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Depth Distribution of Magnetofossils in Near-Surface Sediments From the Blake/Bahama Outer Ridge, Western North Atlantic Ocean, Determined by Low-Temperature Magnetism

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[1] Fe-oxide and Fe-sulfide trace minerals in sediments and sedimentary rocks provide proxy records of biogeochemical processes, record past variations in the geomagnetic field, and can serve as proxies for climatic variations. An important class of these Fe-oxides is produced by bacteria. Magnetic particles produced by magnetotactic bacteria have been proposed as a primary recorder of the geomagnetic field in many terrestrial marine sediments, and have also been suggested to represent fossil evidence of life on the planet Mars. To better understand their distribution and preservation in the sediment column, and their relationship to other biochemical processes, we present rock-magnetic data that document the occurrence and abundance of fossil biogenic magnetite (magnetofossils) in marine sediments from the Blake/Bahama Outer Ridge. Magnetic hysteresis and low-temperature magnetism both indicate that the occurrence of magnetofossils is closely linked to the depth of the modern Fe-redox boundary within the sediment column, and that a fraction of the magnetic minerals in the sediment column above the Fe-redox boundary are in the form of intact and relatively unaltered chains of nanophase magnetite crystals. Below the Fe-redox boundary the abundance of these magnetofossils is markedly decreased. The important conclusions of this work are to demonstrate that nondestructive rock-magnetic methods can be used to successfully document the occurrence and relative abundance of magnetofossils in geologic materials.

1. Introduction

[2] Biogeochemical processes in sediments can produce as well as destroy magnetic minerals and significantly affect sedimentary paleomagnetic records of geomagnetic field behavior or mineral magnetic records of paleoenvironmental change. Microbially mediated chemical reactions involved in the decomposition of organic carbon in marine sediments can result in the dissolution of iron oxides and growth of secondary iron sulfides [*Canfield and Berner*, 1987; *Leslie et al.*, 1990; *Roberts and Turner*, 1993; *Tarduno*, 1994] or form new magnetic phases including magnetite [*Karlin et al.*, 1987; *Karlin*, 1990]. Studies of the effect of changing redox conditions on magnetic mineralogy have focused on shallow-sediment (less than a few meters below the sediment-water interface) diagenesis in suboxic to strongly reducing environments [e.g., *Leslie et al.*, 1990; *Karlin*, 1990; *Canfield et al.*, 1992; *Schwartz et al.*, 1997; *Smirnov and Tarduno*, 2000; *Hilgenfeldt*, 2000; *Robinson*,

2000]. An important source of magnetic minerals in some marine sediments associated with these redox changes is the authigenic biomineralization of fine grained (<100 nm) magnetic minerals by magnetotactic and dissimilatory iron-reducing bacteria [e.g., *Chang and Kirschvink*, 1989; *Hesse and Stolz*, 1999]. For example, magnetotactic bacteria (MTB) are a diverse group of bacteria whose directional swimming is affected by the geomagnetic field. Magnetotactic bacteria mineralize intercellular chains of magnetic inclusions called magnetosomes, which are composed of either magnetite (Fe_3O_4) or greigite (Fe_3S_4). The nanocrystalline iron-mineral particles are single magnetic domains (SD) characterized by narrow, asymmetric, particle size distributions, and uniform, species-specific particle morphologies [e.g., *Bazylinski and Moskowitz*, 1999]. The intercellular magnetosome particles are usually arranged in single or multiple linear chains. The intercellular magnetosome structures are responsible for the cell's response in the geomagnetic field. When the cell dies and lyses, magnetosomes can be deposited in sediment and preserved as magnetofossils [*Chang and Kirschvink*, 1989]. The SD grain sizes (40–120 nm) of these biogenic minerals make them potentially excellent recorders of the paleomagnetic field after deposition, and several unique particle morphologies (e.g., hexagonal prismatic forms) can serve as a potential biosignature for the past presence of magnetotactic

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bacteria in ancient sediments. Magnetotactic bacteria have been found to occur in diverse aquatic environments, and putative magnetofossils have been proposed as the major or sole carrier of natural remanence in a variety of rocks and sediments spanning the last 2.0 Ga [*Chang and Kirschvink*, 1989; *Hesse and Stolz*, 1999].

[3] Modern MTB activity is closely linked to Fe-redox changes within the water column or below the sediment-water interface and large populations of MTB are found near the oxic-anoxic transition zone (OATZ) [*Bazylinski and Moskowitz*, 1999; *Petermann and Bleil*, 1993; *Simmons et al.*, 2004]. Variations in magnetofossil abundance and their morphologies in marine sediments spanning the last few glacial stages have been attributed to climatically mediated redox changes [*Hesse*, 1994; *Lean and McCave*, 1998; *Dinarès-Turell et al.*, 2003]. Furthermore, links between MTB populations and sediment chemistry, and possible migration of these organisms within sediment, suggest that lock-in behavior of post-depositional remanence carried by biogenic minerals could be different from that of detrital minerals [*Tarduno and Wilkison*, 1996; *Tarduno et al.*, 1998]. Reports of contributions by MTB to remanence have been based on merely associating the presence of magnetofossils extracted from the sediment with the occurrence of a well-defined remanence direction [i.e., *McNeill*, 1990]. Similarly, empirical links between scattered remanence directions and chemical alteration of bacterial magnetite by maghemitization have also been proposed by *Vali and Kirschvink* [1989]. In contrast, *Schwartz et al.* [1997] concluded that magnetofossils did not contribute to the NRM in Holocene sediments from the Blake/Bahama Outer Ridge (North Atlantic Ocean), even though magnetofossils were observed to be abundant in the same sediments.

[4] Besides terrestrial occurrences of magnetofossils, magnetite with particle morphologies and sizes similar to those in modern magnetotactic bacteria has been reported in the 4.5 billion year old Martian meteorite ALH-84001, and provides the basis for the hypothesis that these particles represent the fossil remains of ancient Martian life [*Thomas-Keprta et al.*, 2000]. Whether or not these crystals are unequivocal evidence for life on ancient Mars [*Buseck et al.*, 2001], their discovery has raised the possibility that certain types of nanophase particles of magnetite could serve as a biomarker for microbial life on ancient Earth and possibly on other planetary bodies.

[5] The primary means to identify magnetofossils in geological materials has been by magnetic extraction of nanometer-sized magnetic particles from sediments and subsequent electron microscopic observations [*Chang and Kirschvink*, 1989]. This identification is based on the similarities of the particle's shapes and sizes to contemporary magnetosome particles that often have distinctive particle morphologies. Alternative approaches to magnetic extraction and microscopy involve various types of magnetic measurements that can be used to identify magnetofossils in bulk sediments samples [*Moskowitz et al.*, 1993; *Oldfield*, 1994; *Weiss et al.*, 2004; *Egli*, 2004]. These magnetic techniques rely upon isolating the magnetic characteristics of the narrowly sized distributions of SD particles and, possibly the unique particle chain architectures, produced by magnetotactic bacteria. Rock-magnetic techniques

have advantages of being rapid and nondestructive, which allows assaying many samples for possible magnetofossil contributions. However, with all bulk measurements, mixtures of different magnetic minerals, magnetic domain states, or variations in stoichiometry, can often mask the magnetic signature of magnetofossils [*Moskowitz et al.*, 1993; *Smirnov and Tarduno*, 2000; *Passier and Dekkers*, 2002; *Weiss et al.*, 2004; *Pan et al.*, 2005b]. Identification of magnetofossils based on a low-temperature (<300 K) magnetic method proposed by *Moskowitz et al.* [1993] has been applied to natural samples in a few studies with mixed results [*Geiss and Banerjee*, 1997; *Smirnov and Tarduno*, 2000; *Passier and Dekkers*, 2002; *Egli*, 2004; *Weiss et al.*, 2004; *Pan et al.*, 2005a]. We will present results from rock-magnetic measurements, along with existing data on sediment geochemistry and documentation of magnetofossils from marine sediment cores from the Blake/Bahama Outer Ridge (BBOR), in the North Atlantic Ocean [*Schwartz et al.*, 1997]. In particular, our results demonstrate that the method of *Moskowitz et al.* [1993] was successful in identifying stratigraphic variations in magnetofossil content in the near surface BBOR sediments.

2. Sample Description and Rock Magnetic Methods

2.1. Site Areas and Samples

[6] Samples for this study came from the Blake/Bahama Outer Ridge (BBOR), western North Atlantic Ocean. The BBOR samples were taken from cores 88-10P (water depth, 3820 m), 89-1P (water depth, 3180 m), and GGC-24 (water depth, 4250 m), and the geochemistry, paleomagnetism, and rock magnetism of the sediment cores are described by *Schwartz et al.* [1997]. All three BBOR sites consist of hemipelagic drift sediments that have well-documented near-surface redox boundaries, marked by both sediment color changes and by peaks in Mn and Fe [*Schwartz et al.*, 1997], between depths of 60 and 80 cm (core 88-10P), 10 and 40 cm (core 89-1p), and 30 and 50 cm (core GGC24). The redox boundaries occur within the carbonate-rich Holocene (marine isotope Stage 1) sediments in these cores. The Stage 1/Stage 2 boundary in the cores is marked by an abrupt decrease in carbonate content, and occurs at a depth of 95 cm in core 88-10P, 65 cm in core GGC-24, and at 140 cm in core 89-1P [*Schwartz et al.*, 1997]. For all cores, samples were collected in 5- to 25-cm intervals for the uppermost 2–3 m of sediment, and are less than 300 ka in age [*Schwartz et al.*, 1997]. Samples were collected from the archived piston cores as oriented, 8 cm^3 cubic samples by gently inserting plastic cubes into the sediment core with the aid of a scalpel. Splits of these samples, with masses ranging from 80 to 250 mg, were extracted from the sediment cubes and placed into gelatin capsules for measurement of low-temperature remanence and magnetic hysteresis at room temperature. Organic carbon content of these sediments ranges from 0.5 to 2%. Solid phase chemistry and prior work on the magnetic mineralogy indicates that the near surface (depth < 1.0 m) sediments are oxic to suboxic. Sulfate likely becomes reduced at depths between 1.0 m and >5 m depth, as evidenced by color change and a peak in solid-phase sulfur [*Schwartz et al.*, 1997]. Previous paleomagnetic analysis by *Schwartz et al.* [1997] indicated that
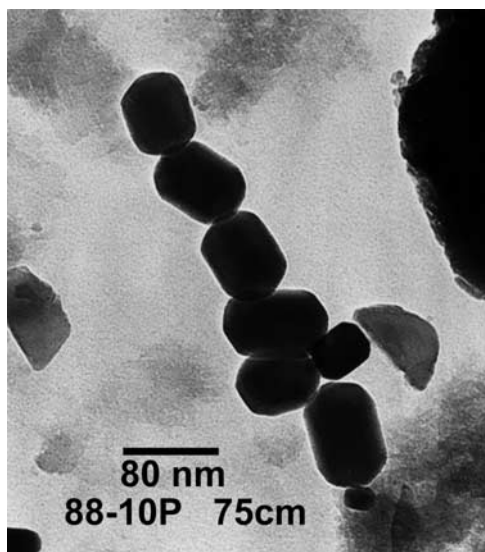
Figure 1. Transmission electron microscopy (TEM) image of magnetite particles extracted from core 88-10P, from 75 cm depth. The shapes of these particles display the truncated cubo-octahedral morphology characteristic of magnetite produced by some strains of magnetotactic bacteria [*Bazylinski and Moskowitz*, 1999]. Image is courtesy of Martha Schwartz.

BBOR cores have well-defined remanence behavior that accurately records the geomagnetic field at the sampling sites. Transmission electron microscopy (TEM) of sediment extracts from 21 sample horizons in the upper 150 cm of the three cores studied here revealed abundant-to-common magnetofossils above the Fe-redox boundaries, in the Holocene carbonate-rich sediments, but few magnetofossils below the redox boundaries [*Schwartz et al.*, 1997]. Magnetofossil identification was based on similarities of size and shapes of magnetite particles to modern magnetosome morphologies and an example is shown in Figure 1.

## 2.2. Low-Temperature Delta-Delta Method

[7] Low-temperature (5–300 K) remanence measurements can provide information about the magnetic mineralogy and domain state of a sample, as many magnetic minerals have low-temperature magnetic or phase-transitions or temperature dependent behavior that produce characteristic changes in their magnetic properties. For example, stoichiometric magnetite undergoes a structural transition from cubic to monoclinic symmetry at $T_v = 125$ K, known as the Verwey transition [e.g., *Dunlop and Özdemir*, 1997]. *Moskowitz et al.* [1993] proposed that magnetosome chains of SD magnetite produced by magnetotactic bacteria can be recognized by distinctive magnetic behavior associated with thermal cycling of remanence through the Verwey transition. This is done by comparing the thermal decay of a saturation remanence in zero field on warming from 20 K to 300 K for two different initial field protocols: (1) Zero field cooled (ZFC remanence) state obtained by initial cooling from 300 K to 20 K in zero-field prior to the application of a 2.5 T field at 20 K, and (2) Field cooled (FC remanence) state obtained by cooling from 300 K to 20 K in a high magnetic field of 2.5 T. *Moskowitz et al.* [1993] suggested

that the difference between the amount of FC and ZFC remanence lost on warming through T_v, quantified as the delta-delta ratio given by $\delta FC/\delta ZFC$, with $\delta = (J(80K) - J(150K))/J(80K)$, can be used to identify and possibly determine the relative abundance of biogenic magnetite in sediments occurring as either magnetosome chains in living cells or magnetofossil chains that not been chemically altered or physically disrupted. For MTB cells with magnetite magnetosomes chains, the field-induced alignment of the c-axes (easy axis) in monoclinic magnetite produces a bifurcation between the ZFC and FC curves below T_v, resulting in an FC remanence higher than the ZFC remanence and delta-delta ratio greater than 1. Warming back through the Verwey temperature, FC and ZFC remanence curves merge as the magnetization flips back along the [111] easy axis defined by the unique chain directions [*Moskowitz et al.*, 1993]. Experimental results on several different pure cultures of freeze-dried magnetotactic bacteria and frozen whole-cell suspensions showed that $\delta FC/\delta ZFC > 2.0$ is an indicator of magnetosome chains. Nonbiogenic SD magnetite or disrupted magnetosome chains had bifurcated ZFC/FC curves but lower delta-delta ratios between 1 and 1.5. Recent confirmation of these results, using other species of MTB has been reported by *Weiss et al.* [2004] and by *Pan et al.* [2005b]. In contrast, pseudo-single domain (PSD) magnetite (grain size, 0.1 to <5 μm), superparamagnetic (SPM) particles (grain size < 30 nm), maghemitized magnetosomes, or other magnetic minerals (i.e., greigite, maghemite, pyrrhotite) produced delta-delta ratios near 1.0 (i.e., no difference between ZFC and FC curves [see also *Kosterov*, 2003]). Conversely, coarse-grained, multidomain magnetite (grain size 100–150 μm) produces an inversion in the ZFC-FC behavior with ZFC remanence greater than the FC remanence and delta-delta ratios <1.0 [*Kosterov*, 2003].

[8] Mixtures of biogenic chains and "nonchain" magnetic phases, typical of natural sediments can reduce delta-delta ratios below 2.0, complicating the use of the delta-delta ratio as a biomarker for magnetofossils [*Moskowitz et al.*, 1993]. Theoretical modeling of FC and ZFC remanence curves for inorganic and biogenic SD magnetite shows that enhanced delta-delta ratios (>2.0) for magnetosome chains is due to a combination of the field-induced easy axis alignment below T_v and very minor amounts (<1%) of nonstoichiometry [*Carter-Stiglitz et al.*, 2004]. Experimental results and theoretical modeling show that at the minimum, elevated delta-delta ratios (>1.0) and bifurcated ZFC/FC curves below T_v with FC > ZFC together are a robust indicator of SD magnetite regardless of origin (biogenic versus inorganic). Therefore any delta-delta ratios greater than 1.0 may still useful for identifying possible sediment zones containing magnetofossils because (1) magnetotactic bacteria are a source of narrowly sized SD particles in sediments and (2) samples displaying elevated ratios can then be preselected for further analysis using electron microscopy for positive magnetofossil identification.

[9] Low-temperature remanence curves were measured with an MPMS-2 SQUID magnetometer at the Institute for Rock Magnetism, University of Minnesota. ZFC and FC thermal demagnetization was carried out with a sweep rate of 5 K/min. The residual field of the superconducting
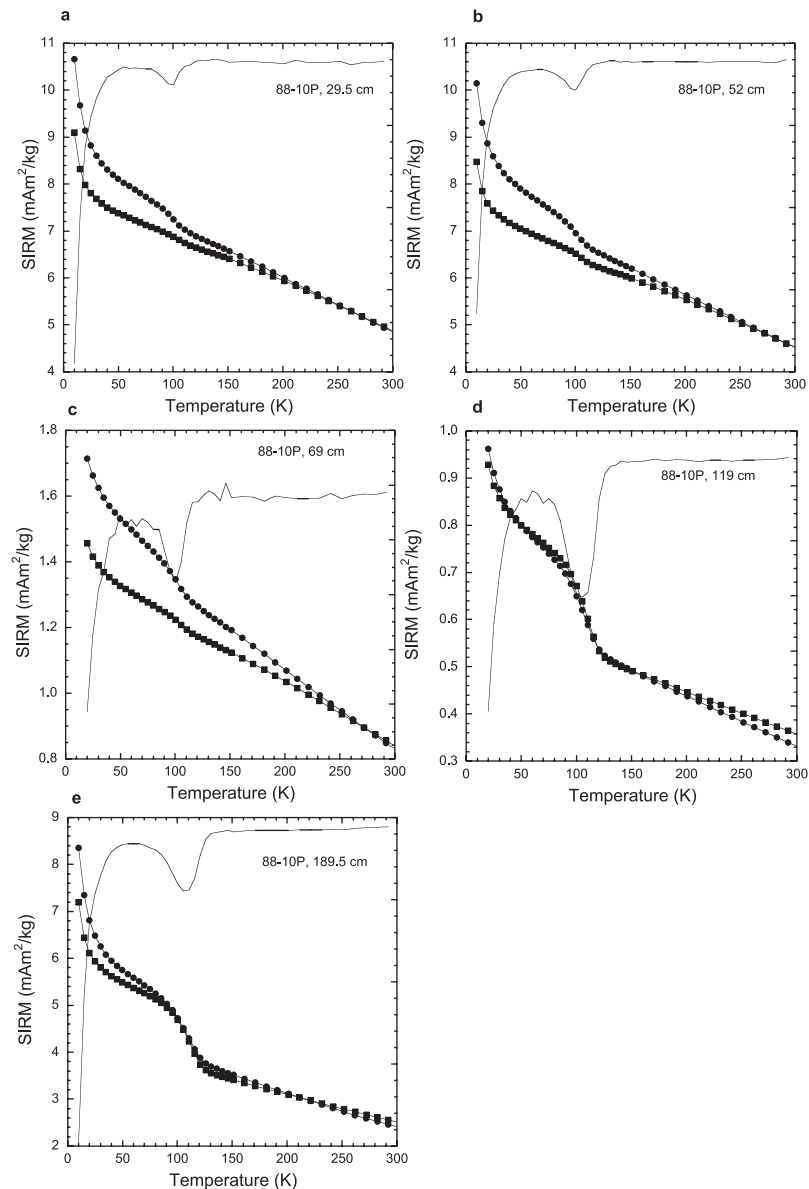
Figure 2. Low-temperature saturation remanence curves after samples were field cooled in a high field (FC, circles) and zero field cooled (ZFC, squares) for representative samples from core 88-10P. The solid line is the first temperature derivative of the FC remanence curve (dM_{fc}/dT).

magnet after a magnet reset from 2.5 T, and with a small dc nulling field applied during measurement, is less than 1 μT.

2.3. Magnetic Hysteresis

[10] One common means of characterizing the magnetic mineralogy of rocks is magnetic hysteresis. These data can be used to extract information regarding the domain-state characteristics of the magnetic minerals within a sample and details regarding possible admixtures of populations of grains with different size-dependent domain states (single domain, multidomain, superparamagnetic) [*Day et al.*, 1977; *Dunlop*, 2002a, 2002b; *Tauxe et al.*, 1996]. In addition to characterizing the domain state, other properties such as coercivity of remanence (B_{cr}) have been used to indicate the possible occurrence of fine-grained magnetic

minerals (including biogenic magnetite) in marine sediments [*Tarduno and Wilkison*, 1996; *Tarduno et al.*, 1998]. Hysteresis data at room temperature were measured for samples from core 88-10P using a Princeton Measurements vibrating sample magnetometer at the Institute for Rock Magnetism.

3. Results and Analysis
3.1. Low-Temperature Remanence

[11] Low temperature remanence experiments on marine sediments from three sites from the BBOR all have Verwey transitions, indicating the presence of magnetite within these sediments. Examples of FC and ZFC warming curves are shown in Figures 2–4. No other distinctive remanence transitions associated with hematite, pyrrhotite, or siderite
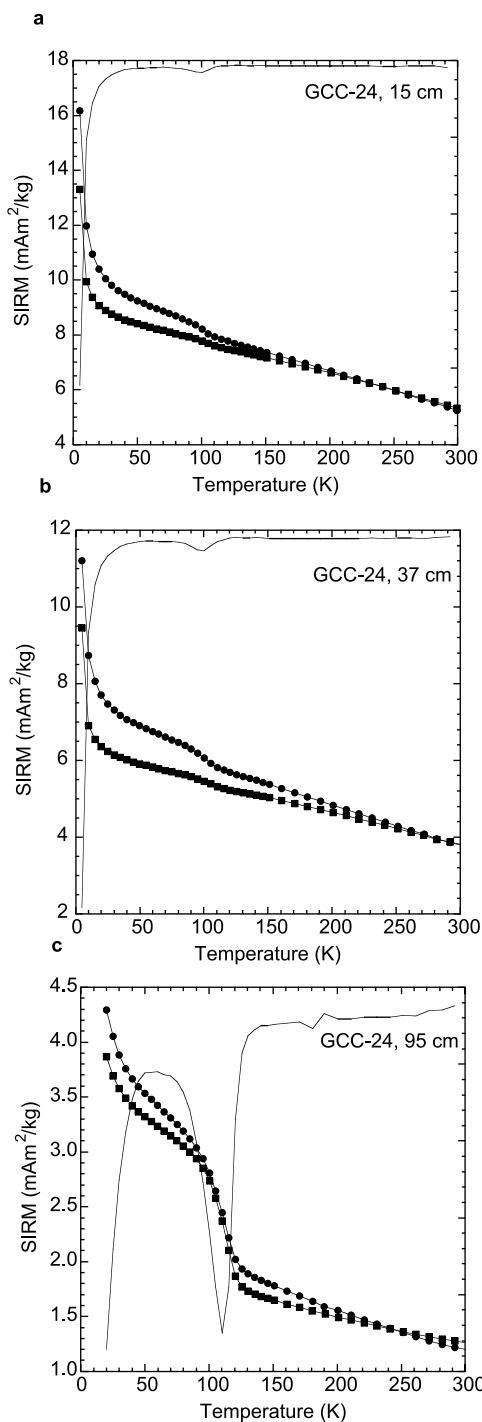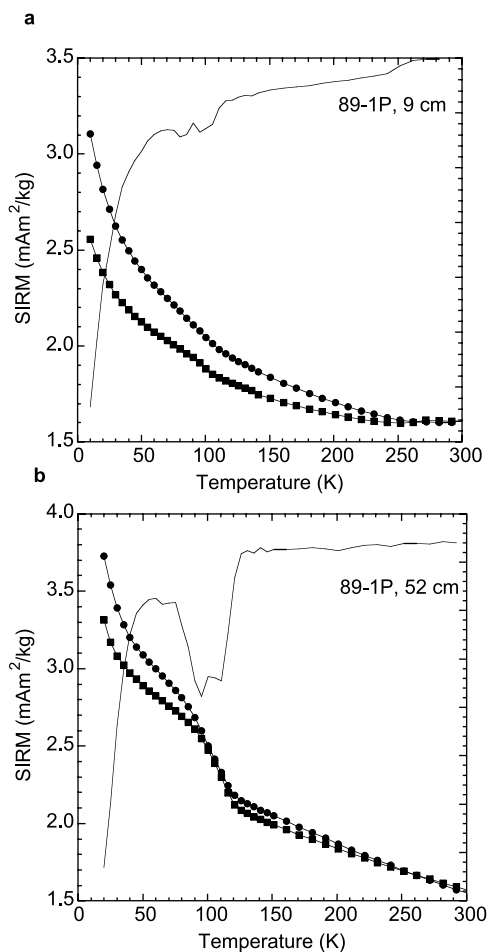
Figure 3. Representative low temperature FC (circles) and ZFC (squares) remanence results from core GGC-24. The solid line is the first temperature derivative of the FC remanence curve (dM_{fc}/dT).

(Figures 2a and 2b), and display more prominent Verwey transitions on the FC warming curves than on the companion ZFC curves (Zone I). Overall, however, the Verwey transitions are broad and weak within this depth range. In contrast, samples in the zone below 80 cm depth have essentially identical FC and ZFC remanences above and below 120 K (Figures 2c and 2d), and display stronger expressions of the Verwey transitions on both FC and ZFC warming curves (Zone II). Although sampling is coarser, a similar FC-ZFC pattern is observed in core GCC-24, with two zones of magnetic behavior but with the transition between Zones I and II occurring between 35–67 cm (Figure 3) Results for core 89-1P fit the general trend but with few data points, the low-temperature behavior is not as convincing as in the other two cores (Figure 4). The transition between magnetic zones I and II occurs within a depth interval that corresponds to the depths of the modern Fe-redox boundaries in each core and is stratigraphically above the transition from carbonate-rich to carbonate-poor sediments associated with the Stage 1/Stage 2 boundary.

[12] FC-ZFC curves from all three cores above their respective Fe-redox boundaries (Zone I) also show variable amounts of separation above the Verwey transition

Figure 4. Representative low temperature FC (circles) and ZFC (squares) remanence results from core 89-1P. The solid line is the first temperature derivative of the FC remanence curve (dM_{fc}/dT).
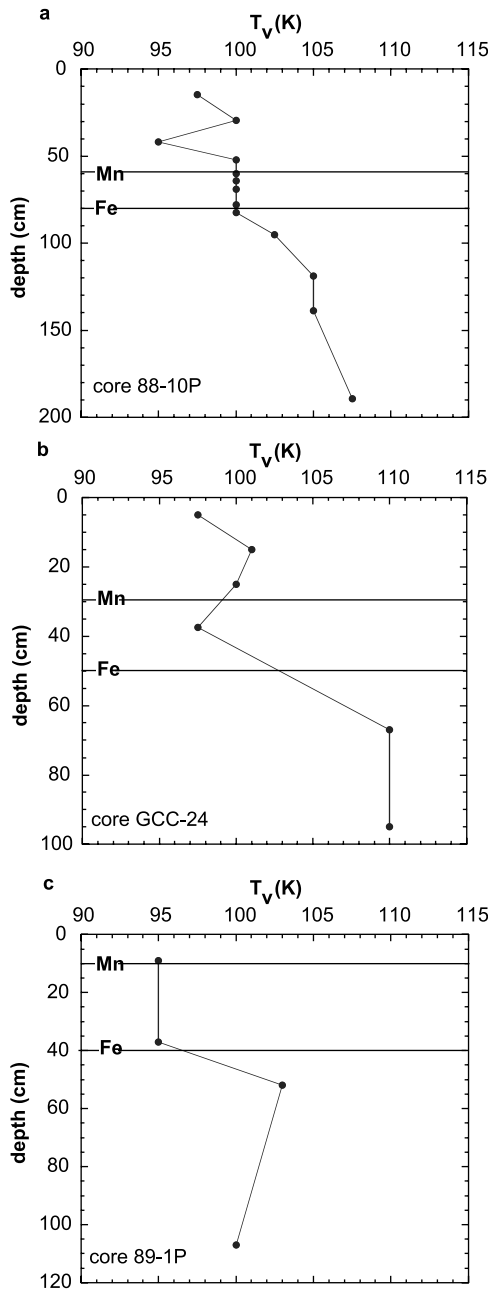
were observed. The samples also show bifurcated FC-ZFC curves below T_v with FC remanence greater than the ZFC remanence indicating the presence of SD magnetite (biogenic or otherwise) and down core changes in the FC-ZFC resulting in two distinct magnetization zones. In core 88-10P samples from 5 to 80 cm depth have FC remanences that are higher than ZFC remanences below 120 K
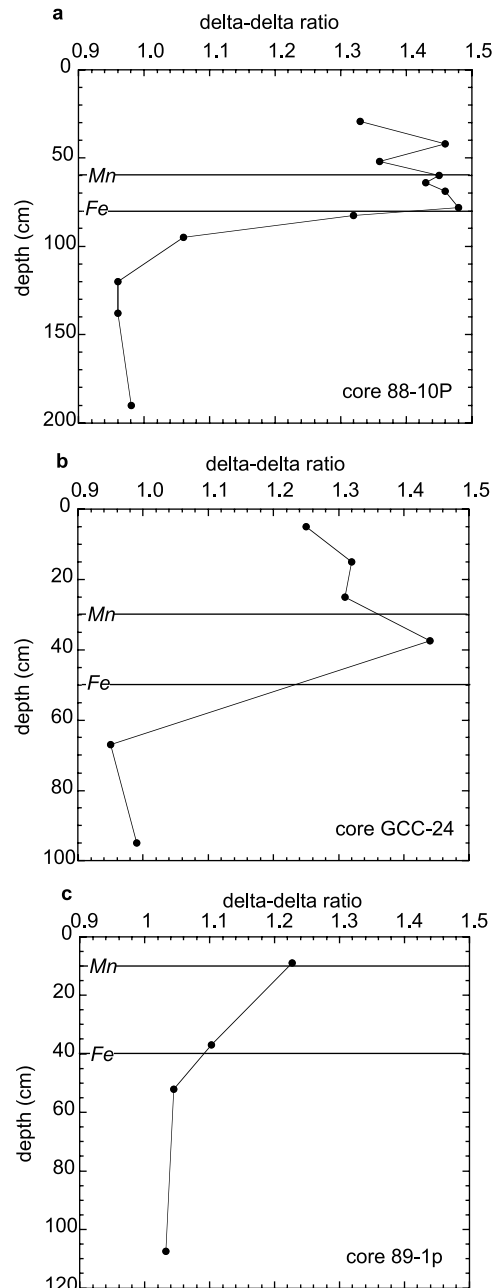
Figure 5. Verwey transition temperature versus depth for (a) core 88-10P, (b) core GCC-24, and (c) core 89-1P. Mn and Fe redox boundaries within the cores are also indicated [*Schwartz et al.*, 1997].

until merging at about 200–300 K (Figures 2–4). At depths below the Fe-redox boundary in each core (Zone II), the high-temperature separation between the FC-ZFC curves is reduced. The high-temperature FC-ZFC divergence is also correlated with estimates of the Verwey transition temperatures defined by the peak of the first temperature derivative of the FC warming curves (dM$_{fc}$/dT). Within Zone I the Verwey transition temperatures are fairly constant in the range of 95–100 K. Near the Fe-redox boundaries and below in Zone II, T$_v$ increases slightly to around 100–110 K (Figure 5). In core 88-10p,

the Verwey transition temperature is remarkably uniform between the Mn and Fe redox boundaries.

[13] Variations in δFC/δZFC ratios are observed to show systematic changes with depth. In core 88-10P, samples above 80 cm depth have δFC/δZFC values between 1.3 and 1.5, samples below 80 cm have δFC/δZFC values around 1.0 (Figure 6a). In core GGC-24, high δFC/δZFC values occur between 0 and 40 cm, with a peak in δFC/δZFC of 1.5 at 37.5 cm; samples below this depth have δFC/δZFC near 1 (Figure 6b). In core 89-1P, the δFC/δZFC values also show a decrease with depth but only one sample (at 9 cm depth) has a δFC/δZFC value greater than 1.2 (Figure 6c).

Figure 6. Delta-Delta ratios as a function of depth for (a) core 88-10P, (b) core GCC-24, and (c) core 89-1P. Mn and Fe redox boundaries within these cores are also indicated [*Schwartz et al.*, 1997].
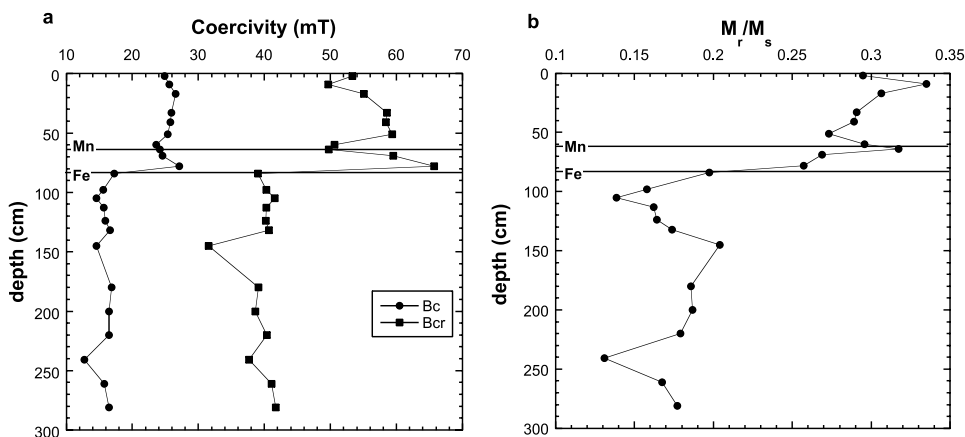
Figure 7. Magnetic hysteresis data for BBOR core 88-10P versus depth. (a) coercivity B_c, and coercivity of remanence B_{cr}, and (b) ratio of saturation remanence to saturation magnetization M_r/M_s. Mn and Fe redox boundaries within these cores are also indicated [*Schwartz et al.*, 1997].

[14] Although complicated by possibly more complex magnetic mineral admixtures, the δFC/δZFC ratios can also be used to estimate an upper limit of the relative volume fraction of SD magnetite chains in these sediments assuming the sediment contains a simple binary mixture of magnetofossil chains and detrital PSD magnetite (see Figure 12 of *Moskowitz et al.* [1993] for details of the model). For samples with δFC/δZFC > 1.0, the δFC/δZFC values indicate that 20% to 60% of the magnetic minerals in these sediments could occur as magnetofossil chains of SD magnetite. In contrast, if the non-magnetofossil magnetic material were composed of either finer-grained SD/PSD maghemite or goethite, then the observed delta-delta ratios would indicate less than a few percent contributions from magnetofossil chains. Nevertheless, in either case, the elevated delta-delta values would still indicate a zone of SD magnetite.

3.2. Hysteresis

[15] All of the hysteresis loops have "normal" shapes, with no evidence of wasp-waisted, pot-bellied, or other anomalous shapes [*Tauxe et al.*, 1996]. Within core 88-10P there are systematic variations of hysteresis parameters with depth. Above 80 cm depth within zone I, coercivity is relatively high (B_c > 20 mT, B_{cr} > 50 mT), with prominent peaks in B_c and B_{cr} observed at 80 cm (Figure 7). The near surface zone of high coercivity also corresponds to a zone of high values of M_r/M_s. Abrupt drops in B_c, B_{cr}, and M_r/M_s occurs below 80 cm depth in Zone II and indicates a coarsening of the median magnetic grain size at the Fe-redox boundary, or demaghemitization [*Smirnov and Tarduno*, 2000].

[16] The samples have tightly grouped M_r/M_s-B_{cr}/B_c values that plot within the PSD region of a Day plot (Figure 8), but depending on depth form two distinct data clusters within core 88-10P that correspond to Zones I and II. Samples from above 80 cm depth have higher M_r/M_s and lower B_{cr}/B_c ratios than do samples from below 80 cm depth (Figure 8). Also plotted in Figure 8 are theoretical hysteresis trends for SD-SPM and SD-MD mixtures from *Dunlop* [2002a, 2002b]. In this case, the SD component can be either biogenic or inorganic because there is very little

difference in M_r/M_s and B_{cr}/B_c values for biogenic versus nonbiogenic SD magnetite [*Moskowitz et al.*, 1993]. Hence hysteresis parameters are not diagnostic for magnetofossils, but are sensitive to SD particles of any origin. Compared with the theoretical results, both sample trends parallel the SD-MD mixing model curve but with the samples from above 80 cm (zone I) displaced closer to the SPM-SD mixing curve. A contribution by ultra fine SPM magnetic minerals with low unblocking temperatures (<100 K) to the
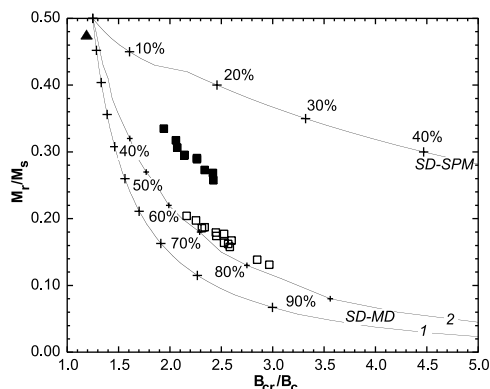
Figure 8. Hysteresis parameters, M_r/M_s and B_{cr}/B_c, plotted on a Day plot. Results from core 88-10P above 80 cm (solid squares), and below 80 cm (open squares) define two clusters. The trend defined by the samples corresponds to that expected for an admixture of MD and SD magnetite. The mixing curves correspond to SD2, 10-nm SPM, and two different MD components given by *Dunlop* [2002a, 2002b]. Curve 1 uses components SD2 and MD2. Curve 2 uses components SD2 and MD data for 15-μm magnetite given by *Dunlop* [2002b]. The percentages along the model curves refer to the volume fraction of the SPM or MD component. The approximate volume fraction for a particular sample can be read off directly from the model curves. The point labeled with a solid triangle corresponds to an average value of M_r/M_s and B_{cr}/B_c for several different types of magnetotactic bacteria [*Moskowitz et al.*, 1993].

88-10P record is possible as indicated by a loss of remanence between 10 and 80 K in the low temperature SIRM results. Using the theoretical results of *Dunlop* [2002a] the volume fraction of the SD component can be estimated from Figure 8. The estimated SD volume fractions based on the hysteresis trends for 88-10P are 45–60% for depths <80 cm, and 20–35% for depths > 80 cm. For the 88-10P section above the Fe-redox boundary, the SD volume fractions estimated from the Day plot agree well with the upper limits of the chain fractions estimated from the low-temperature delta-delta ratios, and support the simple mixing model used to estimate the abundance of bacterial magnetite chains in these sediments.

4. Discussion and Conclusions

[17] The low-temperature remanence measurements from the BBOR site have Verwey transitions, particularly on FC-remanence warming curves, and high $\delta FC/\delta ZFC$ ratios (1.2–1.5) that are together indicative of SD magnetite, possibly aligned within chains produced by magnetotactic bacteria. The zone of high $\delta FC/\delta ZFC$ ratios also corresponds to zones of high ARM, SIRM, and ARM/χ values, and zones of abundant to common magnetosome grains imaged by TEM, as reported by *Schwartz et al.* [1997]. Elevated delta-delta ratios are found within the upper 60–80 cm and occur above or within the oxic-anoxic transition zone (OATZ), marked by the Mn and Fe reduction boundaries. Near the Fe reduction boundary, delta-delta ratios decline (clearly seen in core 88-10P), and below the boundary delta-delta ratios approach 1.0. Elevated delta-delta ratios are also matched by a zone of high B_c, B_{cr}, and M_r/M_s values. In particular the sharp peak at 80 cm (Figure 7) in core 88-10P, is essentially identical to B_c trends obtained from pelagic sediments from the Ontong-Java plateau, where the B_c peak was attributed to the occurrence of SD biogenic magnetite and the abrupt decrease in B_c related to a coarsening of the overall magnetic grain size due to reduction diagenesis and preferential dissolution of the fine-grained fraction [*Tarduno and Wilkison*, 1996; *Tarduno et al.*, 1998]. The 88-10P hysteresis and FC-ZFC data, along with TEM observations [*Schwartz et al.*, 1997] of abundant fine-grained magnetite particles (<100 nm) with shapes and sizes resembling those produced by modern magnetotactic bacteria (Figure 1) are consistent with the occurrence of a significant volume fraction of SD biogenic magnetite (maximum possible amounts of 20–60%) in the near surface sediments above the Fe-redox boundary. Immediately below the redox boundary, magnetofossil abundance declines rapidly as delta-delta ratios approach 1.0, coinciding with the zone where few or no magnetofossils were found with TEM. At the other two BBOR sites, a similar relationship among rock-magnetic indicators of fine-grained biogenic magnetite from low-temperature remanence data, redox boundaries and TEM data is observed.

[18] In contrast to the FC-ZFC magnetization results from BBOR, two previous studies of marine sediments using the delta-delta method to identify magnetofossils produced mixed results due to the possible complicating effects of maghemitization. Pelagic samples from the Ontong-Java plateau (Western Pacific Ocean) showed no pronounced Verwey transitions and inconclusive delta-delta ratios at

depths above the iron redox boundary, even though SD-sized particles with morphologies similar to magnetosomes were identified by TEM [*Smirnov and Tarduno*, 2000]. Additionally, the FC and ZFC remanence curves were divergent all the way to 300 K instead of merging above the Verwey transition, as expected for near-stoichiometric SD magnetite. In another study, sapropel sediments from the eastern Mediterranean Sea again showed no traces of Verwey transitions and divergent FC/ZFC curves to 300 K [*Passier and Dekkers*, 2002]. However, a straightforward calculation of delta-delta ratios in this case showed a stratigraphic variation of delta-delta ratios that correlated elevated values with the location of the modern Fe-redox boundary within the oxidized layer above the sapropel. Although no TEM work was used to identify magnetofossils directly, other magnetic indicators suggest magnetofossils within the unit of elevated delta-delta ratios [*Egli*, 2004; *Passier and Dekkers*, 2002; *Passier et al.*, 2001].

[19] According to *Smirnov and Tarduno* [2000] and *Passier and Dekkers* [2002], the divergence between FC and ZFC warming curves above 120 K is related to the extent of maghemitization of biogenic and detrital magnetite above the Fe-redox boundary. *Smirnov and Tarduno* [2000] attribute the low-temperature behavior to partial maghemitization of PSD magnetite (>100 nm) resulting in the formation of meta-stable SD micromagnetic states during field cooling to 20 K, but multidomain states during zero-field cooling. In this case, the delta ratio would not necessarily provide a proxy record for magnetofossils because the FC/ZFC response would be controlled primarily by the abundance of nonbiogenic PSD sized particles. Maghemitization of the magnetofossil fraction would greatly suppress their FC/ZFC behavior [*Smirnov and Tarduno*, 2000; *Moskowitz et al.*, 1993; *Özdemir et al.*, 1993]. Alternatively, *Passier and Dekkers* [2002] argue that the divergent FC/ZFC behavior is related to a temperature-dependent surface spin disorder effect in SP, SD, and PSD grains composed of a thin shell of maghemite surrounding a core of magnetite. Unlike the *Smirnov and Tarduno* [2000] model, the surface spin disorder model would also affect the magnetofossil population and be enhanced in the fine-grained SPM and SD fraction; hence this may be the reason for the observed stratigraphic distribution of delta-delta ratios in the absence of Verwey transitions.

[20] Variable amounts of high-temperature divergence above the Verwey transition temperatures between the FC and ZFC remanence curves at depths above the Fe-redox boundaries coupled with Verwey transition temperatures near 100 K are observed in all three BBOR cores and suggest possible limited maghemitization of the biogenic magnetite fraction according to the models of *Smirnov and Tarduno* [2000] and *Passier and Dekkers* [2002]. Just below the Fe-redox boundaries, Verwey transition temperatures increase by 5–10 K. This depth trend in Verwey transition temperatures is correlated with the Fe-redox boundaries and is consistent with the reductive dissolution or "demaghemitization" process proposed by *Smirnov and Tarduno* [2000]. However, freeze-dried samples of MTB from pure cultures also show T_v near 100–110 K [*Moskowitz et al.*, 1993; *Weiss et al.*, 2004; *Carter-Stiglitz et al.*, 2004, *Pan et al.*, 2005b], so it is unclear if such depressed values of the Verwey transition temperature from the nominal 120 K

observed for bulk stoichiometric magnetite is by itself an indicator of magnetosome oxidation. Alternatively, goethite, which shows divergent FC-ZFC behavior over the temperature range from 5–300 K [*Guyodo et al.*, 2003], and may be present in the near-surface BBOR sediments based on IRM acquisition and chemical leaching experiments [*Schwartz et al.*, 1997], can also contribute the observed FC-ZFC behavior. Regardless of the exact influences of chemical processes like maghemitization on FC/ZFC magnetizations, the effects of maghemitization appears to be less pervasive on the fossil magnetosome assemblage within the suboxic zone of BBOR sediments, allowing delta-delta ratios to provide information of the depth-distribution of magnetofossils. The results from the BBOR cores show a clear relationship between magnetic indicators of magnetofossils and sediment redox state. Bacterial SD magnetite is abundant and presumably preserved as chains of magnetofossils in shallow sediments above the modern Fe-redox boundaries, and is either absent or no longer in the form of intact chains in sediments below the Fe-redox boundaries. Whether this relationship is due to effects of diagenetic dissolution combined with migration of MTB away from the redox boundary, or is a primary effect of climate-moderated MTB productivity, or is associated with sedimentological changes from carbonate-rich to carbonate-poor sediments, is unclear.

[21] *Schwartz et al.* [1997] observed that in the magnetofossil rich zone (based on TEM observations) in the BBOR sediments low NRM intensities are matched by high values of ARM, SIRM, and ARM/χ. This relationship between magnetization and magnetofossil abundance was interpreted as evidence that the fraction of biogenic magnetite in the form of chains of magnetofossils at the BBOR site was not significantly contributing to the NRM in the sediments, even though the SD size range of magnetofossils would make these particle chains excellent recorders of the geomagnetic field [*Schwartz et al.*, 1997]. One possible explanation why biogenic magnetite might not record the geomagnetic field is that magnetosome chains (as relic cells or chain fragments) electrostatically adhere to clay particles during deposition and are preferentially compacted parallel to bedding, but with semirandom declinations [*Vali and Kirschvink*, 1989; *Schwartz et al.*, 1997]. The remanence that would result from such a process would likely be very weak. Our FC-ZFC results support the conclusions of *Schwartz et al.* [1997] by providing a semiquantitative estimate of magnetofossil abundance from magnetic measurements. The presence of a fraction of biogenic SD material, with an upper limit estimated to be 20–60% on the basis of delta-delta ratios, which makes only a weak contribution to NRM poses difficulties for attempts to estimate geomagnetic field intensities from magnetofossilliferous marine sediments. Such efforts rely on normalization of NRM intensity by another rock-magnetic measure (usually ARM, IRM, or susceptibility) of the amount of magnetic material in the sediment, or by analysis of the NRM and ARM demagnetization spectra (pseudo-Thellier method [*Tauxe et al.*, 1995]). Magnetofossils would make a large contribution to ARM and IRM, but little or no contribution to NRM. Therefore sediments with a significant fraction of magnetofossil chains, possibly bound to clay particles and not

well aligned with the geomagnetic field, would yield underestimates of relative paleointensity. For these sediments additional investigation on possible climatic-related variations in magnetofossil concentration and the contribution these particles make to recording of the geomagnetic field are needed.

[22] Last, our results show that low-temperature delta-delta-ratios have proven to be a viable method for detecting the presence of magnetofossils in the BBOR sediment samples. Owing to their relative ease, and nondestructive nature, these rock-magnetic tests allow assaying many samples for possible magnetofossil contributions. Complications resulting from mixtures of magnetic minerals, magnetic domains states, and oxidation states can all drive the delta-delta ratio below 2, the minimum value observed for pure, fresh cells of magnetotactic bacteria [*Moskowitz et al.*, 1993; *Weiss et al.*, 2004; *Pan et al.*, 2005b]. Nevertheless, at the minimum, delta-delta ratios greater than 1.0 are indicators of SD particles of magnetite. Samples from sediment zones where elevated delta-delta ratios above 1.0 are found can then be selected for closer scrutiny with electron microscopy for possible positive magnetofossil identification.

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