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

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15 **Abstract**

16 The oriented chains of nanoscale Fe-oxide particles produced by magnetotactic
17 bacteria are a striking example of biomineralization. Several distinguishing features of the
18 magnetite particles that comprise bacterial magnetosomes have been proposed to
19 collectively constitute a biosignature of magnetotactic bacteria (Thomas-Keprta et al.,
20 2001). These features include high crystallinity, chemical purity, a single-domain magnetic
21 structure, well-defined crystal morphology, and arrangement of particles in chain
22 structures. Here we show that magnetite derived from inorganic breakdown of
23 nanocrystalline goethite exhibits magnetic properties and morphologies remarkably similar
24 to biogenic magnetite from magnetosomes. During heating in reducing conditions, oriented
25 nanogoethite aggregates undergo dehydroxylation and transform to stoichiometric
26 magnetite. We demonstrate that highly crystalline single-domain magnetite with euhedral
27 grain morphologies produced abiogenically from goethite meets several of the biogenicity
28 criteria commonly used for identification of magnetofossils. Furthermore, the suboxic
29 conditions necessary for magnetofossil preservation in sediments are also conducive to
30 promote reductive alteration of nanogoethite, and to preserve detrital magnetite originally
31 formed from goethite. The findings of this study have potential implications for the
32 identification of biogenic magnetite, particularly in older sediments where diagenetic
33 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*

3

91   Synthetic nanogoethite was produced using the protocol outlined in (Schwertmann

92   and Cornell, 1991). A 0.05 M solution of $FeCl_2 \cdot 4H_2O$ was prepared in a glove box using

93   deoxygenated water and was mixed with a 1 M $NaHCO_3$ solution. A constant flow of air

94   was bubbled through the resulting suspension, which was continuously agitated and

95   became oxidized over 48 h. The goethite precipitate was separated by centrifuging and

96   rinsing with ultrapure (MilliQ) water several times and dried in a vacuum desiccator. The

97   resulting goethite particles are around 10 nm by 50 nm in size, and consist of well-oriented

98   aggregates of crystallites with crystallite sizes around 6 nm (Till et al., 2015).

99   *2.2 Characterization*

100   The starting material and reaction products were characterized by Rietveld

101   refinement of the X-ray diffraction (XRD) powder patterns and imaged by high-resolution

102   transmission electron microscopy on JEOL 2100F microscope with field-emission gun at

103   200 kV accelerating voltage. Electron diffraction patterns were calculated by fast Fourier

104   transforms of high-resolution images. Samples for magnetic measurements were prepared

105   using small amounts of undiluted sample powders packed in gelatin capsules. Low-

106   temperature magnetic measurements of saturation isothermal remanent magnetization

107   (SIRM) curves measured on warming from 10 K after field-cooling (FC) in a 2.5 T field or

108   cooling in zero-field (ZFC), were made on a Quantum Designs Magnetic Properties

109   Measurement System (MPMS XL-5 with EverCool). δ_{FC}/δ_{ZFC} ratios were calculated as $\delta =$

110   $(M_{irm}(80)-M_{irm}(150))/M_{irm}(80)$, where M is the value of magnetic remanence at 80 K and

111   150 K upon warming after either FC or ZFC pre-treatment. First-order reversal curve

112   (FORC) diagrams and hysteresis loops were measured on a Princeton Measurements

113   Corporation vibrating sample magnetometer (VSM) at room temperature. FORC

114   measurements used a maximum field of 0.3 T, which is greater than the samples magnetic

115   saturating field, and a field increment of 1 mT. FORC diagrams were processed and plotted

116   with the FORCinel software package (Harrison and Feinberg, 2008) using the VARIFORC

117   smoothing protocol (Egli, 2013), with smoothing parameters of $S_{c0}=3$, $S_{b0}=2$, and

118   $S_{c1}=S_{b1}=5$.

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

146   were obtained for altered goethite samples containing magnetite in various stages of the

147   reaction. Partially reacted G04 and G03 samples containing approximately 4 and 5 wt%

148   magnetite, based on saturation magnetization (M_s) values in Table 1 and the theoretical

149   value of 92 Am^2/kg for stoichiometric magnetite (Dunlop and Özdemir, 1997), exhibit

150   relatively small interaction fields and a high-coercivity (H_c) "tail" extending along the

151   center horizontal axis (Fig. 2). The FORC distributions of these samples reflect a grain size

152   distribution consisting of a mixture of superparamagnetic and weakly interacting small SD

153   magnetite grains, as determined by Till et al. (2015). Magnetite-rich samples, G02 and G05

154   with approximately 53 and 71 wt% magnetite respectively, display a localized peak with a

155   broader vertical spread indicating higher magnetostatic interaction fields (H_u) and overall

156   higher coercivities, again including a high-coercivity tail with low interaction fields (Fig.

157   2). The teardrop-shaped FORC pattern for sample G02 is characteristic of interacting SD

158   magnetite and is typical for experimentally disaggregated magnetosome particles (Kopp

159   and Kirschvink, 2008; Moskowitz et al., 1993) and some magnetofossil-bearing sediments

160   (Roberts et al., 2012).

161   Pure intact magnetosome chains and sediments dominated by intact magnetofossils

162   display a narrow horizontal central ridge signifying non-interacting SD magnetite in FORC

163   diagrams. In natural sediments, the addition of strongly interacting detrital magnetite can

164   mask the central ridge, requiring certain measurement procedures to isolate the biogenic

165   component of magnetization (Egli et al., 2010). The high-coercivity tails seen for our

166   samples resemble the central ridge displayed by biogenic magnetite, but do not represent a

167   separate mineral component; rather they likely represent magnetite particles embedded in a

168   matrix of incompletely reacted nanohematite that are sufficiently dispersed to be weakly

169   interacting. Interaction effects may be further reduced for highly dispersed magnetite

170   particles in sedimentary material, in contrast to the high magnetite concentrations in our

171   measured samples. Previous work suggests that well-dispersed, fine inorganic magnetite

172   may also display features of non-interacting SD particles in FORC diagrams (Egli et al.,

173   2010), including pedogenic Fe-oxides in soils (Geiss et al., 2008). The close similarities

174   between the FORC diagrams for goethite-derived magnetite in Fig. 2 and those reported for

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

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

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

201 **4. Discussion and conclusions**

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

203   contribute nanoscale magnetic particles to sediments and soils, including thermal alteration

204   by low-grade metamorphism, diagenesis in marine sediments and by wildfire in soils.

205   Elevated temperatures generated in meta-sediments during deep burial will promote

206   breakdown of goethite and may lead to authigenic magnetite formation under reducing

207   conditions. The stability of goethite in anoxic sediments at ambient temperatures is

208   unknown but it is unlikely to be stable under Fe-reducing conditions, so that the possibility

209   of magnetite formation from low-temperature goethite alteration cannot be excluded. This

210   is especially true given that current knowledge of the stability of nanoparticles of goethite

211   and other iron oxides and hydroxides is even sparser (Lagroix et al., 2016).

212   Production of fine magnetic particles and soil magnetic enhancement alteration has

213   been documented to result from goethite alteration during wildfire in various soil types

214   (Anand and Gilkes, 1987; Clement et al., 2011; Ketterings et al., 2000; Nornberg et al.,

215   2009). Nanoparticles produced by fire have high mobility due to both increased surface

216   runoff and sediment delivery to lake catchments (Smith et al., 2013) and from increased

217   wind erosion and aeolian transport following wildfire events (Whicker et al., 2002). These

218   processes represent pathways by which detrital goethite-derived magnetite may enter lake

219   and marine sediments, particularly marine settings with substantial continental inputs from

220   aeolian deposition or submarine fans. Aeolian sediments and detrital material from

221   weathered igneous formations have previously been recognized as potential sources of SD

222   magnetite (Roberts et al., 2012). However, it is often assumed in sediment magnetism

223   studies that the magnetic signature of biogenic magnetite can be distinguished from detrital

224   sources of sedimentary magnetite on the basis of weak magnetic interactions, narrow

225   coercivity and grain size distributions, and magnetosome-like crystal morphologies. Our

226   findings demonstrate that inorganic magnetite particles can exhibit magnetic signatures and

227   crystal morphologies highly similar to disaggregated magnetosomes and isolated

228   magnetofossils in sediments.

229   Further complicating the problem of magnetofossil identification is that the

230   conditions suitable for preservation of inorganic SD magnetite in sediments should be

231   identical to those required for preservation of magnetofossils. Namely, anoxic or suboxic

232 conditions are required to inhibit oxidation, but must not be so reducing that fine magnetite

233 particles begin to dissolve. Reliable identification of suspected magnetofossils should

234 address the robustness measures outlined by Kopp and Kirschvink (2008), including the

235 assessment of high quality paleomagnetic data, to rule out the possibility of secondary

236 magnetizations that would result from authigenic growth of SD magnetite. Detrital SD

237 magnetite that shares physical characteristics of biogenic magnetite will also produce high

238 quality paleomagnetic records but will not meet the key criterion of long, intact chain

239 structures detected either by direct microscopic observation or by various tests that infer

240 chain configurations.

241 Our findings underscore the need for careful characterization of potential

242 magnetofossils and reinforce the assertions of previous studies (Barber and Scott, 2002;

243 Golden et al., 2004; Wang et al., 2015) that cubo-octahedral morphologies in single

244 domain magnetite are not strictly unique to MTB magnetosomes. We contend that

245 observation of isolated magnetite particles and magnetic properties associated with SD

246 particles in sediments are not sufficient evidence for a biogenic origin. Given the

247 widespread occurrence of nanocrystalline goethite in nature, its role as a potential

248 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 (Am²/kg)	M_r (Am²/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.