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Magnetic comparison of abiogenic and biogenic alteration products of lepidocrocite

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ABSTRACT

Lepidocrocite is a potentially important Fe-bearing precursor phase for the production of nanoscale Fe-oxide particles in the environment. We present a detailed magnetic characterization of various alteration products of lepidocrocite resulting from thermal dehydroxylation reactions and bacterially induced bioreduction and remineralization, accompanied by characterization with x-ray diffraction (XRD) and transmission electron microscopy. Dehydroxylation during annealing at moderate temperatures produces a topotactic transformation from lepidocrocite to maghemite when heated in an oxidizing atmosphere, or to magnetite when heated in a reducing atmosphere. The abiotic Fe-oxide products form an oriented framework of strongly interacting superparamagnetic crystallites and are characterized by a distinctive porous nanostructure observed by electron microscopy. Lepidocrocite bioreduction by the iron-reducing bacterium *Shewanella putrefaciens* ATCC 8071 produces nanoscale particles of a strongly magnetic phase. This Fe(II)-bearing mineral produced by bioreduction is highly crystalline and euhedral in shape, with a broad grain size distribution and is indicated by magnetic and XRD measurements to be a cation-excess magnetite. We highlight the distinguishing microscopic characteristics of magnetite from both abiotic and bacterially induced mineralization that should allow them to be identified in natural settings. Moreover, both mechanisms of alteration represent potential pathways for the direct formation of strongly magnetic fine-grained Fe-oxide particles in sedimentary environments.

1. Introduction

Iron oxyhydroxides are important components of soils and other continental sediments as they play a key role in iron cycling in terrestrial systems and are precursor phases to various magnetic Fe-oxide alteration products (Schwertmann and Taylor, 1989; Cornell and Schwertmann, 2003; Maher et al., 2003; Liu et al., 2012). The phenomenon of magnetic enhancement in many soil types relative to their parent material has been recognized for several years (Maher and Thompson, 1991; Dearing et al., 1997; Geiss et al., 2004), and the fine-grained Fe-oxides responsible for the enhanced magnetic signal are generally recognized as being pedogenic in origin (Singer and Fine, 1989; Zhou et al., 1990; Liu et al., 2007). Some evidence suggests that the transformation of metastable Fe-oxyhydroxides may contribute to the enhancement process (Guyodo et al., 2006). However, the question of whether pedogenic production of Fe-oxides is primarily driven by microbial activity or abiotic processes is still unresolved (Maher and Taylor, 1988; Chen et al., 2005).

Lepidocrocite (γ-FeOOH) undergoes a dehydroxylation reaction that results in a topotactic transformation to maghemite, providing a simple mechanism for the production of strongly magnetic Fe-oxide nanoparticles. Natural occurrences of lepidocrocite are often associated with gleyed soil materials found in wet, poorly drained soils in humid, temperate climates (Fitzpatrick et al., 1985; Jordanova et al., 2011). The possibility of lepidocrocite as a significant weathering product of Martian basalts has been demonstrated (Banin et al., 1993) and thus has been suggested as a potential source of both maghemite and hematite particles present in soils on Mars (Morris et al., 1998). Yet aside from a handful of studies (e.g. Hirt et al., 2002), the magnetic properties of lepidocrocite remain poorly studied, in contrast with the extensive work on other oxyhydroxides that usually occur in less crystalline forms, such as goethite (e.g. Dekkers, 1988; Guyodo et al., 2003) and ferrihydrite (e.g. Murad et al., 1988; Guyodo et al., 2006). Because Fe-oxides are involved in a range of biomineralization processes, detailed characterization of different pathways for production of Fe-oxide

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minerals are needed to identify biosignatures that can be used to determine the origin of such minerals in both terrestrial and other planetary settings.

The transformation of lepidocrocite to maghemite during dehydration upon moderate heating under oxidizing conditions has been well-documented (Gehring and Hofmeister, 1994; Chopra et al., 1999; Sudakar et al., 2003; Cudennec and Lecerf, 2005), as well as the subsequent inversion of lepidocrocite-derived maghemite to hematite on heating at higher temperatures (McClelland and Goss, 1993; Gendler et al., 2005). However, in this study, we present the first example of magnetite produced by thermal alteration of lepidocrocite under anoxic conditions and a detailed characterization of the low-temperature magnetic properties of Fe-oxides derived from thermal alteration of lepidocrocite. In addition, we report for the first time on the magnetic properties of Fe-oxides resulting from bacterially induced remineralization during lepidocrocite bioreduction experiments.

2. Methods

2.1. Characterization

Low-temperature ($T < 300$ K) magnetic measurements were made on a Magnetic Properties Measurement System (MPMS XL-5 with EverCool) by Quantum Designs. Magnetic characterization included measurements of susceptibility, χ, as a function of temperature and frequency; low-temperature saturation isothermal remanent magnetization (LTSIRM) curves measured on warming from 10 K to 300 K after cooling in a 2.5 T field (field-cooled, FC) or zero field-cooled (ZFC); and low-temperature hysteresis loops measured with the MPMS at 10 K in a maximum field of 2.5 T. Room-temperature frequency-dependence of susceptibility was calculated as:

$$\chi_{fd} = 100\frac{\chi_{lf} - \chi_{hf}}{\chi_{lf}} \quad (1)$$

where χ_{lf} and χ_{hf} are the susceptibilities at low and high frequencies, respectively. TEM characterization was performed on a JEOL 2100F microscope with field emission gun. Powder X-ray diffraction (XRD) patterns were collected using Co (Kα) radiation on a Panalytical XPert PRO MPD diffractometer. XRD patterns for oxygen-sensitive samples were collected using an anoxic cell with a transparent window so that samples remained in an oxygen-free atmosphere during XRD measurements. XRD was also measured on a coarse-grained industrial synthetic maghemite powder sample (Q-Mh) for comparison. Line-broadening of the XRD peaks was calculated for certain samples and used with Scherrer's formula:

$$\tau = \frac{K\lambda}{\beta\cos\theta} \quad (2)$$

to determine the coherently diffracting domain size, or the average crystallite size, τ, where K is a shape parameter, usually between 0.9 and 1, λ is the wavelength of X-ray radiation, β is the peak full-width at half the maximum intensity, and θ is the Bragg angle.

2.2. Sample synthesis

The lepidocrocite used as starting material for the experiments was synthesized by mixing a 0.228 M solution of $FeCl_2{\cdot}4H_2O$ with a 0.4 M solution of NaOH (Ona-Nguema et al., 2002b). A Fe(II) hydroxide precipitated that was oxidized by continuous magnetic stirring, during which time the color of the suspension changed from dark green to orange. The precipitate was removed from the suspension by centrifuging (4000 rpm for 15 min), rinsed twice in Milli-Q water and vacuum-dried in a desiccator overnight. The resulting lepidocrocite was characterized by TEM and XRD, as well as with low-temperature magnetic measurements. For thermal alteration experiments, synthesis of the starting lepidocrocite was performed by oxidizing the $Fe(OH)_2$ suspension over 3 h. Lepidocrocite used in bioreduction experiments was produced using an identical procedure, except for the oxidation of Fe(II), which was more rapid, leading to color change of the suspension in about 25 min.

2.3. Thermal alteration experiments

Abiotic alteration reactions were investigated with a series of heating experiments in either an oxidizing or a reducing atmosphere. Reduction experiments were performed in a flowing atmosphere of CO–CO_2 mixture (20%/80%) in a furnace inside an Ar-filled glove box to avoid exposing samples to oxygen. Oxidation experiments were performed in air at ambient pressure. Heating temperatures ranged from 150 to 250 °C with heating durations between 1 h and 4 weeks (Table 1). Magnetic characterizations were typically performed immediately after the thermal alteration experiments. Reduction experiments were only performed at or above 210 °C due to uncertainty about the ability of the gas mixture to properly buffer the atmosphere at lower temperatures. Test reduction experiments in the furnace confirmed that the CO/CO_2 mix produces a reducing atmosphere relative to the upper limit of the magnetite stability field at temperatures as low as 210 °C.

2.4. Bioreduction experiments

Biogenic mineral transformations were investigated through a series of bioreduction experiments using the dissimilatory iron-reducing bacteria *Shewanella putrefaciens* (strain CIP 8040T from the Collection Institut Pasteur, France), equivalent to the American Type Culture Collection (ATCC) 8071. The experimental procedures were similar to those followed by Ona-Nguema et al. (2002a) and Ona-Nguema et al. (2009). Three samples of 2 g of lepidocrocite were mixed and suspended in 25 mL of a basic medium for bacteria, the composition of which is given by Ona-Nguema et al. (2002a). The mineral suspensions were adjusted to a pH near 7.5, sterilized by autoclave, and oxygen was removed from the sealed sample bottles by bubbling Ar through the liquid for 40 min in a 60 °C water bath. Sodium formate was added to the samples to act as an electron donor at a concentration of 70 mM. Samples also contained a 0.1 mM concentration of anthraquinone-2,6-disulfonate (AQDS), which increases the rate of the bioreduction reaction by acting as an electron shuttle. To produce a sufficient quantity of bacteria, cells were harvested from agar plates and multiplied in trypticase soy broth (TSB) by continuous magnetic stirring at 1000 rpm at 22 °C. The increase in cell density in the TSB suspension was verified by spectrophotometer absorbance measurements at 600 nm. After 18 h of culture in TSB, the bacterial suspension was centrifuged two times (8000 rpm at 19 °C for 10 min) to harvest and wash the bacteria with a sterile solution of 0.9% NaCl. Cells were then concentrated in 30 mL of sterile NaCl (0.9%). This suspension of *Shewanella putrefaciens* ATCC 8071 was degassed by bubbling Ar through a 0.2 µm sterile filter for 10 min to remove oxygen prior to inoculation. The concentration of bacteria in the suspension used to inoculate the flasks for bioreduction experiments was determined by counting colony-forming units (CFU) formed by plating highly diluted portions of the bacteria suspension.

The sterile, anoxic suspensions of lepidocrocite were inoculated with 3.5 mL of a concentrated suspension of *S. putrefaciens* to reach a final concentration of 1.5×10^{10} CFU/mL and incubated at 30 °C for several weeks. The final volume of the cultures was 45.5 mL. One sample of the lepidocrocite suspension was not inoculated