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Presumed magnetic biosignatures observed in magnetite derived from abiotic reductive alteration of nanogoethite

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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 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 the inorganic breakdown of nanocrystalline goethite exhibits magnetic properties and morphologies remarkably similar to those of biogenic magnetite from magnetosomes. During heating in reducing conditions, oriented nanogoethite aggregates undergo dehydroxylation and transform into 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 the identification of magnetofossils. Furthermore, the suboxic conditions necessary for magnetofossil preservation in sediments are conducive to the reductive alteration of nanogoethite, as well as the preservation of 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 diagenesis commonly disrupts the chain structure of magnetosomes. Our results indicate that isolated magnetofossils cannot be positively distinguished from inorganic magnetite on the basis of their 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 the Cretaceous (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,

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high chemical purity, a single-domain magnetic structure, well-defined crystal morphology, 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 the collapse and the 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 the microscopic observation of magnetic extracts, combined with the 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).

Although the inorganic magnetite fraction in many sediments is not usually considered to include a significant amount of SD material, recent studies have recognized that certain types of detrital particles, such as magnetic inclusions in silicate minerals, are widespread and important contributors to fine-particle magnetism in sediments (Chang et al., 2016b). Additionally, this type of detrital SD magnetite can obscure the rock magnetic signatures of the biogenic magnetite fraction (Chang et al., 2016a). A number of earlier studies demonstrated that various inorganic processes can produce magnetite with certain characteristic morphologies of biogenic magnetite to explain the occurrence of SD magnetite in the ALH84001 Martian meteorite (Barber and Scott, 2002; Bradley et al., 1998; Golden et al., 2004). However, inorganic processes are rarely invoked to explain the biogenic characteristics of SD magnetite in terrestrial environments. Rather it is assumed that because MTB are widespread in modern aqueous environments, they are likely to have been widespread throughout much of Earth's history and hence much ancient sediment may be expected to carry magnetic signatures of magnetofossils. Here, we describe various magnetosome-like properties of nanoscale magnetite particles produced by inorganic alteration of nanocrystalline goethite. We propose that magnetite produced by this reaction pathway could potentially contribute to the SD magnetite signals in sediment magnetic properties that are commonly attributed to biogenic magnetite.

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

2. Procedures

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. After removing the mixed solution from the glove box, 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 a JEOL 2100F microscope with a field-emission gun at a 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 the magnetic remanence at 80 K or 150 K upon warming after either FC or ZFC pre-treatment. First-order reversal curve (FORC) distributions 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 magnetic saturating field of the samples, and a field increment of 1 mT. FORC diagrams

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