



PII S0016-7037(02)00876-1

Evidence for a simple pathway to maghemite in Earth and Mars soils

V. BARRÓN and J. TORRENT*

Departamento de Ciencias y Recursos Agrícolas y Forestales, Universidad de Córdoba, Apdo. 3048, 14080 Córdoba, Spain

(Received September 14, 2001; accepted in revised form February 22, 2002)

Abstract—Soil magnetism is greatly influenced by maghemite ($\gamma\text{-Fe}_2\text{O}_3$), the presence of which is usually attributed to the following: (1) heating of goethite in the presence of organic matter; (2) oxidation of magnetite (Fe_3O_4); or (3) dehydroxylation of lepidocrocite ($\gamma\text{-FeOOH}$). Formation of the latter two minerals in turn requires the presence of Fe(II) in the system. No laboratory experiment or soil study to date has shown whether maghemite can form from ferrihydrite, a poorly crystalline Fe(III) oxide [$\sim\text{Fe}_{4.5}(\text{O},\text{OH},\text{H}_2\text{O})_{13.5}$], below 250°C. However, ferrihydrite is the usual precursor of goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$), the most frequently occurring crystalline Fe(III) oxides in soils. Here is presented in vitro evidence that ferrihydrite can partly transform into maghemite at 150°C. This transformation occurs upon aging of ferrihydrite precipitated in the presence of phosphate or other ligands capable of ligand exchange with Fe-OH surface groups. This maghemite coexists with hematite and is a transient phase in the transformation of ferrihydrite to hematite, which is apparently stabilized by the adsorbed ligands. Its particle size is small (10 to 30 nm), and its X-ray diffraction pattern exhibits superstructure reflections. The possible formation of maghemite in Mars and in different Earth soils can partly be explained in the light of this pathway with minimal ad hoc assumptions. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The magnetic properties of Earth soils are dictated by magnetite and maghemite (Mullins, 1977; Maher, 1986; Schwertmann and Taylor, 1989; Singer et al., 1996); this also seems the case with Mars soils and dust (Banin et al., 1993; Madsen et al., 1999; Morris et al., 2000, 2001). Magnetite and Ti-magnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) inherited from the soil parent material and maghemites resulting from the oxidation of these minerals are major sources of magnetism in many soils. Magnetite in Earth soils can also be the result of synthesis by magnetotactic bacteria (Fassbinder et al., 1990) and, possibly, extracellular synthesis (from Fe oxides and Fe^{2+}) by dissimilatory iron-reducing bacteria (Lovley et al., 1987). Abiotic precipitation has also been suggested as origin of some soil magnetites (Maher and Taylor, 1988). Because of their small size, authigenic magnetite crystals can be oxidized in periods when the soil is aerated (van der Marel, 1951; Schwertmann and Heinemann, 1959; Murad and Schwertmann, 1993) and thus evolve to maghemite. The latter mineral can also be formed in surface soil horizons through fire-induced transformation of goethite in the presence of organic matter and through dehydroxylation of lepidocrocite (Schwertmann and Taylor, 1989). The likely, but not conclusively demonstrated, presence of maghemite in Mars soils has been attributed to thermal conversion of precursor lepidocrocite rather than to oxidation of Ti-magnetite (Banin et al., 1993; Morris et al., 1998). The results of laboratory experiments (Cumplido et al., 2000; Torrent and Barrón, 2000) suggest that lepidocrocite formation and conversion, via meteoritic impact, to maghemite stable at temperatures of $\sim 550^\circ\text{C}$ might be favored by the high P contents ($\sim 3 \text{ g kg}^{-1}$) of Mars rocks (Dreibus et al., 1999).

Maghemite forms from magnetite because its cubic structure

is easily inherited from the inverse spinel structure of magnetite and forms from lepidocrocite because the [051] direction of the latter corresponds to the [111] direction of a distorted maghemite cubic cell (Fasiska, 1967). Eggleton and Fitzpatrick (1988) showed that maghemite formed from ferrihydrite upon heating above 250°C in flowing N_2 . They suggested that this transformation occurs because part of the Fe ions in ferrihydrite, like in maghemite, occur in tetrahedral coordination. The presence of tetrahedrally coordinated Fe ($^{\text{IV}}\text{Fe}$), however, was not supported by extended X-ray absorption fine structure studies (Manceau and Drits, 1993). Nanodiffraction studies suggest, in contrast, the presence of up to 4% $^{\text{IV}}\text{Fe}$ in 2-line ferrihydrites (Janney et al., 2000) but less in 6-line ferrihydrites (Janney et al., 2001). A review by Jambor and Dutrizac (1998) arrives at the conclusion that octahedral coordination represents the “core” of the ferrihydrite structure but part of the surface Fe is $^{\text{IV}}\text{Fe}$ that offers sites amenable to adsorption of foreign species.

Maghemite is relatively abundant in deep horizons of some well-aerated tropical soils, particularly in those that have a high hematite/goethite ratio (Fontes and Weed, 1991; da Costa, 1996). In some of these soils, maghemite is Al substituted, thus excluding formation from lithogenic magnetite, which generally contains little Al (Deer et al., 1962). Because deep horizons are not affected by fire, thermal transformation of an Al-substituted precursor Fe (hydr)oxide (goethite, ferrihydrite, or lepidocrocite) can also be excluded in these soils. It is also unlikely that the solution of a well-aerated, organic matter-poor soil contains enough Fe^{2+} to react with Fe oxides to produce magnetite (Schwertmann and Taylor, 1989). This poses the question whether ferrihydrite, one of the precursors of goethite, and the usual precursor of hematite (the most common Fe oxides), can also transform into maghemite at pedogenic temperatures. We considered this hypothesis when we observed that the products of transformation of some P-doped ferrihydrites exhibited magnetic susceptibility values larger than those

* Author to whom correspondence should be addressed (torrent@uco.es).

of ferrihydrite, hematite, goethite, or lepidocrocite, particularly at temperatures $>100^{\circ}\text{C}$. In this study, we present *in vitro* evidence that ferrihydrite can be transformed into maghemite in aqueous media at 150°C and indirect indication that this transformation can occur at near-pedogenic temperatures.

2. MATERIALS AND METHODS

2.1. Ferrihydrite Preparation and Chemical Analyses

Suspensions of 2-line ferrihydrite were prepared by precipitating 0.1 mol/L $\text{Fe}(\text{NO}_3)_3$ with 1 mol/L KOH to a final pH of 7 in the presence of either phosphate, silicate, tartrate, or citrate. The initial anion/Fe mole ratio ranged between 0 and 0.06. The suspensions were aged in Pyrex bottles at temperatures of 25, 50, and 100°C and in Teflon-lined steel bombs at temperatures of 125, 150, 175, and 200°C (corresponding to pressures of 0.35, 0.60, 1.05, and 1.70 MPa, respectively) over periods of 0.2 to >180 d. One of the series at 175°C was prepared with NaOH instead of KOH to precipitate the Fe(III) salt. At selected times, portions of the suspensions were centrifuged at an acceleration of $1.5 \times 10^4 \text{ m s}^{-2}$ and decanted before washing the sediment several times with deionized water. A small portion of the washed sediment was suspended in water and the rest was freeze dried. Oxalate-soluble Fe (Fe_o) was determined by dissolving the product in 0.2 mol/L NH_4^+ -oxalate with pH of 3 for 2 h in the dark (Schwertmann, 1964). Total Fe (Fe_t) was determined by dissolving 5 mg of the product in 1 mL of cold 11 mol/L HCl. In all extracts, Fe was determined by the *o*-phenanthroline method (Olson and Ellis, 1982).

2.2. Mineralogical Analyses

Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer equipped with $\text{CoK}\alpha$ radiation and a graphite monochromator at a step size of $0.05^{\circ}2\theta$ and a counting time of 20 s. Transmission electron microscope (TEM) specimens of the products were prepared by depositing a drop of the dilute aqueous suspension on C-coated Formvar film supported by a copper grid, which was then examined with a Jeol JEM-200CX instrument. Infrared (IR) spectra of KBr pellets (0.5 wt% sample) were recorded from 380 to 4000 cm^{-1} with a Perkin-Elmer 2000 FTIR spectrometer with 4 cm^{-1} resolution and an average of 100 scans. Magnetic susceptibility, χ , was measured at 10^{-4} T on a physical property measurement system. The frequency dependence of the magnetic susceptibility (χ_{FD}) was calculated as the difference in χ at 0.47 and 4.7 kHz divided by the low-frequency susceptibility. Color was determined with a Varian Cary 1E spectrophotometer equipped with a diffuse reflectance attachment. To prevent particle orientation, color was measured in mixtures of 10 mg of freeze-dried product with 190 mg of white standard BaSO_4 . The reflectance values were taken at intervals of 0.5 nm in the 380- to 900-nm range and converted to the tristimulus X, Y, Z values by the equations provided by Wyszecki and Stiles (1982) and, finally, to the Munsell notation by the free software downloaded from Munsell Color's Web site (www.munsell.com).

In some of the products containing ferrihydrite, hematite, and maghemite, the proportion of maghemite was estimated semiquantitatively by assigning all Fe_o to ferrihydrite and by estimating the proportion of hematite by means of comparing the intensities of the hematite 104 and 110 peaks of the XRD pattern with those of the XRD-pure hematite that was obtained by aging the product for a time long enough for total conversion to hematite.

3. RESULTS

Significant amounts of maghemite were formed when phosphated ferrihydrite was aged at different temperatures if the initial P/Fe atomic ratio was greater than ~ 0.020 . The typical course of this transformation is illustrated by the successive XRD patterns for ferrihydrite with P/Fe = 0.03 aged at 150°C for a period of 120 d (Fig. 1). The reflections of the initial 2-line ferrihydrite became first narrower, suggesting a slight improve-

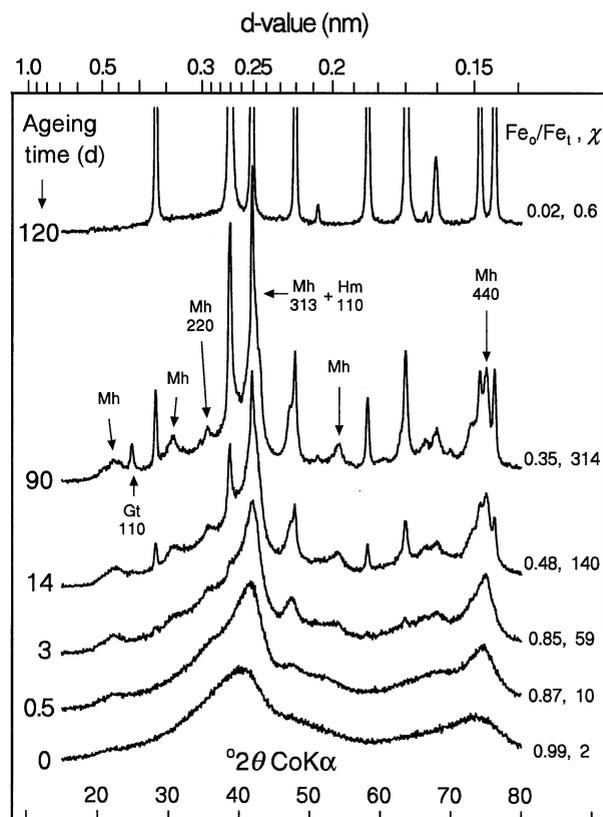


Fig. 1. X-ray diffraction patterns for the successive products obtained by aging phosphated ferrihydrite (P/Fe atomic ratio = 0.03) at 150°C for 120 d. The pattern for the initial product (0 d) is typical of a two-line ferrihydrite. Selected maghemite, hematite, and goethite reflections are denoted by Mh, Hm, and Gt, respectively. The maghemite reflections that are not indexed are attributed to a superstructure. The pattern for the 120-d product exhibits only the reflections for hematite (not marked). The ratio of oxalate extractable to total Fe (Fe_o/Fe_t) and the magnetic susceptibility, χ ($10^{-6} \text{ m}^3 \text{ kg}^{-1}$) for each product are given to the right of the corresponding pattern.

ment in crystallinity/particle size. Then, the ferrihydrite evolved to a mixture of maghemite, hematite, residual ferrihydrite, and some goethite that was observed at 90 d of aging. Maghemite was identified by the reflections at 0.295, 0.251, and 0.147 nm (indexed as 220, 313, and 440). In the products where maghemite was present, three superstructure broad peaks at 0.468, 0.341, and 0.197 were observed (e.g., the 90-d pattern in Fig. 1). The origin of these superstructure reflections is difficult to establish, however. It might be related to ordering of OH groups present in the structure because thermogravimetric analyses (not shown) indicate loss of a substantial amount of water in the 150 to 400°C interval.

The increase in intensity of the maghemite and hematite reflections with time is concomitant with a decrease in the ratio of acid oxalate extractable to total Fe—for example, with an increase in crystallinity of Fe oxides (Schwertmann, 1964). Such a ratio is 0.35 at 90 d. Thus, 35% of the Fe of this sample can be assigned to ferrihydrite on the assumption that neither the well crystallized hematite nor the maghemite in the sample are dissolved by oxalate to a significant extent. The poor solubility of the maghemite in oxalate was confirmed by the

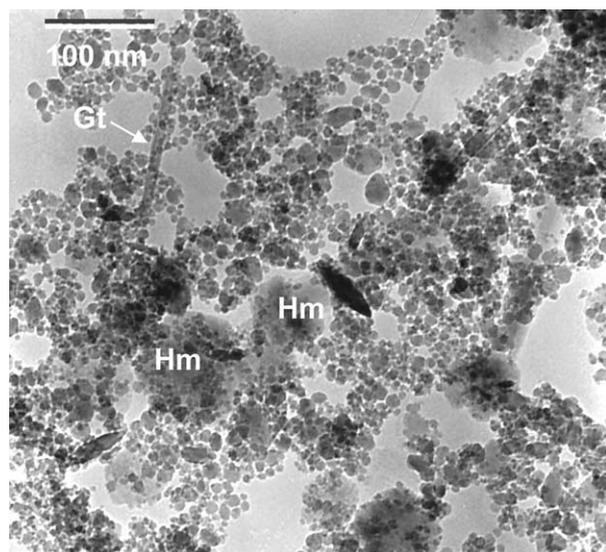


Fig. 2. Transmission electron micrograph of the product obtained by aging phosphated ferrihydrite ($P/Fe = 0.03$) at 150°C for 90 d. The electron diffraction patterns of particles morphologically similar to those denoted by Hm and Gt were those of hematite and goethite, respectively. The subrounded particles of 10 to 30 nm were assigned to maghemite on the basis of the high magnetic susceptibility of the product ($315 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$).

absence of significant change in the ratios between the maghemite and hematite peaks upon oxalate treatment.

The intensity of maghemite reflections peaks at ~ 90 d and then decreases abruptly to zero at 120 d. By this time, only the hematite reflections are observed. On the basis of the position of the reflections (and also on characteristic IR absorption bands at ~ 936 , ~ 971 , ~ 1005 , and $\sim 1037 \text{ cm}^{-1}$), this hematite contains structural P (Gálvez et al., 1999a).

The magnetic susceptibility, χ , of the product (Fig. 1) changes in parallel with the intensity of the maghemite reflections; thus, it peaks at $\sim 315 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ at 90 d, and then decreases to $< 1 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ at 120 d. We estimate χ for the 90-d maghemite to be $\sim 600 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ on the assumptions that (1) the χ values for ferrihydrite, hematite and goethite are negligible; (2) the proportions of ferrihydrite and hematite can be estimated by the methods discussed before; and (3) the proportion of goethite can be neglected. This χ value lies above the 400 to $550 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ range that is usually reported in the literature (de Boer, 1999) but within the 500 to $900 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ range reported by Dearing et al. (1996) for maghemite grains with a diameter of 20 to 40 nm.

The TEM images for the 90-d product (Fig. 2) show large clusters of subrounded small (10 to 30 nm) particles, together with some imperfectly hexagonal hematite plates and few goethite needles (identified from their electron diffraction patterns). This makes it reasonable to assume that the small particles consist of maghemite. Because of their size, these particles are likely to span the superparamagnetic–single domain size (Maher, 1988). This hypothesis is supported by the χ_{FD} value of 3.5% previously found for this sample because χ_{FD} values above 1% are likely to indicate the presence of superparamagnetic particles (Dearing, 1994). In contrast to the 90-d sample, only the rhombohedral and thick hexagonal crys-

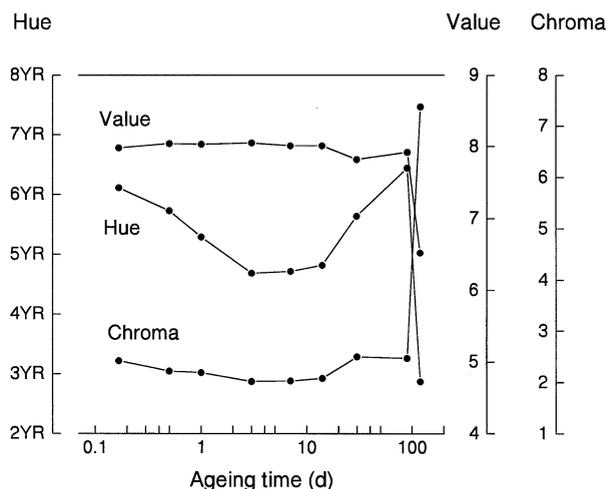


Fig. 3. Munsell hue, value, and chroma notation of the products resulting from the transformation of phosphated ferrihydrite ($P/Fe = 0.03$) at 150°C . Measurements were performed on 5 to 95% mixtures of product–white standard BaSO_4 .

tals typical of many synthetic hematites are seen in the TEM images of the 120-d sample (data not shown).

Figure 3 shows the change in color (Munsell notation) of the products from the experiment at 150°C at $P/Fe = 0.03$. The Munsell value (i.e., lightness) does not depart significantly from 8.0 until day 90 and then drops to ~ 6.5 at 120 d, a time when the product is essentially hematite. This suggests that no magnetite was formed during the transformation of ferrihydrite because magnetite is black (or dark brown, but only in cation-deficient samples), which would have resulted in a strong decrease in lightness. This decrease was not observed in any of the experiments at other temperatures either. The Munsell chroma (i.e., color saturation) increases sharply when hematite becomes dominant. The Munsell hue (i.e., dominant spectral light) increases in redness from the initial ferrihydrite ($H = 5.7$ YR) to the final hematite ($H = 2.9$ YR) but there is an intermediate increase in yellowness at days 30 and 90. This is consistent with the presence of maghemite, which is generally more yellow than ferrihydrite (Scheinost and Schwertmann, 1999).

Maghemite can thus act as a transient phase in the transformation of ferrihydrite into hematite (occasionally, with some goethite). Maghemite readily transforms into hematite (with a concomitant χ decrease) above 150°C despite the required restacking of the oxygen layers from a cubic to an hexagonal closest packing; this transformation is probably favored by the small size of the maghemite particles observed in all of the experiments (Feitknecht and Mannweiler, 1967). The kinetics of maghemite formation (and its further transformation into hematite) is highly dependent on temperature. Experiments at $P/Fe = 0.03$ showed that the time required for χ (taken as a proxy for maghemite content) to peak increased with decreasing temperature (Fig. 4). Such time was ~ 0.9 d at 200°C , ~ 5 d at 175°C , and ~ 90 d at 150°C . At or below 100°C , χ increased significantly with time but reached no maximum over the period studied. The value of χ at 100°C and 180 d ($\sim 8 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$), however, suggests that maghemite is present in

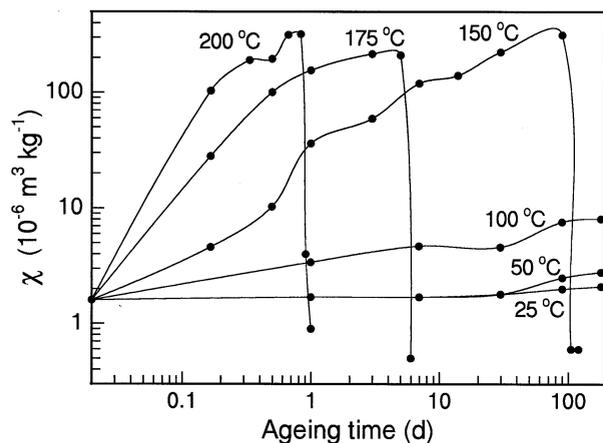


Fig. 4. Magnetic susceptibility as a function of aging time for the products formed from phosphated ferrihydrite ($P/Fe = 0.03$) aged at different temperatures. The lines are intended to help the reader's eye.

the products (Fig. 4). By extrapolating the Arrhenius plot fitted to the products aged at 150 to 200°C, we estimated the time required for the transformation into hematite to be ~ 50 yr at 100°C and ~ 1 Myr at 25°C. Formation and persistence of maghemite thus seem, in principle, possible at pedogenic temperatures.

Maghemite formation is sensitive to the P/Fe ratio in the initial ferrihydrite, as shown by experiments at 150°C (Fig. 5). At 14 d, χ was $< 1 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ at $P/Fe < 0.025$ because ferrihydrite was transformed into hematite. With increasing P/Fe , χ increased abruptly to a maximum of $240 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ at $P/Fe \sim 0.0275$, to finally decrease to $< 20 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ at $P/Fe = 0.06$. This pattern was observed at temperatures different from 150°C provided time was long enough for ferrihydrite to transform. In summary, maghemite is formed only when P/Fe lies within a certain range. Below the optimum P/Fe range for maghemite formation, ferrihydrite is readily transformed into hematite (occasionally with some goethite). Within the optimum range, phosphate that is coprecipitated or ad-

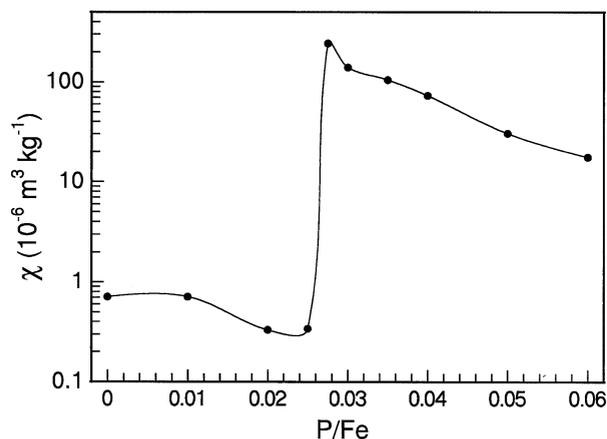


Fig. 5. Magnetic susceptibility as a function of P/Fe for the phosphated ferrihydrite aged at 150°C for 14 d. The line is intended to help the reader's eye.

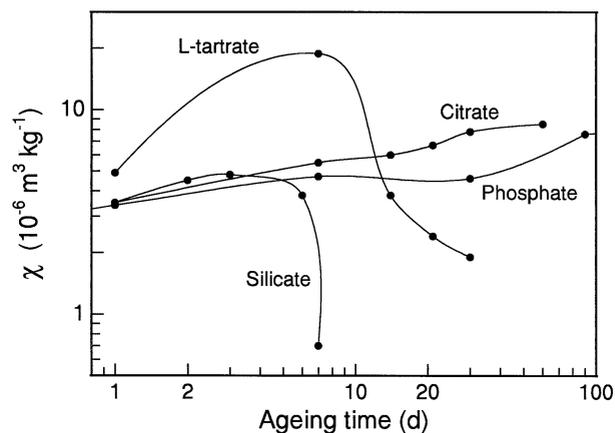


Fig. 6. Magnetic susceptibility as a function of time for the products formed from ferrihydrite prepared in the presence of either phosphate, tartrate, citrate, or silicate (anion/ Fe mole ratio = 0.03) and aged at 100°C. The lines are intended to help the reader's eye.

sorbed by ligand exchange hinders both the aggregation of ferrihydrite that precedes its transformation into hematite and the dissolution of ferrihydrite required for goethite to form (Schwertmann and Taylor, 1989). This probably favors the alternative transformation into maghemite; such transformation might be triggered by the possible (but not conclusively proven) existence of small amounts of ^{IV}Fe in the ferrihydrite. Amounts of phosphate in excess of a certain threshold indeed prevent any significant transformation of ferrihydrite, as is also the case for other strongly adsorbing ligands (Cornell and Schwertmann, 1996).

Figure 6 shows that some maghemite (as evidenced by the χ values of the products) was also formed in experiments at 100°C with L-tartrate and citrate. These anions, like phosphate, are strongly adsorbed by ligand exchange on Fe oxides. The differences in the effect of these two anions (Fig. 6) are possibly due to differences in the number and arrangement of OH and COOH groups adsorbed on the oxide surface. In fact, Cornell and Schwertmann (1979) found that L-tartrate favored the transformation of ferrihydrite into hematite more than citrate. This difference can explain why χ increases rapidly with time and then decreases abruptly (hematite formation) in the tartrate system, whereas χ always increases with time (albeit at a slow rate) in the 60-d experiment with citrate (Fig. 5). Experiments at $> 125^\circ\text{C}$ (not shown) indicate similarity between the XRD patterns of samples prepared in the presence of citrate and phosphate. With silicate, no significant amounts of maghemite form before ferrihydrite becomes hematite (Fig. 6). This anion has very little capacity to prevent hematite formation and to stabilize maghemite formed from ferrihydrite probably because it is less strongly adsorbed than phosphate (Sigg and Stumm, 1980). In other experiments to examine the effect of foreign ions, we used NaOH instead of KOH to precipitate the Fe(III) salt, given that Na is much more abundant than K in some environments, such as in soils on Mars (Rieder et al., 1997). We found that the products of a series prepared at 150°C with NaOH did not differ significantly from those prepared with KOH.

4. DISCUSSION

The ferrihydrite-to-maghemite pathway described in this work occurs under conditions that differ substantially from those reported by Eggleton and Fitzpatrick (1988). These authors obtained maghemite by heating dry 6-line ferrihydrite in a N₂ atmosphere to >250°C. Campbell et al. (1997) reported that heating ferrihydrite in a pure (99.999%) N₂ atmosphere resulted in maghemite formation only when a reductant (glucose) was present. Madsen et al. (1999) obtained maghemite by heating an ochre (ferrihydrite) from a water treatment plant containing 4% weight of C. These three sets of experiments have in common the absence of oxidizing conditions that may favor the initial formation of magnetite that evolves to maghemite when the conditions become oxidizing again. In our experiments, reduction of the ferrihydrite Fe(III) and magnetite formation is not likely because they were carried out in an air atmosphere. This contention is supported, as previously discussed, by the absence of a significant decrease in lightness (resulting from magnetite production) of the products at the time when maghemite is being formed (Fig. 3).

Our results indicate that ferrihydrite can partly transform into maghemite when sufficient amounts of strongly adsorbing ligands "block" ferrihydrite to an extent to interfere with the mechanisms by which hematite and goethite are formed. Below a certain ligand concentration, the metastable maghemite phase is not formed and hematite is the product of ferrihydrite transformation, as shown by control experiments with little or no phosphate (Fig. 5). In our experiments, maghemite formed at much lower temperatures than those reported by the former authors; the extent to which the hypothetical presence of ⁵⁷Fe on the ferrihydrite surface can contribute to favor the ferrihydrite-maghemite transformation cannot be elucidated on the basis of current data.

One apparent consequence of the blocking effect of the ligands adsorbed on ferrihydrite is the slow kinetics of maghemite formation. As previously indicated, extrapolation of the results obtained at >150°C to pedogenic temperatures yields times above 10⁵ yr for ferrihydrite to significantly transform into maghemite in the presence of the most effective ligands (phosphate and citrate). Consequently, if the proposed pathway operates in soils, one should expect pedogenic maghemite of this origin to occur in significant amounts only in relatively old soils. This is consistent with the common presence of maghemite in highly weathered soils and soil materials of tropical and subtropical regions. Examples are different Oxisols from Brazil (Fontes and Weed, 1991; da Costa, 1996) and New Caledonia (Schwertmann and Latham, 1986), the oldest members of Alfisols chronosequences in California (Singer et al., 1996), nodules and clays of South Africa and Australia (Fitzpatrick, 1988), and paleosols in loess-paleosols sequences of different regions (Liu et al., 1992; Heller and Evans, 1995; Maher, 1998; Tsatskin et al., 1998).

The ligands that, according to our experiments, favor the ferrihydrite-maghemite transformation also favored hematite over goethite in the crystallization of ferrihydrite (Cornell and Schwertmann, 1996; Gálvez et al., 1999b). This occurred probably because these ligands hinder ferrihydrite dissolution, a step postulated to be previous to goethite nucleation (Schwertmann and Taylor, 1989). Therefore, if the proposed pathway

operates in soils, then one would expect maghemite to occur in hematitic rather than goethitic soils. This is the case with Oxisols from Brazil (Fontes and Weed, 1991; da Costa, 1996) and New Caledonia (Schwertmann and Latham, 1986), where the hematitic soils often are maghemite rich but the goethitic soils contain generally no maghemite. In the Chinese loess-paleosols sequences, enhanced magnetic susceptibility (attributed to maghemite) is recorded in the paleosols where hematite is the dominant crystalline Fe oxide (Fine et al., 1995; Tsatskin et al., 1998).

Direct transformation of ferrihydrite into maghemite might partly account for the magnetic enhancement observed in humic soil horizons in paleosols of some loess-paleosols sequences (Virina et al., 2000), where low-molecular-weight organic acids probably occurred in significant concentration during soil formation.

Because the proposed pathway implies formation of both maghemite and hematite, it provides an amazingly simple explanation for the supposed maghemite-hematite assemblage in Mars soils, which exhibit a hematite-like spectral signature and magnetic properties consistent with the presence of maghemite (Madsen et al., 1999; Morris et al., 2000). Indeed, the high (~0.05) P/Fe ratio of the Martian mafic rocks (Dreibus et al., 1999) would favor the proposed evolution of ferrihydrite to maghemite. Interestingly, as postulated by Torrent and Barrón (2000), this high P/Fe ratio might also play a crucial role in a well-known competitive pathway—that is, lepidocrocite formation and conversion to maghemite-hematite via meteoritic impact (Banin et al., 1993; Morris et al., 1998). In fact, the presence of phosphate resulted in first, the formation of lepidocrocite rather than goethite when Fe(II)SO₄ neutralized with bicarbonate was oxidized (Cumplido et al., 2000), and second, the partial transformation of ferrihydrite into lepidocrocite at P/Fe >0.025 (Gálvez et al., 1999b). The question remains whether the environmental conditions affecting the weathering of Fe(II) silicates on the surface of Mars would result in lepidocrocite, ferrihydrite or magnetite as maghemite precursors. Whether neof ormation of Fe oxides resulting in the appearance of maghemite has more importance than the frequently preconized oxidation of lithogenic magnetite or Ti-magnetite to maghemite (Morris et al., 2000, 2001) is a question yet unresolved.

Acknowledgments—This work was supported by the Spanish Ministry of Science and Technology (project PB98-1015). We thank Dr. J. L. Martínez (ICMM, Madrid) for his help with the magnetic measurements. We acknowledge the constructive criticism offered by Prof. U. Schwertmann and Dr. H. Stanjek, Technische Universität München, and Dr. R. V. Morris, NASA.

Associate editor: P. A. Maurice

REFERENCES

- Banin A., Ben-Shlomo T., Margulies L., Blake D. F., Mancinelli R. L., and Gehring A. U. (1993) The nanophase iron mineral(s) in Mars soil. *J. Geophys. Res.* **98**, 20831–20853.
- Campbell A. S., Schwertmann U., and Campbell P. A. (1997) Formation of cubic phases on heating ferrihydrite. *Clay Miner.* **32**, 615–622.
- Cornell R. M. and Schwertmann U. (1979) Influence of organic acids in the crystallization of ferrihydrite. *Clays Clay Miner.* **27**, 402–410.
- Cornell R. M. and Schwertmann U. (1996) *The Iron Oxides*. VCH.

- Cumplido J., Barrón V., and Torrent J. (2000) Effect of phosphate on the formation of nanophase lepidocrocite from Fe(II) sulfate. *Clays Clay Miner* **48**, 503–510.
- da Costa A. C. S. Iron oxide minerals of soils derived from volcanic rocks in the Paraná River Basin, Brazil. Ph.D. thesis. 1996. Ohio State University.
- de Boer C. B. Rock-magnetic studies on hematite, maghemite and combustion-metamorphic rocks. Ph.D. thesis. 1999. Utrecht University, The Netherlands.
- Deer W. A., Howie R. A., and Zussman J. (1962) *Rock Forming Minerals* Vol. 5. Longmans.
- Dearing J. (1994) Environmental Magnetic Susceptibility. Using the Bartington MS 2 System. Chi Publishing, Kenilworth, UK.
- Dearing J. A., Dann R. J. L., Hay K., Lees J. A., Loveland P. J., Maher B. A., and O'Grady K. (1996) Frequency-dependent susceptibility measurements of environmental materials. *Geophys. J. Int* **124**, 228–240.
- Dreibus G., Brueckner J., Lugmair G. W., Rieder R., and Waenke H. (1999) Possible indication of sedimentary products at the Mars Pathfinder landing site: Phosphorus in APXS X-ray spectra. *EOS Trans. AGU* **80**, (Supplement) p. 46. Poster P32A-06.
- Eggleton R. A. and Fitzpatrick R. W. (1988) New data and a revised structural model for ferrihydrite. *Clays Clay Miner* **36**, 111–124.
- Fasiska E. J. (1967) Structural aspects of the oxides and oxidehydrates of iron. *Corros. Sci.* **7**, 833–839.
- Fassbinder J. W. E., Stanjek H., and Vali H. (1990) Occurrence of magnetic bacteria in soil. *Nature* **343**, 161–163.
- Feitknecht W. and Mannweiler U. (1967) Der Mechanismus der Umwandlung von γ - $\text{zr}\alpha$ -Eisensesquioxid. *Helv. Chim. Acta.* **50**, 570–581.
- Fine P., Verosub K. L., and Singer M. J. (1995) Pedogenic and lithogenic contributions to the magnetic susceptibility record of Chinese loess/paleosol sequence. *Geophys. J. Int.* **122**, 97–107.
- Fitzpatrick R. W. (1988) Iron compounds as indicators of pedogenic processes: Examples from the southern hemisphere. In *Iron in Soils and Clay Minerals* (eds. J. W. Stucki, B. A. Goodman, and U. Schwertmann), pp. 351–396. Reidel Pub. Co, Dordrecht, Holland.
- Fontes M. P. F. and Weed S. B. (1991) Iron oxides in selected Brazilian Oxisols: I. Mineralogy. *Soil Sci. Soc. Am. J.* **55**, 1143–1149.
- Gálvez N., Barrón V., and Torrent J. (1999a) Preparation and properties of hematite with structural phosphorus. *Clays Clay Miner* **47**, 375–385.
- Gálvez N., Barrón V., and Torrent J. (1999b) Effect of phosphate on the crystallization of hematite, goethite, and lepidocrocite from ferrihydrite. *Clays Clay Miner* **47**, 304–311.
- Heller F. and Evans M. E. (1995) Loess magnetism. *Rev. Geophys.* **33**, 211–240.
- Jambor J. L. and Dutrizac J. E. (1998) Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. *Chem. Rev.* **98**, 2549–2585.
- Janney D. W., Cowley J. M., and Buseck P. R. (2000) Structure of synthetic 2-line ferrihydrite by electron nanodiffraction. *Am. Mineral.* **85**, 1180–1187.
- Janney D. W., Cowley J. M., and Buseck P. R. (2001) Structure of synthetic 6-line ferrihydrite by electron nanodiffraction. *Am. Mineral.* **86**, 327–335.
- Liu X., Shaw J., Liu T., Heller F., and Yuan B. (1992) Magnetic mineralogy of Chinese loess and its significance. *Geophys. J. Int.* **108**, 301–308.
- Lovley D. R., Stolz J. F., Nord Jr. G. L., and Phillips E. J. P. (1987) Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism. *Nature* **330**, 252–254.
- Madsen M. B., Hviid S. F., Gunnlaugsson H. P., Knudsen J. M., Goetz W., Pedersen C. T., Dinesen A. R., Mogensen C. T., Olsen M., and Hargraves R. B. (1999) The magnetic properties experiments on Mars Pathfinder. *J. Geophys. Res.* **104**, 8761–8779.
- Maher B. A. (1986) Characterization of soils by mineral magnetic measurements. *Phys. Earth Planet. Inter.* **42**, 76–91.
- Maher B. A. (1988) Magnetic properties of some synthetic submicron magnetites. *Geophys. J.* **94**, 83–96.
- Maher B. A. (1998) Magnetic properties of modern soils and Quaternary loessic paleosols: paleoclimatic implications. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **137**, 25–54.
- Maher B. A. and Taylor R. M. (1988) Formation of ultrafine-grained magnetite in soils. *Nature* **336**, 368–370.
- Manceau A. and Drits V. A. (1993) Local structure of ferrihydrite and feroxyhite by EXAFS spectroscopy. *Clays Clay Miner* **28**, 165–184.
- Morris R. V., Golden D. C., Shelfer T. D., and Lauer J. H. V. (1998) Lepidocrocite to maghemite to hematite: A pathway to magnetic and hematitic Martian soil. *Meteorit. Planetary Sci.* **33**, 743–751.
- Morris R. V., Golden D. C., Bell III J. F., Shelfer T. D., Scheinost A. C., Hinman N. W., Furniss G., Mertzman S. A., Bishop J. L., Ming D. W., Allen C. C., and Britt D. T. (2000) Mineralogy, composition, and alteration of Mars Pathfinder rocks and soils: Evidence from multispectral, elemental, and magnetic data on terrestrial analogue, SNC meteorite, and Pathfinder samples. *J. Geophys. Res.* **105**, 1757–1817.
- Morris R. V., Golden D. C., Ming D. W., Shelfer T. D., Jorgensen L. C., Bell J. F., Graff T. G., and Mertzman S. A. (2001) Phyllosilicate-poor palagonitic dust from Mauna Kea Volcano (Hawaii): A mineralogical analogue for magnetic Martian dust? *J. Geophys. Res.* **106**, 5057–5083.
- Mullins C. E. (1977) Magnetic susceptibility of the soil and its significance in soil science: A review. *J. Soil Sci.* **28**, 223–246.
- Murad E. and Schwertmann U. (1993) Temporal stability of a fine-grained magnetite. *Clays Clay Miner* **41**, 111–113.
- Olson R. V. and Ellis Jr. R. (1982) Iron. In *Methods of Soil Analysis, Part 2* (eds. A. L. Page, R. H. Miller, and D. R. Keeney), pp. 301–312. American Society of Agronomy and Soil Science Society of America, Madison, WI.
- Rieder R., Economou T., Wänke H., Turkevich A., Crisp J., Brückner J., Dreibus G., and McSween Jr. H. Y. (1997) The chemical composition of Martian soil and rocks returned by the mobile alpha proton X-ray spectrometer: Preliminary results from the X-ray mode. *Science* **278**, 1771–1774.
- Scheinost A. C. and Schwertmann U. (1999) Color identification of iron oxides and hydroxysulfates: Use and limitations. *Soil Sci. Soc. Am. J.* **63**, 1463–1471.
- Schwertmann U. (1964) Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. *Z. Pflanzenernähr. Düng. Bodenkd.* **105**, 194–202.
- Schwertmann U. and Heinemann B. (1959) Über das Vorkommen und die Entstehung von Maghemit in nordwestdeutschen Böden. *Neues Jahrb. Miner. Monatsh.* **8**, 174–181.
- Schwertmann U. and Latham M. (1986) Properties of iron oxides in some New Caledonian Oxisols. *Geoderma* **39**, 105–123.
- Schwertmann U. and Taylor R. M. (1989) Iron oxides. In *Minerals in Soil Environments* (eds. J. B. Dixon and S. B. Weed), pp. 379–438. Soil Science Society of America.
- Sigg L. and Stumm W. (1980) The interaction of anions and weak acids with the hydrous goethite (α -FeOOH) surface. *Colloids Surf* **2**, 101–117.
- Singer M. J., Verosub K. L., Fine P., and TenPas J. (1996) A conceptual model for the enhancement of magnetic susceptibility in soils. *Quat. Int.* **34–36**, 243–248.
- Torrent J. and Barrón V. (2000) Key role of phosphorus in the formation of the iron oxides in Mars soils? *Icarus* **145**, 645–647.
- Tsatskin A., Heller F., Hailwood E. A., Gendler T. S., Hus J., Montgomery P., Sartori M., and Virina E. I. (1998) Pedosedimentary division, rock magnetism and chronology of the loess/paleosol sequence at Roxolany (Ukraine). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **143**, 111–133.
- van der Marel H. W. (1951) γ -Ferric oxide in sediments. *J. Sed. Petrol.* **21**, 12–21.
- Virina E. I., Faustov S. S., and Heller F. (2000) Magnetism of loess-paleosol formations in relation to soil-forming and sedimentary processes. *Phys. Chem. Earth.* **25**, 475–478.
- Wyszecki G. and Stiles W. S. (1982) *Color Science: Concepts and Methods, Quantitative Data and Formulae*. Wiley, New York.