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

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14  
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  $\text{NaHCO}_3$  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).  $\delta_{FC}/\delta_{ZFC}$  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-CO<sub>2</sub> 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 Am<sup>2</sup>/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  $\delta_{FC}/\delta_{ZFC}$  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.  $\delta_{FC}/\delta_{ZFC}$  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 <sup>2</sup> /kg)	$M_r$ (Am <sup>2</sup> /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.