

POTENTIAL PATHWAYS TO MAGHEMITE IN MARS SOILS: THE KEY ROLE OF PHOSPHATE. V. Barrón and J. Torrent, Departamento de Ciencias y Recursos Agrícolas y Forestales, Universidad de Córdoba, Apdo. 3048, 14080 Córdoba, Spain, vidal@uco.es, torrent@uco.es.

Introduction: Maghemite is considered to be a firm candidate to account for the magnetic behavior of Mars soils [1]. The need thus exists to establish the physical and geochemical conditions that may have favored its formation on the red planet. Maghemite rarely abounds in terrestrial soils, where it forms mainly by (a) thermal transformation of goethite and ferrihydrite in the presence of organic matter, (b) oxidation of biogenic magnetite, (c) oxidation of lithogenic magnetite, and (d) dehydroxylation of lepidocrocite [2]. Because pathways (a) and (b) require the presence of significant amounts of organic matter, they can in principle be dismissed for Mars. Pathway (c) is possible since the Martian environment is oxidizing and (titano)magnetite is a likely constituent of Mars rocks [3]. Finally, pathway (d) requires the prior formation of lepidocrocite.

Based on data from SNC meteorites [4], and from the X-ray fluorescence analyses of the Pathfinder [5], Martian rocks are richer in P than are terrestrial rocks; therefore, one can speculate that the hypothetical formation of maghemite in Mars is favored by the presence of phosphate. We report here the results of various laboratory experiments revealing that phosphate plays a key role in the formation of lepidocrocite from Fe(II) salts and in the direct formation of maghemite via ferrihydrite precipitated from Fe(III) salts in the presence of phosphate.

Materials and Methods: *Synthesis of Fe oxides from Fe(II) salts.* Solutions of 0.05M FeSO₄·7H₂O and 0.01M KH₂PO₄ were mixed (P/Fe atomic range 0–0.2) and then neutralized with 1M NaHCO₃, the pH being kept constant with a pH stat. The resulting green-rust precipitate was oxidized by bubbling air. Similar experiments were conducted with mixtures of Fe(II) and Fe(III) salts.

Synthesis of Fe oxides from Fe(III) salts. Suspensions of 2-line ferrihydrite prepared by neutralizing 0.1M Fe(NO₃)₃ with 1M KOH in the presence of phosphate (P/Fe range 0–0.06) were aged at different temperatures from 25 to 200 °C.

The products resulting from the different synthesis tests were washed with deionized water, freeze dried, and characterized by X-ray and electron diffraction, Mössbauer, UV–visible and infrared spectroscopy, chemical analysis, and magnetic (saturation and susceptibility) measurements, as described in detail elsewhere [6–9].

Results *Synthesis from solutions of Fe(II) salts.* Phosphate favored the formation of lepidocrocite and inhibited that of goethite at P/Fe atomic ratios above 0.02, even if the solutions were saturated with HCO₃[–]—which strongly favors goethite formation in P-free systems. The resulting lepidocrocite nano-crystals (5–25 nm in size) contained occluded (possibly structural) P, as suggested by the P-induced changes in unit cell parameters [6].

From solutions of Fe(II) and Fe(III) salts. The hydrolysis of these mixtures resulted in the formation of magnetite in the absence of phosphate and in that of a mixture of poorly crystalline lepidocrocite and magnetite when phosphate was present at 0.05>P/Fe>0.01 [9].

From Fe (III) salts. Crystallization of P-doped 2-line ferrihydrite with P/Fe >~0.025 was inhibited at room temperature; a poorly crystalline magnetic phase and/or hematite was formed, however, after a long enough time at temperatures above 50 °C [7]. Under certain time and temperature conditions, the products with P/Fe >0.025 exhibited a high magnetic susceptibility. The magnetic phase occurred as 7–30 nm sub-rounded particles with lattice fringes, XRD reflections and Mössbauer features consistent with cubic maghemite (Fig.1).

Such a phase, designated “hydromaghemite” because it lost >3% water between 110 and ~350 °C [8], was an intermediate step in the transformation of ferrihydrite into hematite.

In summary, the presence of phosphate in aqueous media where Fe oxides are being formed significantly favors the formation of maghemite (via ferrihydrite) or of its precursor lepidocrocite over that of the more stable oxides (goethite and hematite). This provides a simple explanation for the hypothetically high concentration of maghemite in Mars soils relative to most Earth soils, since, as noted earlier, the former originated from rocks that were richer in P than the latter.

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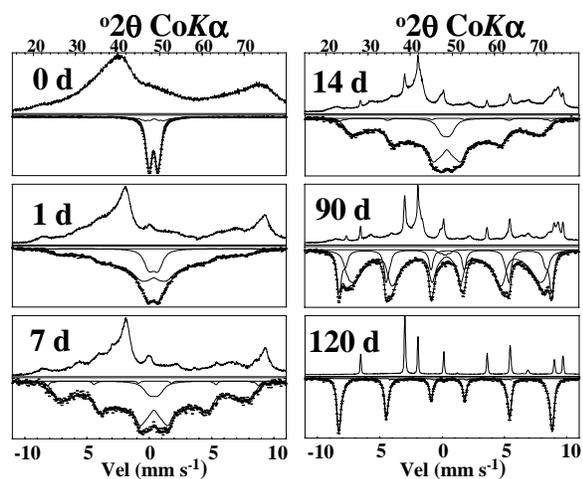


Fig.1. X-ray diffraction pattern (top) and Mössbauer spectrum (bottom) for the products obtained by aging phosphated 2-L ferrihydrite (P/Fe = 3%) at 150 °C for different times. The magnetic susceptibility (χ , in 10^{-6} m 3 kg $^{-1}$ units) of the product was 2, 36, 119, 140, 314, and 0.6 at 0, 1, 7, 14, 90, and 120 days, respectively.