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Intermediate magnetite formation during dehydration of goethite

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Abstract

The dehydration of goethite has been studied by low-temperature induced magnetization (LTIM) and X-ray diffraction on well-characterized acicular crystals. Fresh samples were heated in air to temperatures between 155°C and 610°C. Goethite and hematite were the magnetically dominant phases after all runs except 500°C and 610°C, for which only hematite was found. However, partially dehydrated goethites after the 238–402°C runs had broad peaks or inflections in the LTIM curves around 120 K, suggesting the formation of an intermediate spinel phase. These samples were next given a saturation remanence in a field of 2 T at 10 K and the remanence was measured continuously during zero-field warming to 300 K. There was a decrease in remanence at the Verwey transition (120 K), diagnostic of magnetite. The possible formation of a small amount of magnetite is of serious concern in studies of goethite-bearing sediments and rocks. Chemical remanent magnetization (CRM) of this strongly magnetic spinel phase could significantly modify the direction as well as the intensity of the original goethite CRM. As well, it would be a new source of paleomagnetic noise as far as primary remanence carried by other mineral phases is concerned. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Goethite, although a minor carrier of stable paleomagnetic remanence, is a major constituent of terrestrial soils, sediments, and oolitic iron ores [1,2], as well as a common weathering product in rocks of all types. Goethite may also occur in Martian soils [3]. Fibrous varieties of goethite are unusual in that the angle of the optic varies

with both wavelength and temperature. These distinctive optical properties make goethite easily recognizable in spectral signatures of planetary surfaces [3,4].

Goethite has a hexagonal closed-packed (hcp) lattice of oxygen ions, with ferric iron ions in octahedral interstices. Hydroxyl bonds form zig-zag chains between the oxygen planes. When heated, goethite dehydrates to hematite by removing hydroxyl sheets and some of the oxygen in strips parallel to the *c*-axis to form water [5]. In this transformation the [100], [010] and [001] directions in goethite become the [001], [110] and [1 $\bar{1}$ 1] directions in the trigonal hematite cell.

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Since the transformation temperatures and proportions of the two phases depend on environmental conditions, the phase assemblage may be useful in deducing paleoclimate. Goethite \rightarrow hematite dehydration is common in moist tropical climates where organic matter decomposes rapidly [6]. The hematite/goethite ratio in soil is thus an indicator of the carbon regime and climate [7]. Pollack et al. [8] studied the kinetics of the dehydration reaction and suggested that the chemical equilibrium in the goethite–hematite system determines the time-average abundance of water vapor on Mars.

The topotactic conversion of goethite to hematite has been the subject of numerous structural and kinetic studies [5,9–12]. Dehydration of goethite involves removal of hydrogen and one quarter of the oxygen, without disturbing the network of remaining oxygen, and atomic rearrangement of Fe^{3+} to form hematite: $2\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ [5]. Several mechanisms have been suggested. Watari et al. [11] and Goss [12] were of the opinion that the transformation proceeds by the direct dehydration of goethite to hematite without an intermediate phase. Their high-resolution transmission electron microscopy (TEM) studies show that early in the reaction, a skin of hematite coats the grains and a porous reaction product forms. This early stage is one of proton/ion transfer across the reaction interface.

On the other hand, dehydration could lead to an intermediate product, as proposed by Ball and Taylor [13] and Lima-de-Faria [9]. In this inhomogeneous dehydration process, the crystal develops separate ‘donor’ and ‘acceptor’ regions. Hydroxyl ions migrate from acceptor regions and combine with protons to form water, gradually transforming the donor regions into pores. This process can produce an intermediate phase, with a periodic variation of the structure factor along the c -axis caused by unequal distribution of Fe^{3+} ions and protons between the close-packed oxygen layers. A transitional structure with intermediate proportions of Fe^{2+} and Fe^{3+} is energetically possible because the transformation mechanism is one of cation migration [13,14].

We studied the $\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3$ transformation by making low-temperature magnetic

measurements on partially dehydrated mixtures of the two phases, produced by heating 11 different fresh goethite samples in air at temperatures ranging from 155°C to 610°C. Previous studies used non-magnetic techniques such as TEM, differential thermal analysis (DTA), differential thermogravimetry (DTG) and X-ray diffraction (XRD), but magnetic measurements have greater resolution than these techniques in detecting minute quantities of iron oxides in a mixture.

Magnetite and hematite have distinctive remanence transitions: magnetite at $T_V = 110\text{--}125$ K (the Verwey transition), and hematite at $T_M = 250\text{--}260$ K (the Morin transition). As magnetite cools through T_V , its structure changes from cubic to monoclinic and the easy directions of magnetization switch from [111] to [001] [15,16]. In cooling through T_M , hematite undergoes a magnetic phase transition from weakly ferromagnetic to antiferromagnetic and the spins rotate 90° from the basal plane to the [111] trigonal c -axis [17]. The Verwey and Morin transitions are signatures by which magnetite and hematite can be identified in rocks and sediments.

2. Sample characterization and experimental procedure

Our starting material is a synthetic goethite manufactured by Pfizer Inc. with acicular particles of average diameter 32 ± 9 nm and length 500–900 nm. X-ray analysis using a diffractometer with Cu– $K\alpha$ radiation and a silicon standard gave XRD patterns with numerous reflections characteristic of goethite. The orthorhombic unit cell dimensions were $a = 4.6$ Å, $b = 9.9$ Å and $c = 3.0$ Å, in close agreement with standard values (ASTM data file 17-536).

The ^{57}Fe Mössbauer spectrum was measured using a constant-acceleration spectrometer, with ^{57}Co as a source of 14.4 keV γ rays. At 77 K, the spectrum shows a single set of six sharp lines with a hyperfine field of 503.5 kG, in good agreement with previous results [18,19]. The Mössbauer spectrum confirms that our goethite is well-crystallized and uncontaminated by other forms of FeOOH or iron oxides [20].

Goethite is an antiferromagnet with a weak ferromagnetism below the Néel temperature $T_N = 120^\circ\text{C}$ [21,22]. The magnetization M measured in a 1-T field had a broad peak just above 100°C marking the antiferromagnetic \rightarrow paramagnetic transition at T_N (Fig. 1). Dehydration of goethite to hematite around 250°C was marked by an irreversible decrease in M . By way of comparison, DTG of αFeOOH similar to ours [4] showed a weight decrease due to loss of water between 220 and 250°C . M remained relatively constant above 300°C .

Dehydration experiments were carried out on 1×1 cm cylindrical samples containing 50% by weight of αFeOOH dispersed in non-magnetic CaF_2 . In each run, we heated a single fresh sample for 2.5 h in air at one of 11 different temperatures between 155°C and 610°C in a water-cooled resistance furnace. The choice of these temperatures was guided by the dehydration data of Fig. 1. After cooling the samples, low-temperature induced magnetization (LTIM) was measured in a field of 100 mT during warming from 20 K to 300 K using a Quantum Design MPMS2 SQUID magnetometer.

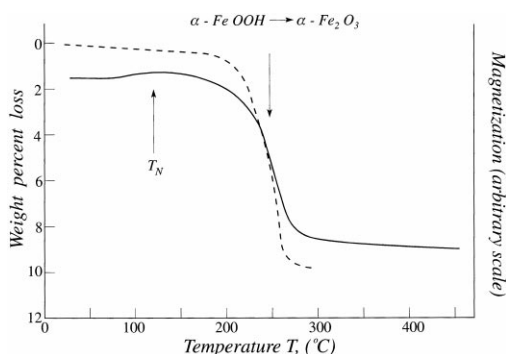


Fig. 1. Thermomagnetic curve (solid line) of our goethite heated in air. The broad peak just above 100°C marks the Néel temperature. The sharp decrease in magnetization between 220°C and 270°C is due to the $\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3$ transformation. Thermogravimetric analysis of goethite (dashed curve, after [4]) records a 10% weight loss between 200°C and 250°C resulting from loss of H_2O molecules in the crystal structure during dehydration.

3. Experimental results

3.1. Induced magnetization

LTIM curves for samples dehydrated at 155°C , 222°C and 238°C , as well as for fresh unheated goethite, are shown in Fig. 2A. The LTIM curves for the 155°C and 222°C samples are very similar to the curve for unheated goethite (labeled 20°C) except for a decrease in the intensity of M . The goethite heated at 238°C has a similar curve, with the addition of a small peak centered on 112 K, in the range $T_V = 110$ – 125 K of reported Verwey transition temperatures for magnetite.

The LTIM of the sample dehydrated at 255°C (Fig. 2B) increased sharply between 100 and 120 K, leveled out in the range 140–170 K, and finally increased slowly up to 300 K. The LTIM curve for this sample has a very different shape from those of samples heated at lower temperatures, probably indicating microstructural changes around the maximum dehydration temperature (Fig. 1).

Partially dehydrated goethites after the 275°C , 304°C and 325°C heatings have well-defined LTIM peaks around T_V , indicating intermediate magnetite formation (Fig. 2B,C). T_V increased from 112 K for the 238°C sample to 118 K for the 275°C sample and to 120 K for the 304°C and 325°C samples. The magnetization decreased steadily between T_V and 300 K for the 275°C and 304°C samples.

The LTIM curve for the 354°C sample has, in addition to the sharp peak at 120 K due to magnetite, a second broader peak centered on 260 K, the Morin transition temperature of hematite (Fig. 2C). The 120-K LTIM peak was weak for the 402°C sample (Fig. 2D). The samples heated at 500°C and 610°C showed well-defined Morin transitions around 250 K, where magnetization increased sharply with the onset of weak ferromagnetism. The sharp transition indicates well-crystallized hematite.

3.2. X-ray analysis

X-ray powder diffraction patterns were taken for the dehydrated goethites after 222°C , 238°C ,

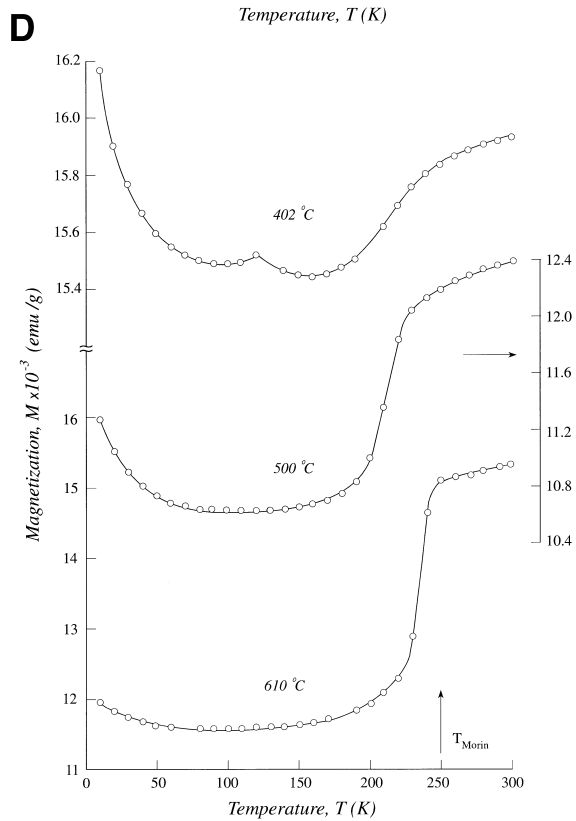
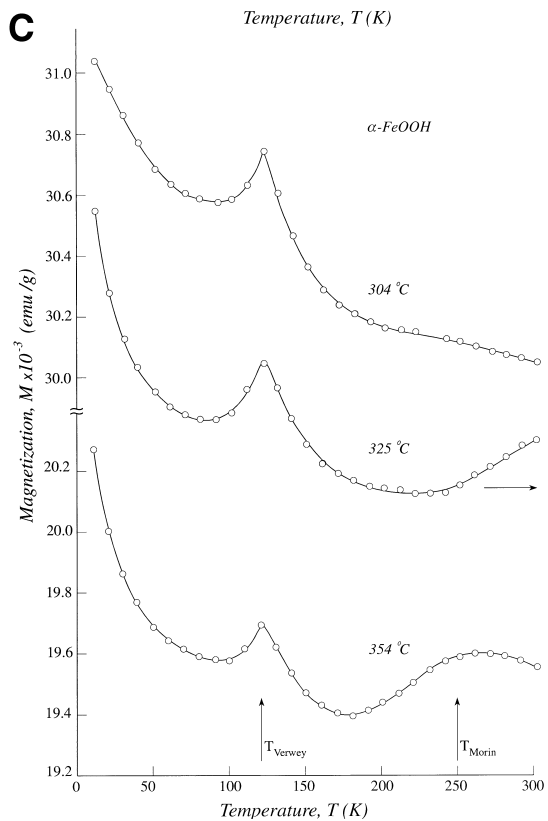
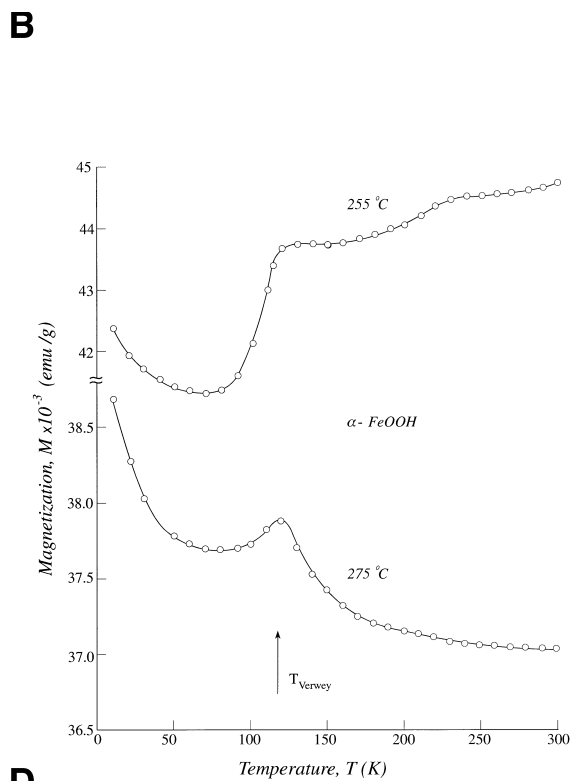
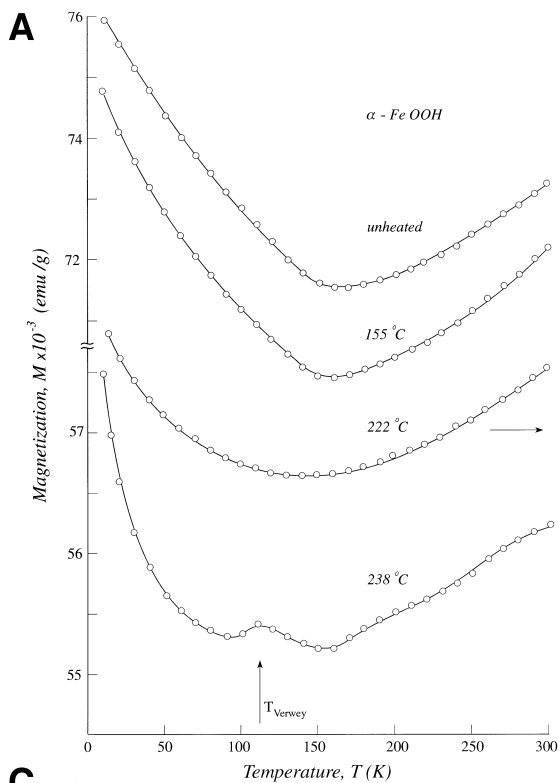


Fig. 2. LTIM curves of goethite samples dehydrated at temperatures of (A) 155°C, 222°C, 238°C, (B) 255°C, 275°C, (C) 304°C, 325°C, 354°C, and (D) 402°C, 500°C, 610°C. The goethites partially dehydrated at 238–405°C show LTIM peaks at the Verwey transition, indicating formation of magnetite. The peak marking the hematite Morin transition in the LTIM curve for the sample dehydrated at 354°C run is very broad, because of either fine particle size or lattice strain or defects introduced during recrystallization. After high-temperature dehydration (500°C, 610°C), the LTIM peak at the Morin transition becomes sharper, indicating well-crystallized hematite.

255°C, 354°C, 402°C and 610°C heatings. The positions of the diffraction peaks after the 222°C run were nearly the same as for unheated goethite, but the intensities of the peaks decreased and the weak (020), (120) and (250) goethite reflections disappeared. After the 238°C heating, broad diffuse diffraction peaks due to hematite appeared in addition to the goethite peaks. No spinel phase was detected for this sample.

X-ray patterns for the goethites heated at 255°C and 354°C were dominated by rhombohedral reflections corresponding to hematite, together with a few diffuse goethite peaks. The (102), (104) and (204) peaks broadened and the (110), (113) and (111) peaks became sharper. The newly forming spinel phase is identifiable as magnetite from two major lines, $d_{(311)}$ at 2.54 Å and $d_{(440)}$ at 1.48 Å. Both peaks were weak and diffuse. The broader hematite peaks sharpened after the 402°C, 500°C and 610°C heatings. Increasing dehydration temperature improves hematite crystallinity, resulting in sharper diffraction profiles.

3.3. Low-temperature demagnetization of SIRM

Heated and unheated goethites were given a saturation isothermal remanent magnetization (SIRM) in a field of 2.5 T at 20 K, then warmed to 300 K in approximately zero field (Fig. 3). The SIRM of the unheated goethite decreased almost linearly with temperature. The SIRM of the goethite heated at 238°C decreased rapidly from 20 to 50 K, as ultrafine particles became superparamagnetic and lost their remanence. Between 100 and 120 K approximately, the SIRM again decreased rapidly, as the intermediate magnetite phase passed through its Verwey transition. The transition was not sharp and occurred at lower temperatures than reported for stoichiometric magnetite. The thermal decay curve of SIRM after 325°C heating was similar to that of the 238°C sample.

However, there was almost no SIRM decrease below 50 K: the ultrafine particles present after 238°C heating must have grown to much larger stable single domain sizes.

The low-temperature SIRM results show that the spinel product in the partially dehydrated goethites is magnetite. The broadened remanence transition and depressed T_V values are likely due to slightly non-stoichiometric or cation-deficient magnetite of fine particle size [23].

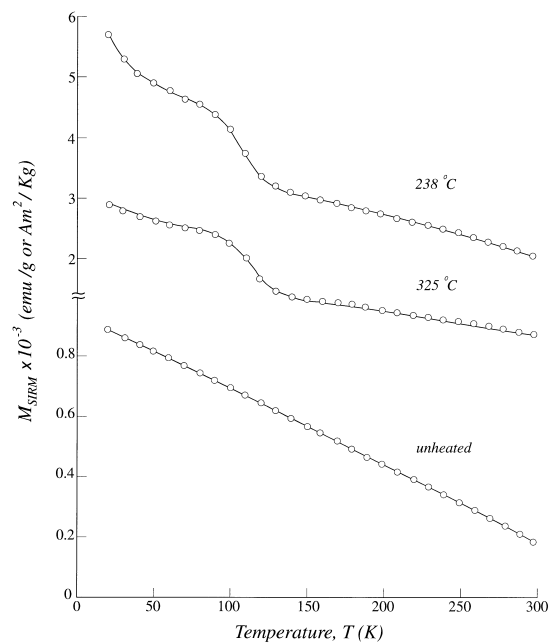


Fig. 3. SIRM warming curves of unheated goethite and of samples heated at 238°C and 325°C. The partially dehydrated goethites lose part of their SIRM at the magnetite Verwey transition; there is no sign of any transition for unheated goethite. The Verwey transition is broadened because of the fine particle size of the intermediate magnetite phase. The decrease of SIRM between 20 and 50 K in the 238°C sample is due to unblocking of nearly superparamagnetic size particles. Heating to 325°C causes grain growth and the initial SIRM decrease disappears.

4. Discussion

In the present study, the dehydration of goethite to hematite resulted in the formation of an intermediate spinel phase. The transformation occurs in several stages. In the first stage (155–238°C heatings), X-ray powder patterns continue to be dominated by goethite reflections, but the peaks broaden and their heights decrease. The shape of the LTIM curves remains essentially the same over this range of dehydration temperatures (Fig. 2A).

The second or intermediate stage (255–405°C) is characterized by mixtures of hematite and goethite, together with formation of an intermediate spinel phase. Rapid transformation of αFeOOH to $\alpha\text{Fe}_2\text{O}_3$ in heating at 255°C is evidenced by a weight loss in DTG and a sharp decrease in magnetization (Fig. 1). All the XRD lines for these partially dehydrated samples belong to hematite and goethite. Some of the hematite peaks become broader, indicating the formation of micropores [24]. Crystal strain and imperfections such as stacking faults [9] and the finely twinned nature of the product [12] could also cause broadening of the X-ray peaks. High-resolution TEM shows that the transformation proceeds from the surface inwards, forming a skin or a shell of hematite [11,12]. The undehydrated and dehydrated parts of the grain are distinct and the pores are associated with the dehydration product. The central core of goethite cannot further dehydrate to hematite because water is prevented from escaping by the increasing water pressure in the outer voids [11].

A spinel phase first appeared after heating at 238°C, as evidenced by a small hump in the LTIM curve near 110 K (Fig. 2A). X-ray analysis revealed no spinel reflections, probably because the newly formed magnetite is fine-grained, imperfectly crystalline, and present only in minute amounts. Growth in the amount and grain size of magnetite, as well as improved crystallinity and stoichiometry, result in a sharper Verwey transition and a shift of T_V to higher temperatures, around 120 K, after the 275°C, 304°C, 325°C and 354°C heatings (Fig. 2B,C). Weak spinel (311) and (440) XRD peaks also appear as a result of these heatings.

The LTIM peak at T_V originates in the following way. The Verwey transition is both a crystallographic and an order–disorder transition. The fundamental cause of the transition is ordering of Fe^{3+} and Fe^{2+} ions on octahedral sites. The ordering in turn gives rise to a distortion of the spinel lattice to a monoclinic lattice below T_V , with an accompanying large increase in magnetocrystalline anisotropy. It is the anisotropy change that produces a discontinuity in magnetization across T_V , the size of the discontinuity depending on the strength of the field and its orientation relative to the monoclinic c -axis. For a full discussion of the transition and data on accompanying magnetization peaks, see Cullen and Callen [25], Samiullah [26], Özdemir and Dunlop [16], Dunlop and Özdemir [27].

Formation of Fe_3O_4 during $\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3$ transformation is somewhat puzzling. The dehydration mechanism involves removal of H_2O and rearrangement of ions and protons by cation transfer across the reaction interface into the developing oxide layer. In partially dehydrated grains, the surface hematite layer effectively halts further dehydration of the goethite core [11,12]. The formation of magnetite may be promoted by the sluggish reaction kinetics at this interface. In addition, there may be internal interfaces between water-poor (acceptor) and water-rich (donor) regions [9,13], the latter ultimately developing into water-filled pores. There is evidence for pore formation in the broadening we observed for some of the hematite XRD lines, and pores are a prominent feature in TEM pictures of dehydrated goethites. The long-range nature of cation and proton migration may make possible some conversion of Fe^{3+} to Fe^{2+} during migration between acceptor and donor regions. In addition, some degree of ordering of Fe^{3+} and Fe^{2+} between oxygen layers would be needed to form an intermediate magnetite phase.

Watanabe and Ishii [28] proposed a mechanism in which the transformation from hematite to magnetite occurs by restacking and removal of oxygen and migration of iron ions. When $\alpha\text{Fe}_2\text{O}_3$ transforms to Fe_3O_4 , the hcp stacking sequence of oxygen in $\alpha\text{Fe}_2\text{O}_3$ changes by shearing to the face-centered cubic stacking of Fe_3O_4 . Octahedral

sites in the hematite lattice change to tetrahedral sites after the restacking, weakening the Coulomb force between the iron and oxygen ions. During the removal of oxygen from the restacked $\alpha\text{Fe}_2\text{O}_3$, part of the Fe^{3+} ions become Fe^{2+} to maintain electrical neutrality. Finally, the iron ions are rearranged to form the Fe_3O_4 lattice. Experimentally, Watari et al. [11] observed magnetite formation in partially dehydrated goethite; reduction may have been promoted by the carbon film on the TEM grid. However, magnetite is also produced when the dehydration of goethite takes place in vacuum or in an inert atmosphere [29,30].

In the final stage of our experiments, for heatings at and above 402°C , the intermediate spinel regions disappeared as the magnetite oxidized to hematite. With increasing dehydration temperature, cracks appear in the hematite skin as a result of volume reduction [12]. Cracks allow the water of dehydration to escape and create new reaction surfaces for further dehydration. After the particles are completely transformed to hematite, recrystallization and grain growth proceed with further heating, but inhomogeneously, leading to heterogeneity in particle size and shape [11]. After our 402°C , 500°C and 610°C heatings, all the goethite X-ray diffraction peaks disappeared and the broad hematite peaks became sharper, indicating formation of well-crystallized hematite.

The LTIM curves for the samples heated at temperatures from 354°C to 610°C show that the Morin transition also becomes sharper with increasing dehydration temperature. The Morin transition was first observed after the 354°C heating as a broad peak between 200 and 300 K. The broad transition region probably reflects inhomogeneities such as lattice strain and defects [31,32], arising in our study from pore formation and perhaps crystal twinning. After the 500°C and 610°C heatings, when dehydration is complete, the transition becomes sharper in the LTIM curves (Fig. 2D), indicating improved crystallinity and larger hematite grain size. After the heatings at 402°C to 610°C , the Morin transition shifted to higher temperatures. However, $T_M = 225$ K, the highest value reached, is still lower than the usual 250–260 K for pure hematite. This shift in T_M is

probably also due to lattice strain or defects and fine particle size [32,33].

5. Relevance to nature

Conditions in our laboratory dehydration experiments differed from conditions prevailing in nature in several respects:

1. The goethites used were synthetic fine crystals 25–40 nm in diameter and 500–900 nm in length. Natural goethites are often coarse and impure polycrystalline aggregates. Their variable crystallite sizes and shapes, degree of crystallinity, impurities, and excess water could affect the reaction kinetics and the formation of an intermediate spinel phase during dehydration.
2. Our dehydration experiments were carried out at above-ambient temperatures in order to achieve reasonable transformation rates, and the time scales used were a few hours. In nature, goethite forms and dehydrates at ambient temperatures over thousands of years or more.

Despite these differences, magnetite formation during transformation of $\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3$ is not limited to synthetic goethites heated in the laboratory but has also been reported for naturally occurring goethites. Goss [12] observed magnetite formation during transformation of natural goethite, both in small equidimensional flakes about 14 nm in size and in large thin flakes about 48 nm thick. DTG of these goethite flakes gave an additional peak corresponding to the formation of magnetite. Gehring and Heller [2] found that upon heating in air, goethites in Jurassic iron oolitic limestones transformed to a metastable iron oxide. Lowrie and Heller [34] identified magnetite with a maximum blocking temperature of 550°C forming during thermomagnetic analysis of Franconian limestones containing goethite.

Although these natural goethites were all dehydrated in the laboratory, similar intermediate spinel phases may well accompany goethite dehydration in nature. An important related question needing study is the time scale for natural goethite

dehydration. The dehydration kinetics have been studied in the laboratory [8,12] but kinetics under natural conditions are not well known. Dehydration occurring thousands or tens of thousands of years after sediment deposition would produce chemical remanent magnetization (CRM) in an intermediate spinel phase, but the direction would be similar to that of the goethite remanence. A time delay of a million years or more, on the other hand, might result in a CRM sufficiently distinctive (e.g., because of reversed polarity) to potentially date weathering and dehydration processes.

6. Conclusions

From the above, the following conclusions can be drawn:

1. The LTIM curves of goethites that had been partially dehydrated at temperatures between 238°C and 400°C showed sharp peaks or inflections around 120 K indicative of a spinel phase. Even more conclusive was a marked decrease in SIRM during zero-field heating through the magnetite Verwey transition around 120 K.
2. In the final stages of goethite dehydration (402–600°C heatings), well-crystallized hematite was identified by a sharp increase in LTIM at the Morin transition, $T_M \approx 225$ K. This value of T_M is lower than the 250–260 K of pure hematite, probably because of lattice strain and defects such as pores produced during the dehydration process.
3. LTIM measurements are an effective way of identifying a small amount of magnetite or hematite in a mixture of phases.
4. The formation of a small amount of magnetite has serious implications for paleomagnetic studies of goethite-bearing sediments and rocks. CRM of the strongly magnetic intermediate spinel phase could significantly modify the original goethite CRM. Magnetite's strong M_s makes it a potent contributor of CRM even if present in trace amounts. Magnetite might also act as an intermediate coupled phase,

modifying the direction of the ultimate hematite CRM.

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