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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

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

37 **1. Introduction**

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

52 While all of the above criteria are typically observed in cultured strains of MTB and
53 live bacteria sampled from modern aqueous environments, studies of older sediments often
54 fail to observe intact chain structures in fossil magnetosomes due to collapse and
55 disaggregation of the chains either through diagenesis or by laboratory protocols of
56 magnetic mineral extraction for microscopic investigation. In some cases, methods such as
57 ferromagnetic resonance or low-temperature magnetic measurements can be used to infer
58 the presence of magnetic chain structures (Weiss et al., 2004a). However many studies on
59 ancient sediments rely on microscopic observation of magnetic extracts, combined with
60 analysis of sediment magnetic properties to detect single domain (SD) magnetite (e.g.
61 (Abrajevitch et al., 2015; Larrasoana et al., 2014; Savian et al., 2016)), which has few
62 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 ($T = 210\text{-}270^\circ\text{C}$).
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*

91 Synthetic nanogoethite was produced using the protocol outlined in (Schwertmann
92 and Cornell, 1991). A 0.05 M solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 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 $S_{c1}=S_{b1}=5$.

119 *2.3 Alteration experiments*

120 Alteration experiments were performed by heating synthetic nanogoethite powder
121 at temperatures between 210 and 270°C for up to 2.5 hours in a constant flow of a 20%-
122 80% CO-CO₂ gas mixture. The furnace used for heating experiments was enclosed inside
123 an Ar-filled glove box, and samples were prepared and maintained under anoxic conditions
124 to minimize samples oxidation. Magnetic characterization was performed immediately
125 after each alteration experiment. Conditions for each experimental run as well as detailed
126 results of XRD and other magnetic measurements were reported by Till et al. (2015) and
127 are summarized in Table 1.

128 **3. Results**

129 *3.1 Magnetite morphology*

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

143 *3.2 Magnetic properties*

144 To examine the distribution of magnetic domain states and degree of magnetostatic
145 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 $92 \text{ Am}^2/\text{kg}$ 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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252

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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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389

390 **Figure Captions:**

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

398

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

403

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