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Abstract

The oriented chains of nanoscale Fe-oxide particles produced by magnetotactic bacteria are a striking example of biomineralization. Several distinguishing features of the magnetite particles that comprise bacterial magnetosomes have been proposed to collectively constitute a biosignature of magnetotactic bacteria (Thomas-Keprta et al., 2001). These features include high crystallinity, chemical purity, a single-domain magnetic structure, well-defined crystal morphology, and arrangement of particles in chain structures. Here we show that magnetite derived from inorganic breakdown of nanocrystalline goethite exhibits magnetic properties and morphologies remarkably similar to biogenic magnetite from magnetosomes. During heating in reducing conditions, oriented nanogoethite aggregates undergo dehydroxylation and transform to stoichiometric magnetite. We demonstrate that highly crystalline single-domain magnetite with euhedral grain morphologies produced abiogenically from goethite meets several of the biogenicity criteria commonly used for identification of magnetofossils. Furthermore, the suboxic conditions necessary for magnetofossil preservation in sediments are also conducive to promote reductive alteration of nanogoethite, and to preserve detrital magnetite originally formed from goethite. The findings of this study have potential implications for the identification of biogenic magnetite, particularly in older sediments where diagenetic alteration commonly disrupts the chain structure of magnetosomes. Our results indicate

that isolated magnetofossils cannot be positively distinguished from inorganic magnetite on the basis of magnetic properties and morphology, and that intact chain structures remain the only reliable distinguishing feature of fossil magnetosomes.

1. Introduction

Magnetotactic bacteria (MTB) are a diverse group of microbes that produce chains of magnetic nanoparticles called magnetosomes for the purpose of navigation. MTB have been identified in an extensive variety of freshwater and marine environments (Faivre and Schuler, 2008), and the preserved magnetosome components of such bacteria, also known as magnetofossils, have been identified in sediments dating at least as far back as Cretaceous in age (Montgomery et al., 1998). The stoichiometric magnetite that comprises most bacterial magnetosomes consistently exhibits certain features, including a high degree of crystallinity with few crystallographic defects, high chemical purity, a single-domain magnetic structure, well-defined crystal morphology, a tendency for particle elongation along [111] directions, and arrangement of particles in chain structures (Kopp and Kirschvink, 2008). These collective attributes have been proposed as a biosignature of magnetotactic bacteria and have been applied as criteria for the identification of magnetofossils in sediments, sedimentary rocks, and even meteorites (Thomas-Keprta et al., 2001).

While all of the above criteria are typically observed in cultured strains of MTB and live bacteria sampled from modern aqueous environments, studies of older sediments often fail to observe intact chain structures in fossil magnetosomes due to collapse and disaggregation of the chains either through diagenesis or by laboratory protocols of magnetic mineral extraction for microscopic investigation. In some cases, methods such as ferromagnetic resonance or low-temperature magnetic measurements can be used to infer the presence of magnetic chain structures (Weiss et al., 2004a). However many studies on ancient sediments rely on microscopic observation of magnetic extracts, combined with analysis of sediment magnetic properties to detect single domain (SD) magnetite (e.g. (Abrajevitch et al., 2015; Larrasoana et al., 2014; Savian et al., 2016)), which has few known inorganic sources in sediments.

63 Previous studies have demonstrated how inorganic processes may produce certain
64 characteristic morphologies of biogenic magnetite that can explain the occurrence of SD
65 magnetite in the ALH84001 Martian meteorite (Barber and Scott, 2002; Bradley et al.,
66 1998; Golden et al., 2004). However, inorganic processes are rarely invoked to explain
67 biogenic characteristics of SD magnetite in terrestrial environments. Rather it is assumed
68 that because MTB are widespread in modern aqueous environments, they are likely to have
69 been widespread throughout much of Earth's history and hence much ancient sediment
70 may be expected to carry magnetic signatures of magnetofossils. Here we describe the
71 various magnetosome-like properties of nanoscale magnetite particles produced by
72 inorganic alteration of nanocrystalline goethite. We propose that magnetite produced by
73 this reaction pathway could potentially contribute to the SD magnetite signals in sediment
74 magnetic properties that are commonly attributed to biogenic magnetite.

75 The Fe-oxyhydroxide goethite occurs in nanocrystalline form in a wide range of
76 soils, aeolian material, and lake and marine sediments (van der Zee et al., 2003). In many
77 sedimentary systems, it is the dominant substrate available for Fe-redox reactions (Hansel
78 et al., 2004; van der Zee et al., 2003). Nanogoethite is predicted to be thermodynamically
79 unstable with respect to dehydroxylation to Fe-oxide at ambient temperatures on geologic
80 time scales (Diakonov et al., 1994; Langmuir, 1971), although the kinetics are sufficiently
81 slow that no reaction occurs below 100°C on laboratory time scales (Diakonov et al.,
82 1994). Recently, a study by Till et al. (2015) reported that nanogoethite readily alters to
83 sub-micron magnetite under reducing conditions upon moderate heating (T = 210-270°C).
84 They identified a two-step process involving dehydroxylation of goethite to nanohematite,
85 and subsequent rapid reduction and recrystallization of nanohematite to fine-grained
86 magnetite. We analyzed the magnetite produced in these experiments in detail using
87 transmission electron microscopy (TEM) and magnetic measurements and describe the
88 results below.

89 **2. Procedures**

90 *2.1 Synthesis*

Synthetic nanogoethite was produced using the protocol outlined in (Schwertmann and Cornell, 1991). A 0.05 M solution of $FeCl_2 \cdot 4H_2O$ was prepared in a glove box using deoxygenated water and was mixed with a 1 M $NaHCO_3$ solution. A constant flow of air was bubbled through the resulting suspension, which was continuously agitated and became oxidized over 48 h. The goethite precipitate was separated by centrifuging and rinsing with ultrapure (MilliQ) water several times and dried in a vacuum desiccator. The resulting goethite particles are around 10 nm by 50 nm in size, and consist of well-oriented aggregates of crystallites with crystallite sizes around 6 nm (Till et al., 2015).

2.2 Characterization

The starting material and reaction products were characterized by Rietveld refinement of the X-ray diffraction (XRD) powder patterns and imaged by high-resolution transmission electron microscopy on JEOL 2100F microscope with field-emission gun at 200 kV accelerating voltage. Electron diffraction patterns were calculated by fast Fourier transforms of high-resolution images. Samples for magnetic measurements were prepared using small amounts of undiluted sample powders packed in gelatin capsules. Low-temperature magnetic measurements of saturation isothermal remanent magnetization (SIRM) curves measured on warming from 10 K after field-cooling (FC) in a 2.5 T field or cooling in zero-field (ZFC), were made on a Quantum Designs Magnetic Properties Measurement System (MPMS XL-5 with EverCool). δ_{FC}/δ_{ZFC} ratios were calculated as $\delta = (M_{irm}(80)-M_{irm}(150))/M_{irm}(80)$, where M is the value of magnetic remanence at 80 K and 150 K upon warming after either FC or ZFC pre-treatment. First-order reversal curve (FORC) diagrams and hysteresis loops were measured on a Princeton Measurements Corporation vibrating sample magnetometer (VSM) at room temperature. FORC measurements used a maximum field of 0.3 T, which is greater than the samples magnetic saturating field, and a field increment of 1 mT. FORC diagrams were processed and plotted with the FORCinel software package (Harrison and Feinberg, 2008) using the VARIFORC smoothing protocol (Egli, 2013), with smoothing parameters of S_{c0}=3, S_{b0}=2, and S_{c1}=S_{b1}=5.

2.3 Alteration experiments

Alteration experiments were performed by heating synthetic nanogoethite powder at temperatures between 210 and 270◦C for up to 2.5 hours in a constant flow of a 20%-80% CO-CO_2 gas mixture. The furnace used for heating experiments was enclosed inside an Ar-filled glove box, and samples were prepared and maintained under anoxic conditions to minimize samples oxidation. Magnetic characterization was performed immediately after each alteration experiment. Conditions for each experimental run as well as detailed results of XRD and other magnetic measurements were reported by Till et al. (2015) and are summarized in Table 1.

3. Results

3.1 Magnetite morphology

TEM images of the pure magnetite end product indicate that the majority of grains are rounded and elongated, ranging from about 20 to 60 nm in width (Fig. 1A). Although many of grains have irregular or non-distinct shapes, a small but significant portion exhibit striking similarities to magnetite particles found in magnetosomes. Among the latter are elongated, tapered particles (Fig. 1C) that resemble bullet-shaped magnetosome particles found in certain MTB strains (Kopp and Kirschvink, 2008). A number of equant and slightly elongated euhedral particles were also found that strongly resemble cubo-octahedral magnetosome morphologies (Fig. 1B and E). Short ”chains” of particles are even observed occasionally in TEM (Fig. 1A and D), although the spontaneously formed chain configurations in our samples can be distinguished from chains formed by MTB by the lack of repeated regular grain shapes and close spacing of the particles. In high-resolution TEM images, the magnetite crystals are highly crystalline and free of defects, with the exception of occasional twinning.

3.2 Magnetic properties

To examine the distribution of magnetic domain states and degree of magnetostatic interactions in goethite-derived magnetite, first-order reversal curve (FORC) diagrams

were obtained for altered goethite samples containing magnetite in various stages of the reaction. Partially reacted G04 and G03 samples containing approximately 4 and 5 wt% magnetite, based on saturation magnetization (M_s) values in Table 1 and the theoretical value of 92 Am^2/kg for stoichiometric magnetite (Dunlop and Özdemir, 1997), exhibit relatively small interaction fields and a high-coercivity (H_c) "tail" extending along the center horizontal axis (Fig. 2). The FORC distributions of these samples reflect a grain size distribution consisting of a mixture of superparamagnetic and weakly interacting small SD magnetite grains, as determined by Till et al. (2015). Magnetite-rich samples, G02 and G05 with approximately 53 and 71 wt% magnetite respectively, display a localized peak with a broader vertical spread indicating higher magnetostatic interaction fields (H_u) and overall higher coercivities, again including a high-coercivity tail with low interaction fields (Fig. 2). The teardrop-shaped FORC pattern for sample G02 is characteristic of interacting SD magnetite and is typical for experimentally disaggregated magnetosome particles (Kopp and Kirschvink, 2008; Moskowitz et al., 1993) and some magnetofossil-bearing sediments (Roberts et al., 2012).

Pure intact magnetosome chains and sediments dominated by intact magnetofossils display a narrow horizontal central ridge signifying non-interacting SD magnetite in FORC diagrams. In natural sediments, the addition of strongly interacting detrital magnetite can mask the central ridge, requiring certain measurement procedures to isolate the biogenic component of magnetization (Egli et al., 2010). The high-coercivity tails seen for our samples resemble the central ridge displayed by biogenic magnetite, but do not represent a separate mineral component; rather they likely represent magnetite particles embedded in a matrix of incompletely reacted nanohematite that are sufficiently dispersed to be weakly interacting. Interaction effects may be further reduced for highly dispersed magnetite particles in sedimentary material, in contrast to the high magnetite concentrations in our measured samples. Previous work suggests that well-dispersed, fine inorganic magnetite may also display features of non-interacting SD particles in FORC diagrams (Egli et al., 2010), including pedogenic Fe-oxides in soils (Geiss et al., 2008). The close similarities between the FORC diagrams for goethite-derived magnetite in Fig. 2 and those reported for

magnetofossil-bearing sediments (e.g., (Roberts et al., 2012)) may confound the identification of magnetofossils in natural sediments. The close comparison with natural samples also suggests that material similar to that produced from goethite in our experiments could be sufficient to account for the magnetic signature of certain sediments.

The Moskowitz test (Moskowitz et al., 1993) is a commonly used magnetic measurement for detecting intact magnetosome chains. The δ_{FC}/δ_{ZFC} ratio is based on the loss in remanence on warming through the Verwey crystallographic transition around 120 K (Verwey, 1939) and is greater than 2 for intact magnetosome chains, while values between 1 and 2 indicate that SD magnetite is present in other forms, including disaggregated or oxidized magnetosomes. δ_{FC}/δ_{ZFC} values for our magnetite-bearing samples are between 1.1 and 1.3. These values fall in the same range as the magnetite-bearing carbonate globules in Martian meteorite ALH84001 (Weiss et al., 2004b), experimentally disaggregated magnetosomes (Li et al., 2012), and marine sediment cores containing partially oxidized magnetofossils (Housen and Moskowitz, 2006).

The sharpness of the Verwey transition around 120 K for the pure magnetite end-product (sample G05) indicates a high degree of oxygen stoichiometry and the absence of substitutional impurities (Weiss et al., 2004b), as expected from the high purity of the starting goethite material. Although natural goethite commonly occurs in aluminous form with up to 30 mole% Al substitution (Tardy and Nahon, 1985), the stabilizing effect of aluminum (Ruan and Gilkes, 1995) suggests that Al-free goethite will alter to magnetite more readily and that Al-substituted magnetite produced by this pathway should be less common. Despite the success of some studies in producing magnetosomes doped with small amounts of metals (e.g. (Prozorov et al., 2014)), cation substitution in magnetofossils remains an important counter-indicator of biogenicity (Amor et al., 2015), and the occurrence of aluminum substitution in particular would strongly support an origin from detrital or authigenic goethite.

4. Discussion and conclusions

Till et al. 2015 recently identified various pathways by which altered goethite may

contribute nanoscale magnetic particles to sediments and soils, including thermal alteration by low-grade metamorphism, diagenesis in marine sediments and by wildfire in soils. Elevated temperatures generated in meta-sediments during deep burial will promote breakdown of goethite and may lead to authigenic magnetite formation under reducing conditions. The stability of goethite in anoxic sediments at ambient temperatures is unknown but it is unlikely to be stable under Fe-reducing conditions, so that the possibility of magnetite formation from low-temperature goethite alteration cannot be excluded. This is especially true given that current knowledge of the stability of nanoparticles of goethite and other iron oxides and hydroxides is even sparser (Lagroix et al., 2016).

Production of fine magnetic particles and soil magnetic enhancement alteration has been documented to result from goethite alteration during wildfire in various soil types (Anand and Gilkes, 1987; Clement et al., 2011; Ketterings et al., 2000; Nornberg et al., 2009). Nanoparticles produced by fire have high mobility due to both increased surface runoff and sediment delivery to lake catchments (Smith et al., 2013) and from increased wind erosion and aeolian transport following wildfire events (Whicker et al., 2002). These processes represent pathways by which detrital goethite-derived magnetite may enter lake and marine sediments, particularly marine settings with substantial continental inputs from aeolian deposition or submarine fans. Aeolian sediments and detrital material from weathered igneous formations have previously been recognized as potential sources of SD magnetite (Roberts et al., 2012). However, it is often assumed in sediment magnetism studies that the magnetic signature of biogenic magnetite can be distinguished from detrital sources of sedimentary magnetite on the basis of weak magnetic interactions, narrow coercivity and grain size distributions, and magnetosome-like crystal morphologies. Our findings demonstrate that inorganic magnetite particles can exhibit magnetic signatures and crystal morphologies highly similar to disaggregated magnetosomes and isolated magnetofossils in sediments.

Further complicating the problem of magnetofossil identification is that the conditions suitable for preservation of inorganic SD magnetite in sediments should be identical to those required for preservation of magnetofossils. Namely, anoxic or suboxic

conditions are required to inhibit oxidation, but must not be so reducing that fine magnetite particles begin to dissolve. Reliable identification of suspected magnetofossils should address the robustness measures outlined by Kopp and Kirschvink (2008), including the assessment of high quality paleomagnetic data, to rule out the possibility of secondary magnetizations that would result from authigenic growth of SD magnetite. Detrital SD magnetite that shares physical characteristics of biogenic magnetite will also produce high quality paleomagnetic records but will not meet the key criterion of long, intact chain structures detected either by direct microscopic observation or by various tests that infer chain configurations.

Our findings underscore the need for careful characterization of potential magnetofossils and reinforce the assertions of previous studies (Barber and Scott, 2002; Golden et al., 2004; Wang et al., 2015) that cubo-octahedral morphologies in single domain magnetite are not strictly unique to MTB magnetosomes. We contend that observation of isolated magnetite particles and magnetic properties associated with SD particles in sediments are not sufficient evidence for a biogenic origin. Given the widespread occurrence of nanocrystalline goethite in nature, its role as a potential precursor to sedimentary magnetite should be considered in future studies.

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386 **Table 1.** Room-temperature hysteresis parameters and experimental conditions for altered
387 samples.

Sample	Temp (°C)	Heating time (min)	M_s (Am^2/kg)	M_r (Am^2/kg)	H_c (mT)
G02	250	150	49	15	17
G03	230	150	4.3	1.1	10
G04	210	155	3.8	0.59	4.6
G05	270	75	65	18	19

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Figure Captions:

Figure 1: Examples of magnetite produced by reductive dehydroxylation of nanogoethite aggregates imaged by TEM. A) Clusters of magnetite particles demonstrating dominantly rounded, elongated shapes. B) Equant grains of highly crystalline magnetite with approximately cubo-octahedral morphologies. C) Elongated tapered magnetite grains resembling bullet-shaped magnetosome particles. D). Magnetite particles arranged in short irregular chains. E). Highly euhedral magnetite grains with cubo-octahedral morphologies. Insets are simulated electron diffraction patterns for particles in each image.

Figure 2: FORC measurement diagrams (top) for altered goethite G04, G03, G02 samples and gradient curves of magnetic remanence acquisition obtained from FORC measurements (bottom) for increasing stages of the magnetite-producing reaction from left to right. A smoothing factor of 3 has been applied to each FORC diagram.

Figure 3: Measurements of low-temperature saturation isothermal magnetic remanence (SIRM) measured on warming from 10 K after zero-field cooling (ZFC) or field cooling (FC) in a 2.5 T field for various stages of reductive alteration products of nanogoethite. Solid grey lines represent derivatives of FC remanence curves with local minima indicating the temperature of the Verwey transition.