed spindle type hematite particles. *Journal of Colloid and Interface Science*, **137**, 546–549.
- Paige, C.R., Snodgrass, W.J., Nicholson, R.V., Scharer, J.M., and He, Q.H. (1997) The effect of phosphate on the transformation of ferrihydrite into crystalline products in alkaline media. *Water, Air, and Soil Pollution*, **97**, 397–412.
- Reeves, N.J. and Mann, S. (1991) Influence of inorganic and organic additives on the tailored synthesis of iron oxides. *Journal of the Chemical Society Faraday Transactions*, **87**, 3875–3880.
- Schwertmann, U. (1964) Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-lösung. *Zeitschrift für Pflanzenernährung, Düngung und Bodenkunde*, **105**, 194–202.
- Schwertmann, U. (1969) Der Einfluss einfacher organischer Anionen auf die Bildung von Goethit und Hämatit aus amorphem Fe(III)-hydroxid. *Geoderma*, **3**, 207–214.
- Schwertmann, U. and Murad, E. (1983) Effect of pH on the formation of goethite and hematite from ferrihydrite. *Clays and Clay Minerals*, **31**, 277–284.
- Sugimoto, T., Muramatsu, A., Sakata, K., and Shindo, D. (1993) Characterization of hematite particles of different shapes. *Journal of Colloid and Interface Science*, **158**, 420–428.
- Torrent, J. (1997) Interactions between phosphate and iron oxide. In *Soils and Environment, Advances in GeoEcology 30*, K. Auerswald, H. Stanjek, and J.M. Bigham, eds., Catena Verlag, Reiskirchen, Germany, 321–344.
- Willett, I.R., Chartres, C.J., and Nguyen, T.T. (1988) Migration of phosphate into aggregated particles of ferrihydrite. *Journal of Soil Science*, **39**, 275–282.

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