

The identification and biogeochemical interpretation of fossil magnetotactic bacteria

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Abstract

Magnetotactic bacteria, which most commonly live within the oxic-anoxic transition zone (OATZ) of aquatic environments, produce intracellular crystals of magnetic minerals, specifically magnetite or greigite. The crystals cause the bacteria to orient themselves passively with respect to the geomagnetic field and thereby facilitate the bacteria's search for optimal conditions within the sharp chemical gradients of the OATZ. The bacteria may also gain energy from the redox cycling of their crystals.

Because magnetotactic bacteria benefit from their magnetic moments, natural selection has promoted the development of traits that increase the efficiency with which the intracellular crystals impart magnetic moments to cells. These traits also allow crystals produced by magnetotactic bacteria (called magnetofossils when preserved in sediments) to be distinguished from abiogenic particles and particles produced as extracellular byproducts of bacterial metabolism. Magnetofossils are recognizable based on their narrow size and shape distributions, distinctive morphologies with blunt crystal edges, chain arrangement, chemical purity, and crystallographic perfection. This article presents a scheme for rating magnetofossil robustness based on these traits.

The magnetofossil record extends robustly to the Cretaceous and with lesser certainty to the late Archean. Because magnetotactic bacteria predominantly live in the OATZ, the abundance and character of their fossils can reflect environmental changes that alter the chemical stratification of sediments and the water column. The magnetofossil record therefore provides an underutilized archive of paleoenvironmental information. Several studies have demonstrated a relationship between magnetofossil abundance and glacial/interglacial cycles, likely mediated by changes in pore water oxygen levels. More speculatively, a better-developed magnetofossil record might provide constraints on the long-term evolution of marine redox stratification. More work in modern and ancient settings is necessary to explicate the mechanisms linking the abundance and character of magnetofossils to ancient biogeochemistry.

Keywords: bacteria, magnetite, greigite, biomineralization, biogeochemistry

1. Introduction

Traditionally, paleobiology has focused on studying the products of biologically-controlled mineralization (BCM), the process of inducing minerals to precipitate following a template established by organic molecules (Lowenstam, 1981). Such products are clear indications of the existence and nature of past life. A fossil shell, for instance, is an unequivocal biosignature that conveys information about the paleoenvironment of its formation and hints to the evolutionary complexity of the organism that created it. BCM is rare, however, in microbes. Thus, the study of ancient microbes usually relies upon alternative techniques, each with distinctive strengths and weaknesses: techniques such as the study of stromatolites and carbonaceous microfossils, the interpretation of organic biomarker compounds and isotopic signatures, and the phylogenetic analysis of genomic data.

Though many prokaryotes precipitate carbonate, sulfide, or oxide minerals as extracellular metabolic byproducts, magnetotactic bacteria are among the few prokaryotes to engage in BCM (Blakemore, 1975). These bacteria are defined by the ability to precipitate intracellular crystals of ferrimagnetic minerals, specifically magnetite and greigite, and have been found from several divisions of the Proteobacteria (DeLong et al., 1993; Maratea and Blakemore, 1981; Simmons et al., 2004) and from the Nitrospira (Spring et al., 1993; Spring and Schleifer, 1995). Like fossil shells, bacterial magnetite and greigite bear the signs of natural selection's optimizing influence. They can therefore be identified in sediments, where they are given the name magnetofossils. Like the presence of more

conventional fossils, the presence of magnetofossils reflects environmental conditions, specifically conditions that facilitate magnetotactic bacteria growth and magnetofossil preservation. Magnetofossils are therefore a largely untapped proxy for ancient biogeochemistry.

2. Ecology of magnetotactic bacteria

2.1. *Magnetotaxis and Redox Zonation*

Magnetotactic bacteria produce membrane-bound magnetite or greigite crystals within vesicles called magnetosomes (Bazylinski and Frankel, 2004; Gorby et al., 1988; Komeili et al., 2006; Komeili et al., 2004; Matsunaga and Okamura, 2003).¹ The crystals provide the bacteria with a net magnetic moment, which they employ for magnetotaxis, movement directed by the local magnetic field. Many magnetotactic bacteria grow preferentially under specific, narrow redox conditions (Figure 1). Magnetite producers are often microaerophiles or nitrate-reducers found in the suboxic conditions of the oxic-anoxic transition zone (OATZ) (Bazylinski and Moskowitz, 1997). Simmons et al. (2004) found that, in Salt Pond, Massachusetts, magnetite producers were particularly concentrated at the top of the OATZ, where oxygen diffusing from above and iron diffusing from below produce a peak in particulate Fe(III) abundance. There are exceptions to this typical distribution, however. Some magnetite producers can grow under aerobic conditions (e.g. Schüler and Baeuerlein, 1998), although they do not produce magnetite at high oxygen levels. At least one magnetite producer, *Desulfovibrio*

¹ Whether the magnetosomes are invaginations of the cytoplasmic membrane or true organelles is a matter of current debate (Kobayashi et al., 2006; Komeili et al., 2006).

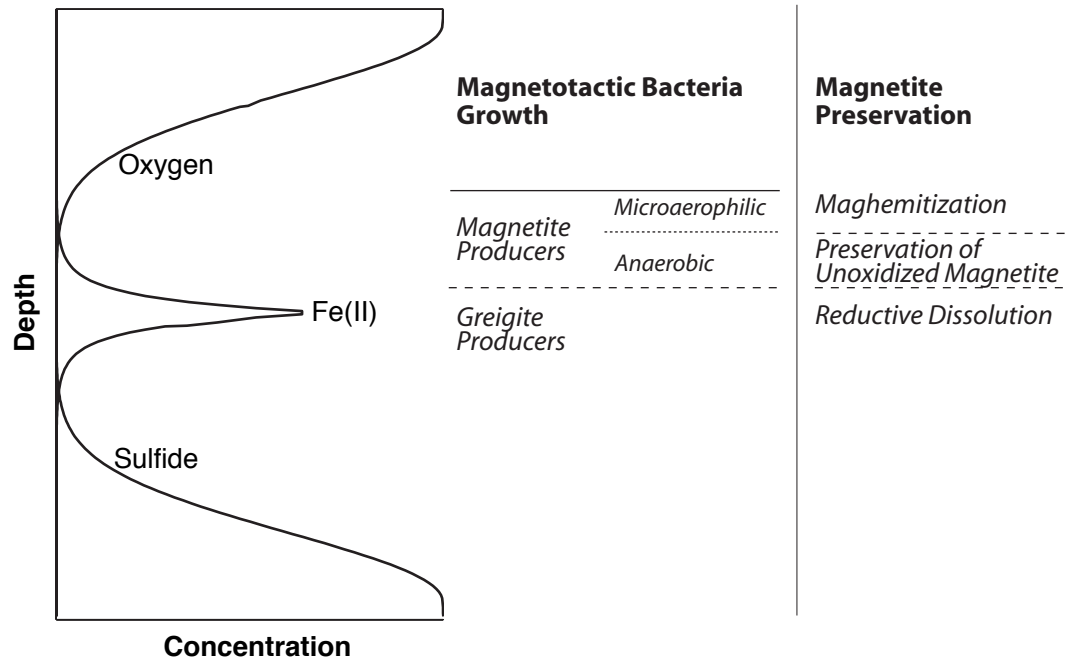


Figure 1: Schematic representation of chemical gradients, typical optimal growth positions of different types of magnetotactic bacteria, and typical diagenetic fates of magnetite. Redox gradients can exist over scales from millimeters to meters.

magneticus RS-1, is a strictly anaerobic sulfate reducing bacterium (Sakaguchi et al., 2002; Sakaguchi et al., 1993), although it is only weakly magnetotactic and may use its magnetosomes for an alternate purpose (Pósfai et al., 2006).

Greigite producers prefer more reduced conditions and are likely strictly anaerobic sulfate reducers (DeLong et al., 1993). Simmons et al. (2004) found that greigite-producing multicellular magnetotactic prokaryotes (MMPs) grew in greatest abundance near the dissolved Fe(II) concentration peak at the base of the OATZ, while other greigite producers grew in deeper, more sulfidic waters. One sulfate-reducing greigite bacterium, found in microbial mats associated with methane-seep carbonate concretions in the Black Sea, is a member of a syntrophic partnership engaged in anaerobic oxidation of methane (Reitner et al., 2005). A

magnetotactic bacterium found in Pettaquamscutt River Estuary, Rhode Island, produces both greigite and magnetite, with a greater proportion of greigite particles produced under more reducing conditions (Bazylinski et al., 1995).

In environments with sharp redox gradients, magnetotaxis likely provides magnetotactic bacteria with a selective advantage by allowing them to search in one dimension instead of in three dimensions for optimal geochemical conditions (Kirschvink, 1980). The cells' magnetic moment causes them to align passively with the local magnetic field. Redox gradients are often nearly vertical, and, except at the geomagnetic equator, the geomagnetic field has a vertical component. For cells with moments $> 10^{-15}$ Am², equivalent to that produced by ~17 cubic magnetite crystals with 50 nm edge lengths, >90% of the cell's velocity is directed along

magnetic field lines (Frankel and Blakemore, 1989). However, because other gradient organisms thrive in spite of performing three-dimensional biased random walks to find optimal conditions, additional functions for the magnetosomes have been proposed, including iron storage (Chang and Kirschvink, 1989) and energy storage (Vali and Kirschvink, 1991). The discovery of membrane-bound iron oxide inclusions in the non-magnetotactic, iron-reducing bacterium *Shewanella putrefaciens* (Glasauer et al., 2002) lends credence to these suggestions.

2.2. Magnetotaxis as a way to short-circuit diffusion

For most organisms living at sharp redox gradients, metabolism is limited by the diffusive fluxes of nutrients, but, as reviewed by Schulz and Jørgensen (2001), several species of large colorless sulfur bacteria have found ways of bypassing diffusive limitations. These microaerophilic or nitrate-reducing organisms employ two distinctive strategies: (1) overcoming diffusive limitation of electron donors and acceptors through various approaches to motility, and (2) storage of intracellular electron donor and acceptor reserves as a buffer against external variability. *Thioploca*, for instance, forms elevator-like sheaths many centimeters long, within which filaments swim up and down (Jørgensen and Gallardo, 1999). The sheaths provide it with direct paths between electron-donor rich and electron-acceptor rich environments. *Thioploca* can accumulate nitrate in storage vacuoles at concentrations as high as 0.5 M when at the more oxidized end of their shafts, then use the nitrate to oxidize sulfide when at the more reduced end. Conversely, they can also partially oxidize sulfide to form elemental sulfur granules as an electron donor reserve.

Magnetotaxis performs a function analogous to that of the sheaths of *Thioploca*: namely, enabling the magnetotactic bacteria to swim rapidly and directly between electron donor rich and electron acceptor rich regions. Moreover, as in the colorless sulfur bacteria, sulfur globules have been found in a number of magnetotactic bacteria (Cox, 2002; Moench, 1988; Spring et al., 1993). As Spring et al. (1993) suggested, these globules may act as electron donor reserves. Some magnetotactic bacteria also contain additional energy storage compounds, such as polyphosphate granules and polyhydroxyalkanoates (Keim et al., 2005).

Indeed, magnetosome crystals themselves may act as intracellular storage batteries, becoming partially oxidized while the bacterium is in oxidizing waters and reduced back to stoichiometric magnetite while the bacterium is in reducing waters (Vali and Kirschvink, 1991). Thermodynamic and growth rate calculations indicate that such a pathway is a feasible supplementary metabolism at the centimeter and sub-centimeter length scales characteristic of sedimentary redox zonation (Kopp, 2007). If correct, this magnetosome battery hypothesis would explain why magnetotactic bacteria live predominantly near sharp redox gradients and why some bacteria (e.g., Spring et al., 1993) produce many more magnetosomes than are necessary for magnetotaxis. It also suggests that magnetotaxis might have been an evolutionary exaptation, a metabolic pathway adapted for sensitivity to the geomagnetic field after its initial evolution.

3. Traits and identification techniques for magnetotactic bacteria

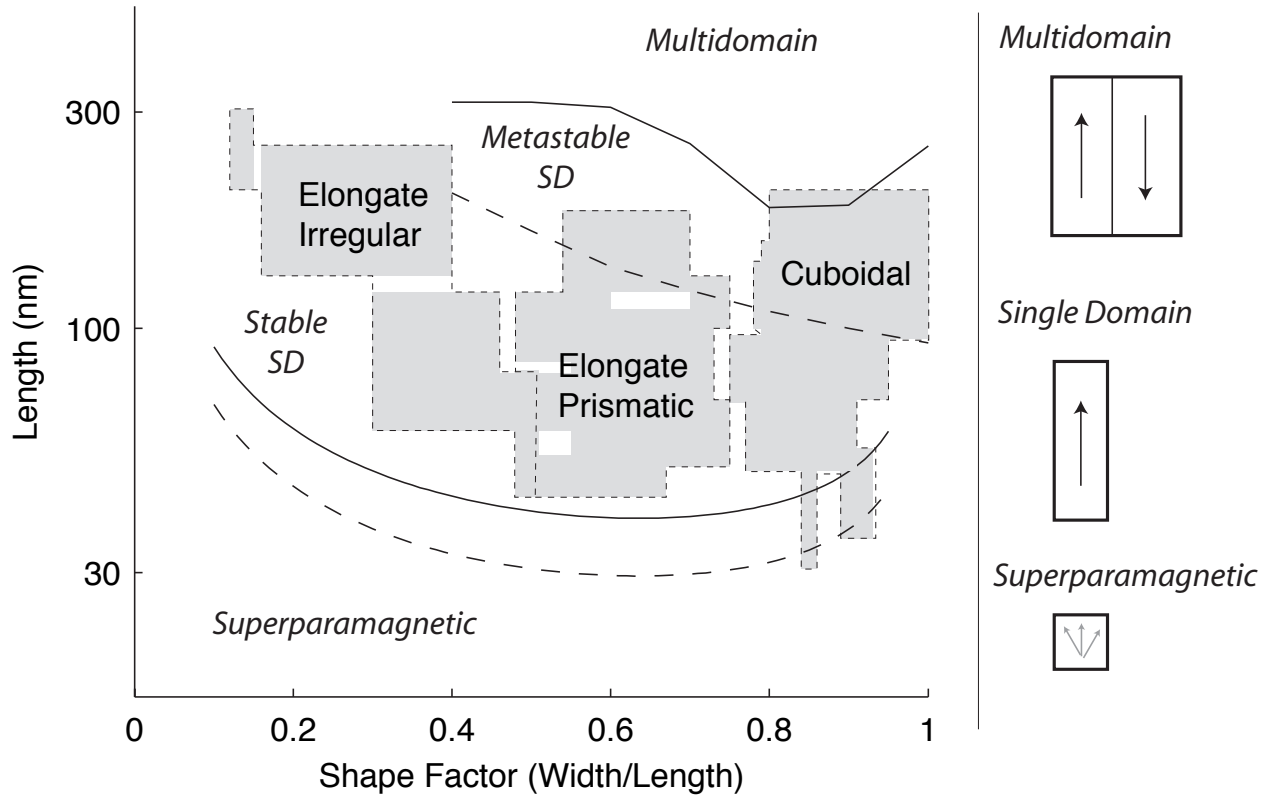


Figure 2: Single domain stability field of magnetite as a function of shape factor (width/length ratio) and length. Diagrams on the right schematically represent the arrangement of magnetic moments in two domain, single domain, and superparamagnetic particles. The lower, SD/superparamagnetic boundary is determined for rectangular parallelepipeds with unblocking times of 100 s (dashed line) and 4.5 Gy (solid line) following Butler and Banerjee (1975) and Diaz-Ricci and Kirschvink (1992). Because the calculation ignores magnetocrystalline anisotropy, it overestimates the minimum SD length at shape factors close to 1. The dashed upper boundary of the stable SD field and the solid upper boundary of the metastable SD field are taken from the micromagnetic models of Witt et al. (2005) for characteristic magnetosome crystal shapes. Shaded regions mark size and shape of crystals from magnetotactic bacteria (Arató et al., 2005; Bazylinski et al., 1995; Devouard et al., 1998; Farina et al., 1994; Meldrum et al., 1993a; Meldrum et al., 1993b; Moench, 1988; Sakaguchi et al., 1993; Thornhill et al., 1994; Vali and Kirschvink, 1991).

3.1. The fingerprint of natural selection

In the modern world, Fe is often a scarce nutrient, its availability limited by its insolubility under oxic conditions. Because natural selection has not eliminated magnetosome production, magnetotactic bacteria must gain some adaptive advantage from the sequestration of this precious resource in magnetosomes. Natural selection should therefore favor traits that maximize the efficiency with which the bacteria employ Fe. Since magnetotaxis requires that the cells'

magnetic moments are strong enough that the magnetic aligning effect dominates thermal agitation, selection should favor traits that maximize the moment produced per atom of Fe used.

The most fundamental characteristic of biologically controlled mineralization is that it occurs under biological control. Magnetosome crystals are produced within membrane-bound vesicles in a process orchestrated by a mechanism that genetic studies are just starting to reveal (Bazylinski and Frankel, 2004;

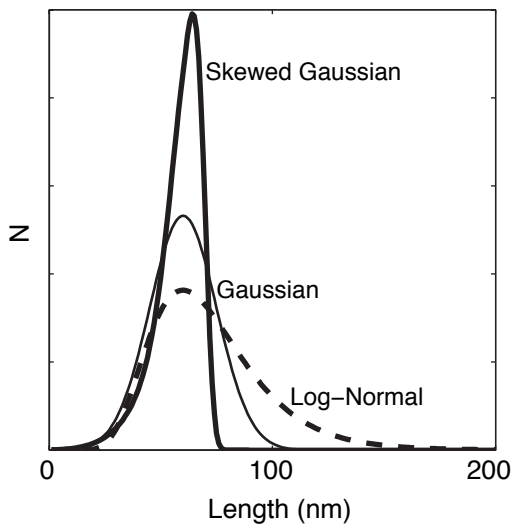


Figure 3: Schematic representation of particle size distributions. Most magnetotactic bacteria produce skewed Gaussian distributions, although some produce Gaussian distributions. Open system chemical growth processes give rise to log-normal distributions.

Komeili et al., 2006; Komeili et al., 2004; Matsunaga and Okamura, 2003; Scheffel et al., 2006). Biochemical regulation allows magnetotactic bacteria to produce crystals with three broad categories of adaptive traits: (1) narrow size and shape distributions, (2) chain arrangement, and (3) chemical purity and crystallographic perfection. Several aspects of these traits were previously discussed by Thomas-Keprta et al. (2000). Some of these traits can be partially assessed at a bulk level through the techniques of rock magnetism and ferromagnetic resonance (FMR) spectroscopy (e.g., Kopp et al., 2006b), while others traits require detailed electron microscopy to identify.

3.2. Size and Shape Distributions

Magnetosome crystals typically exhibit species-specific, narrow distributions of size and shape factor (length/width ratio) (e.g.

Arató et al., 2005; Devouard et al., 1998; Kirschvink and Lowenstam, 1979). Almost all magnetotactic bacteria produce crystals that, at least in the arrangement that naturally occurs in the cell, act as single domain (SD) particles (Figure 2). While the moments of smaller, superparamagnetic (SP) particles are buffeted by thermal noise and those of larger, multidomain (MD) particles are reduced by the formation of domains with moments aligned in different directions, in single domain particles the entire crystal contributes to producing a stable net magnetization. Natural selection would predict such an outcome in organisms that are capable of controlling the microenvironment in which the crystals form and that gain a selective advantage from their magnetic moment.

Whereas open system chemical growth processes lead to log-normal size distributions, magnetotactic bacteria produce distributions with sharper cutoffs at larger sizes. Cultured bacteria generally produce negatively skewed crystal size distributions, although a few bacteria produce Gaussian size distributions (Arató et al., 2005; Devouard et al., 1998; Pósfai et al., 2001) (Figure 3).

Common magnetosome magnetite morphologies include equidimensional cubo-octahedra, elongate hexaoctahedral prisms, and irregular and elongate tooth, bullet (Thornhill et al., 1994), and arrowhead (Bazylinski et al., 1995) shapes (Figure 4), while common magnetosome greigite morphologies include equidimensional cubo-octahedra and elongate rectangular prisms (Bazylinski et al., 1994). (Cubo-octahedra are frequently labeled as “cuboidal” and elongate hexaoctahedra are frequently labeled as “prismatic,” a convention we adopt for linguistic simplicity. In the literature, where crystals have not been examined closely, cubo-octahedra have sometimes been identified as cubic or

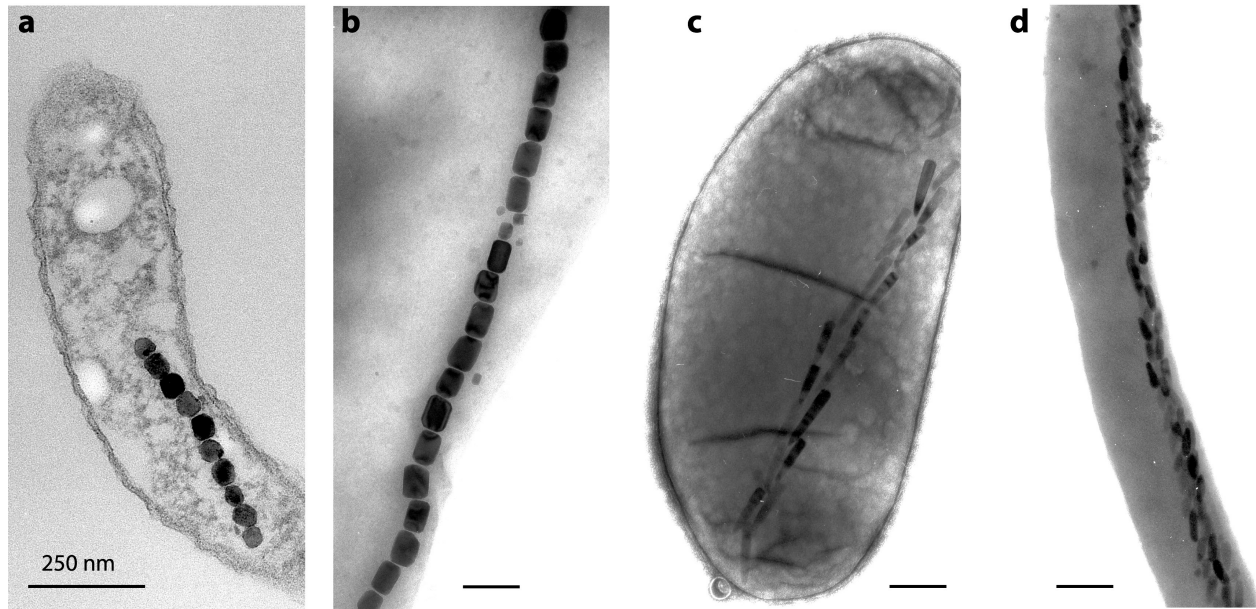


Figure 4: TEM images of magnetite-producing magnetotactic bacteria exhibiting different magnetosome crystal morphologies. (a) Cubooctahedral magnetite in laboratory-grown *Magnetospirillum magnetotacticum* MS-1, (b) hexaoctahedral prismatic magnetite from bacteria living in the sediments of Lake Ammersee, Germany, (c-d) irregular elongate magnetite from bacteria living in the sediments of Lake Chiemsee, Germany. Scale bar is 250 nm in all images. Images courtesy A. Kobayashi (a) and H. Vali (b-d).

octahedral.) The characteristic magnetosome crystal shapes have less sharp edges than do equidimensional octahedral or rectangular parallelepipeds. This ‘rounding’ reduces the outward warping of magnetization at the crystal ends, which produces magnetic ‘flower’ structures in straight-edged particles (Kirschvink, 2001; Witt et al., 2005). It thereby extends the size to which single-domain crystals can grow (Witt et al., 2005). Because the bending of magnetization in flower structures reduces net crystal magnetization, the elimination of sharp edges also directly increases the magnetic moment per iron atom (Kirschvink, 2001).

Magnetic anisotropy energy causes the magnetization of a domain to align preferentially in certain crystallographic directions. In SD particles, it therefore controls the particle’s coercivity, the field required to remagnetize the particle (Diaz-

Ricci and Kirschvink, 1992; Kopp et al., 2006a). In equidimensional magnetite and greigite particles, magnetic anisotropy and thus coercivity are controlled by the inherent magnetocrystalline anisotropy. In stoichiometric magnetite, magnetocrystalline anisotropy leads to room-temperature bulk coercivities of ~15 mT. Increasing the anisotropy of a particle increases coercivity and permits larger particles to remain within the single domain field. Shape anisotropy increasingly governs magnetic anisotropy for crystals with width-to-length ratios less than ~0.9. A 50 nm long magnetite particle with a width-to-length ratio of 0.5, for instance, has a room-temperature bulk coercivity of ~50 mT. At 0 K, an infinitely long magnetite rod would have a bulk coercivity of ~150 mT, the maximum possible for magnetite.

In magnetotactic bacteria with elongate magnetite particles, the crystals are typically

elongated along a [111] axis (but for exceptions see Mann et al., 1987; Taylor and Barry, 2004; Taylor et al., 2001; Vali and Kirschvink, 1991). Because [111] axes are the magnetocrystalline easy axes, this choice of axis causes the magnetocrystalline anisotropy to enhance the shape anisotropy produced by elongation. Greigite crystals are often elongated along a [100] axis (Bazylinski et al.,

1995; Heywood et al., 1990; Pósfai et al., 1998), fueling speculation that [100] axes are the greigite magnetocrystalline easy axes (Bazylinski and Moskowitz, 1997).

The most direct method of assessing size and shape factor distributions, but also the most labor-intensive and subject to sampling biases, involves direct measurement of particles in magnetic extracts under

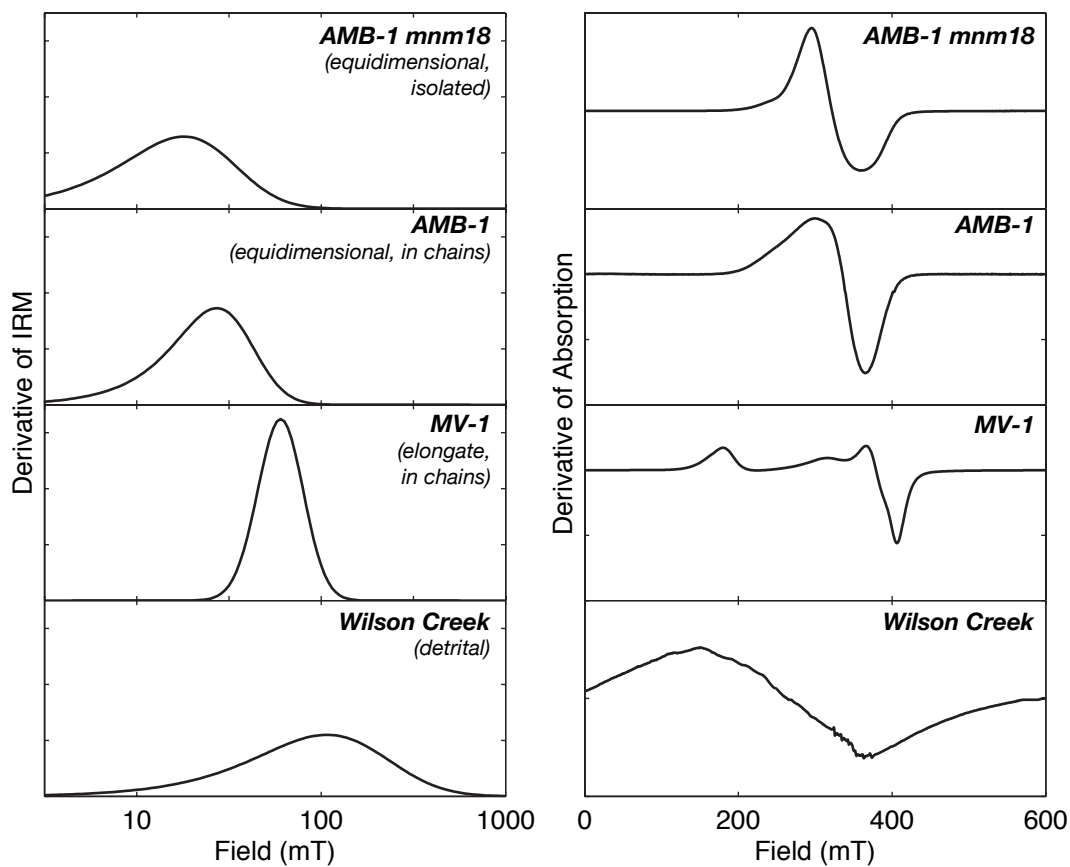


Figure 5: Example coercivity spectra (left) and FMR spectra (right). From top to bottom, spectra are shown for *AMB-1* mutant *mnm18* (which predominantly produces isolated particles of cuboidal magnetite), wildtype *AMB-1* (which produces chains of cuboidal magnetite), *MV-1* (which produces chains of elongate prismatic magnetite), and detrital magnetic particles from the Wilson Creek Formation of Mono Basin, California. Comparison of the wildtype *AMB-1* and *MV-1* coercivity spectra demonstrates the effect of elongation on particle coercivity, while comparison of the bacterial and detrital coercivity spectra illustrates the narrower coercivity distribution of biologically controlled magnetite. Whereas magnetocrystalline anisotropy causes the FMR spectrum of *mnm18* to be slightly asymmetric in the high field direction, the stronger anisotropy produced by particle elongation and chain arrangement causes the spectrum of *MV-1* to be much broader and strongly low-field extended. Wildtype *AMB-1*, with anisotropy dominated by chain arrangement, is more mildly low-field extended. The detrital magnetic particles of the Wilson Creek sediments, being more heterogeneous in size, shape, and arrangement, produce an extremely broad but fairly symmetric spectrum.

transmission electron microscopy (TEM). A variety of magnetic techniques allow the construction of coercivity spectra of samples, which are functions of both size and shape. The characteristically narrow distributions of biologically controlled magnetic minerals can sometimes be observed in the dispersion of the coercivity (Egli, 2004) (Figure 5). Anisotropy fields play a major role in controlling the width and asymmetry of FMR spectra, which can be used to identify elongate magnetic particles as well as the narrow distributions characteristic of biological control (Kopp et al., 2006a; Kopp et al., 2006b) (Figure 5).

3.3. Chain Arrangement

In most magnetotactic bacteria, the magnetosomes are maintained aligned in one or more chains by a cytoskeletal structure (Komeili et al., 2006), an organic sheath (Kobayashi et al., 2006), and anchoring proteins (Scheffel et al., 2006). The chain axis is typically aligned with the easy axes of the individual particles (Dunin-Borkowski et al., 2001). The chain serves the same basic physical function as particle elongation: it increases the stability of the state in which particle moments are aligned along the chain axis by enhancing magnetic anisotropy. Whereas mutant AMB-1 producing isolated particles of nearly equidimensional magnetite has a room-temperature bulk coercivity of ~13 mT, AMB-1 producing short chains of equidimensional particles has a room-temperature coercivity of ~25 mT (Kopp et al., 2006a).

Linear strings of magnetic particles can also be produced by physical processes (Kopp et al., 2006b). Biologically produced chains are distinguished by being composed of particles from a size and shape factor distribution characteristic of magnetotactic

bacteria and having few branch points. If the particle size distribution of the magnetic crystals is known, sampling statistics can assess the probability that the crystals within a chain are not a random sub-sample of the distribution. Chains with these traits are highly suggestive of a biological origin. Techniques for identifying these chains are therefore key to developing the fossil record of magnetotactic bacteria.

TEM imaging of magnetic extracts is currently the only technique for producing high-resolution images of chains. Magnetic extraction, however, involves disrupting the matrix containing the magnetic particles, and the extraction process provides a good mechanism for physically forming strings of particles. Thus, short chains found in extracts are ambiguous as to their origins; only long chains with characteristic magnetofossil traits are indicative of biological origin. Scanning electron microscopy (SEM) permits imaging particles in situ (Friedmann et al., 2001; Maher et al., 1999) but lacks the resolution needed to characterize particle shape and so is only useful for magnetofossil identification when combined with TEM of extracts (e.g., Figure 6, c-d).

For unoxidized magnetite, the Moskowitz test, which compares the thermal demagnetization behavior of low temperature saturation remanence magnetizations acquired after cooling in zero field and that acquired after cooling in a strong field, can also indicate the presence of chains (Moskowitz et al., 1993; Weiss et al., 2004b). At the Verwey transition, which occurs at 125 K in stoichiometric magnetite, magnetite shifts from having cubic symmetry at higher temperatures to having uniaxial symmetry at lower temperatures. Magnetite chains exhibit relatively greater demagnetization of the field-cooled remanence upon warming through the Verwey transition

than do other arrangements of magnetite. The effect likely results from the influence of the chain structure on the selection of an elongation axis during cooling below the Verwey temperature (Moskowitz et al., 1993). However, the physics underlying this observation (Carter-Stiglitz et al., 2002; Carter-Stiglitz et al., 2004) is only partially understood, and the test is subject to false negatives generated by limited particle oxidation.

Ferromagnetic resonance spectroscopy is sensitive to the magnetic anisotropy produced by particle chains as well as the homogeneity that distinguishes biological chains from physical strings (Kopp et al., 2006a; Kopp et al., 2006b) (Figure 5). It is rapid and insensitive to particle oxidation, and thus is currently the best bulk technique capable of screening samples for the presence of likely magnetofossil chains.

3.4. Chemical Purity and Crystallographic Perfection

In general, magnetite produced by magnetotactic bacteria is nearly pure iron oxide, with concentrations of trace elements like Ti, Al, and Cr significantly lower than in most abiotic magnetite (Thomas-Keprta et al., 2000). Such purity is expected based both on selection for efficiency in the use of Fe, as trace elements reduce the magnetic moment of magnetite particles, and on the extensive use of pure iron as a specific metal cofactor in numerous enzymatic systems. Some bacteria do produce magnetite that is slightly oxidized; the Verwey transition can be reduced from the 125 K of stoichiometric magnetite to temperatures as low as ~100 K, which indicates up to 0.4% cation depletion (Kopp et al., 2006a; Moskowitz et al., 1993). Chemical

purity can be assessed most accurately by analytical techniques coupled to TEM, such as energy dispersive X-ray spectroscopy (EDS), but can also be assessed in magnetite at a bulk level from shifts in the Verwey transition temperature and Néel temperature. However, these transition temperatures are also affected by diagenetic oxidation.

With the exception of twinning along the [111] easy axis, crystallographic defects also reduce the magnetic moment of magnetite particles. Thus, crystallographic defects are rare in magnetosome magnetite (Devouard et al., 1998). The absence of such defects can be assessed only by high-resolution TEM.

Greigite magnetosome crystals are often less strictly controlled than magnetite crystals, both chemically and crystallographically. Some greigite-producers can incorporate up to ~10 atomic percent Cu into their magnetosome crystals (Bazylinski et al., 1993; Pósfai et al., 1998). Greigite magnetosome crystals also commonly exhibit planar defects along (222)-type planes, believed to be associated with the conversion of mackinawite into greigite (Pósfai et al., 1998). These differences suggest that greigite precipitation by magnetotactic bacteria may be less regulated than magnetite precipitation and could hinder identification of greigite magnetofossils.

3.5. Scoring magnetofossil identifications

We suggest the following scheme for rating possible magnetofossils:

Context and Robustness: Magnetofossil identifications are more reliable if the samples under consideration come from an understood stratigraphic, geochemical, and paleomagnetic context or were collected as part of a broader study aimed at understanding this context.

Magnetofossil reports from localities lacking robust paleomagnetic data should be viewed cautiously, as they are more likely to have undergone diagenetic or metamorphic processes that altered primary magnetic carriers, including any possible magnetofossils. Our suggested criteria for considering a magnetofossil identification to be robust are given in Table 1. Table 2 lists reports of pre-Quaternary magnetofossils from samples collected with contextual information, while Table 3 lists reports of pre-Quaternary magnetofossils from grab samples lacking such information. For samples where paleomagnetic information is available, we also report a paleomagnetic quality (PQ) score follow the criterion of van der Voo (1990). PQ ranges from zero to seven, where samples with $PQ \geq 4$ are considered robust. For demonstrably remagnetized units, PQ is listed as “*”.

Single domain (criterion SD): As a basic requirement, all claims of magnetofossils should be supported by magnetic or electron microscopy evidence indicating the presence of a significant amount of single domain magnetite, maghemite, or greigite.

Size and shape (score S): Beyond the basic single domain criterion, we score the size and shape of particles in a sample based on (1) coercivity or FMR spectra indicating narrow distributions of size and shape, (2) TEM evidence for SD particles with truncated edges (cubo-octahedral or hexa-octahedral morphologies, for example), (3) TEM evidence for elongate SD particles (such as hexa-octahedral and irregular elongate particles), and (4) statistical TEM evidence for SD populations with narrow size and shape distributions. Each of these four lines of evidence contributes one point to score S, which ranges from zero to four.

Chains (score C): We grade the quality of chain identification from zero to four. Zero

Table 1: Proposed magnetofossil robustness criteria

| Context | Criteria |
|--|--|
| <i>Environment analogous to younger magnetofossil-bearing environments; Paleomagnetic data robust</i> | $S \geq 3$; or $S \geq 2$ and $C \geq 3$; or $S \geq 2$ and $C \geq 2$ and ChP |
| <i>Environment analogous to younger magnetofossil-bearing environments; Paleomagnetic data not robust</i> | $S \geq 3$ and ChP; or $S \geq 3$ and $C \geq 3$; or $S \geq 3$ and $C \geq 2$ and ChP |
| <i>Environment analogous to younger magnetofossil-bearing environment; Sediments have undergone burial metamorphism or paleomagnetic data remagnetized</i> | $S = 4$ and ChP; or $S \geq 3$ and $C \geq 3$ and ChP; or $S \geq 3$ and $C \geq 2$ and ChP and CrP |
| <i>Unique environment</i> | $S = 4$ and $C \geq 3$ and ChP and CrP |

indicates the absence of any evidence for chains, while one indicates that either SEM or low-temperature thermal demagnetization indicates the presence of chains. Two indicates either (a) that FMR indicates the presence of chains or (b) that short chains of ambiguous origin were imaged in the TEM of magnetic extracts. Three indicates either (a) the TEM identification of short chains and FMR data indicating that they are a significant, in situ component of the sample, or (b) the TEM identification of long chains in magnetic extracts. Four indicates the TEM identification of long chains in magnetic extracts combined with SEM or FMR evidence confirming that the chains occur in situ.

Chemical perfection (criterion ChP): Criterion ChP reflects whether the particles relatively pure and, in particular, Ti-free. Among other techniques, EDS and low-temperature magnetometry can assess purity.

Crystallographic perfection (criterion CrP): Criterion CrP reflects whether high

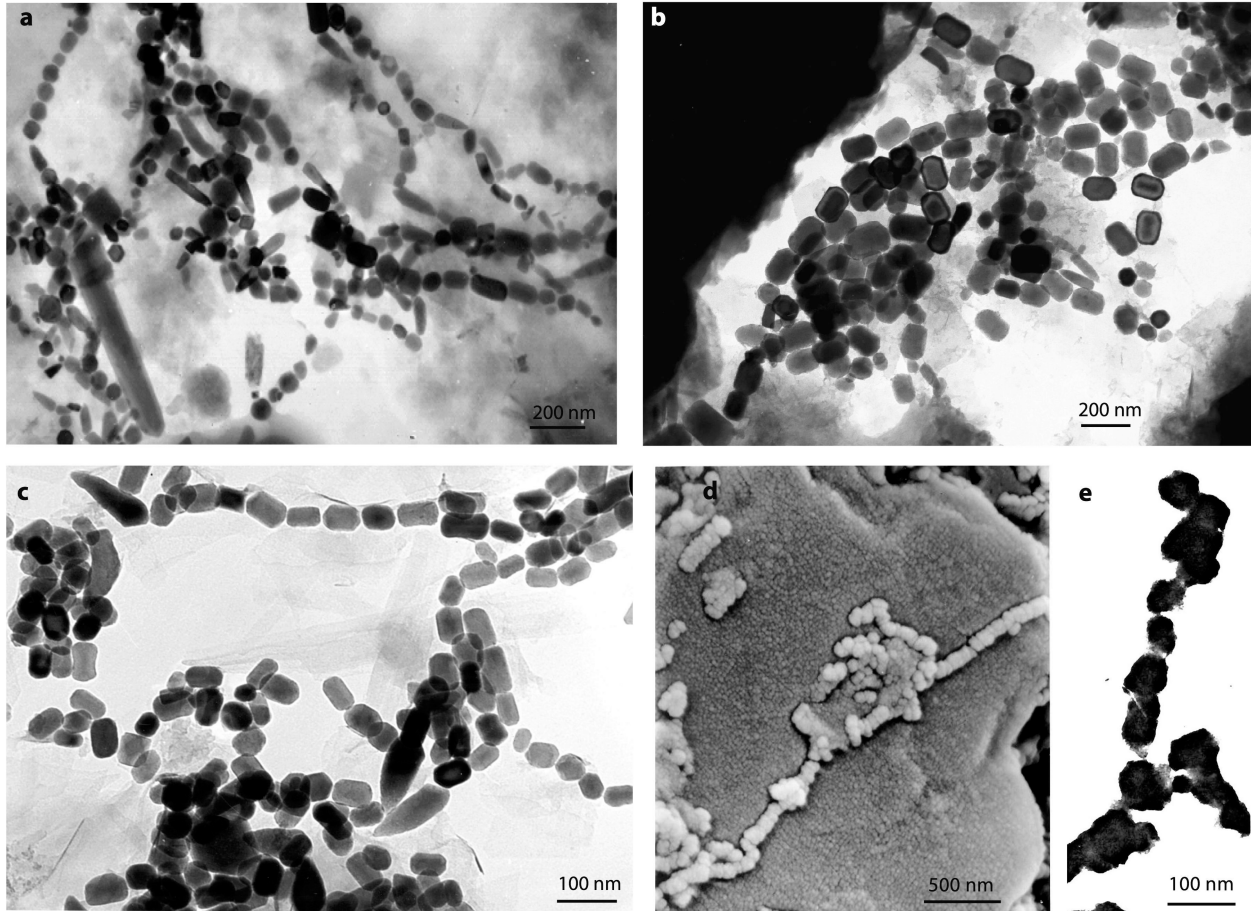


Figure 6: TEM images of magnetofossils. (a) Quaternary magnetofossils in a magnetic extract from nannofossil ooze from Ocean Drilling Project Hole 1006D, Santaren Channel, west of the Great Bahama Bank. Cuboidal, prismatic, and bullet morphologies are visible (scale bar = 200 nm). (b) Prismatic Miocene magnetofossils from clay-rich sediments, DSDP Leg 73, Angola Basin, South Atlantic Ocean (scale bar = 200 nm). (c-d) Cretaceous magnetofossils from chalk beds at Culver Cliff, United Kingdom. (c) shows prismatic and irregular elongate magnetosome morphologies in a magnetic extract from Culver Cliff chalk, with some intact chains of prismatic crystal (scale bar = 100 nm), while (d) shows intact magnetite chains imaged in situ with SEM (scale bar = 500 nm). (e) Putative 1.9 Ga magnetofossils from the Gunflint Formation, Ontario, Canada (scale bar = 100 nm). (Images courtesy M. Hunslow (a, c-d) and H. Vali (b). (e) reproduced from Chang (1988).)

resolution TEM indicates the absence of crystallographic defects other than twinning around the magnetic easy axis.

3.6. Example magnetofossil scores

As an example application of this scoring system, consider the magnetofossils from the Cretaceous chalk deposits of southern England (Table 2 and Figure 6, c-d) (Hounslow

and Maher, 1996; Maher et al., 1999; Montgomery et al., 1998). These magnetofossils were identified in the course of a broad paleomagnetic study that yielded robust results, with a paleomagnetic quality index of 5. Rock magnetic experiments revealed that the magnetic carrier in these samples is a low coercivity phase, such as magnetite, and TEM confirmed that the dominant carrier is SD magnetite. Thus, the samples pass the SD test.

The TEM images show predominantly hexaoctahedral prisms and lesser quantities of cubo-octahedral and bullet-shaped crystals. However, no coercivity or FMR spectra are available, nor have size and shape distributions been compiled from TEM images. Thus, the samples earn points for particles with truncated edges and for elongate SD particles, yielding a S score of 2. TEM images of magnetic extracts show particles in chains, while SEM images confirm that these chains occur in situ, yielding a C score of 4. No analyses have been performed to test the chemical purity or crystallographic perfection of the magnetite particles.

Because the Cretaceous sediments yield robust paleomagnetic data, we would test the magnetofossils against the first set of criteria in Table 1. With a S score of 2 and a C score of 4, we would therefore judge these magnetofossils to be robust.

As another example, consider the putative magnetofossils from the Paleoproterozoic Gunflint Formation of Canada (Table 3 and Figure 6e). These samples are not placed within stratigraphic context at a resolution finer than the formation level. Rock magnetic data indicate the presence of significant SD magnetite, an observation confirmed by TEM. The samples thus pass the SD test. The SD particles present are crudely cubo-octahedral in shape, although they appear to be corroded; one might generously grant a S score of 1. TEM of magnetic extracts reveal short chains of ambiguous origin, yielding a C score of 2. No analyses have tested the chemical purity or crystallographic perfection of the crystals. Regardless of the leniency with which one picks a set of robustness criteria from Table 1, these magnetofossils are not robust.

4. Fossil record of magnetotactic bacteria

4.1. Phanerozoic Magnetofossils

Magnetofossils are a common contributor to sedimentary magnetism in a variety of Quaternary environments (e.g., Figure 6a). Magnetite magnetofossils, often partially oxidized to maghemite, have been found as a major magnetic component of lacustrine (Dearing et al., 1998; Kim et al., 2005; Oldfield et al., 2003; Pan et al., 2005; Peck and King, ; Snowball, 1994), microbial mat (Stolz et al., 1989), hemipelagic (Dinares-Turell et al., 2003; Housen and Moskowicz, 2006; Stolz et al., 1986), pelagic (Hesse, 1994; Hilgenfeldt, 2000; Lean and McCave, 1998; Petersen et al., 1986; Yamazaki and Ioka, 1997; Yamazaki et al., 1991) and carbonate platform (Maloof et al., 2007; McNeill, 1990; McNeill et al., 1988; Sakai and Jige, 2006) sediments. Greigite magnetofossils have not yet been identified in Quaternary sediments.

The pre-Quaternary magnetofossil record, in contrast, is sparse; more magnetofossil-bearing localities have been identified in the Quaternary than in all the rest of Earth history. The most robust pre-Quaternary identifications come from Mesozoic and Cenozoic sediments, although possible magnetofossils have also been found in rocks as old as the late Archean (Tables 2, 3). To date, pre-Quaternary magnetofossils have been identified in carbonate platform sediments, basinal sediments, and continental shelf deposits.

Carbonate platform and atoll sediments. In weakly magnetic Quaternary carbonate sediments, magnetofossils are frequently the primary carrier of syndepositional remanence magnetization, and the limited data available

suggest the same is true of ancient carbonate sediments.

Magnetofossils have been robustly identified in Pliocene platform and atoll sediments. In Pliocene to Recent limestones and dolstones from San Salvador Island, Bahamas, TEM investigation of magnetic extracts reveals that the dominant magnetic particles are cuboidal and bullet-shaped SD magnetite crystals, sometimes arranged in short chains (McNeill et al., 1988). Similarly, in a core of Pliocene limestones and dolstones of the Mururora atoll, Aissaoui et al. (1990) found predominantly cuboidal and prismatic SD magnetite particles, mixed with fragments of lithogenic, multidomain titanomagnetite. Coercivity spectra suggested that the single domain particles dominate the samples' magnetic properties.

Plausible Jurassic (Bathonian-Sinemurian) magnetofossils that marginally fail to meet our robustness criteria have been found in carbonate platform sediments of the Paris and Jura Basins (Belkaaloul and Aissaoui, 1997; Vali et al., 1987). In both basins, single domain magnetite, which constitutes a minor component (~15% in the Paris Basin; "low concentrations" in the Jura) of the bulk magnetic mineralogy, is present in cuboidal and prismatic shapes. Magnetic extracts from the Jura Basin carbonates contain short chains of SD particles (Vali et al., 1987), while the Paris Basin extracts contain pairs and clusters of particles (Belkaaloul and Aissaoui, 1997). The Jura samples were collected without paleomagnetic data, and Vali et al. (1987) do not report any stratigraphic information that would allow their samples to be tied to other samples from the well-studied Northern Calcareous Alps. The Paris Basin carbonates carry robust paleomagnetic data, and despite the dominance by volume of detrital and authigenic MD magnetite,

coercivity data indicate that biogenic SD magnetite is the main remanent magnetization carrier (Belkaaloul and Aissaoui, 1997).

Lower Cambrian (Tommotian) limestones of the Pestrosvet Formation, Siberia Platform, similarly contain plausible magnetofossils that marginally fail to meet our robustness criteria. The sediments are well preserved, having experienced no metamorphism, and provide robust paleomagnetic data (Kirschvink and Rozanov, 1984). Their magnetic properties reflect a dominant role for SD magnetite (Chang et al., 1987), and TEM investigation reveals that the magnetite particles occur in cuboidal and prismatic shapes. At least in extract, the magnetite crystals occasionally form short chains.

Basinal sediments. Most robust reports of Phanerozoic magnetofossils come from basinal sediments, predominantly unlithified sediments from marine drill cores but also including lithified sediments exposed on land.

In Pliocene to Recent clays from the North Pacific, deposited below the lysocline at depths in excess of 5000 m, Yamazaki and Ioka (1997) found that the magnetic mineralogy was a mixture of SD, SP, and PSD magnetite, as well as maghemite and hematite. TEM images revealed that the SD fraction consisted of cuboidal and prismatic crystals, sometimes aligned in chains, while the larger grains were irregularly shaped. Yamazaki and Ioka identified the SD particles as magnetofossils and proposed an aeolian origin for the larger grains.

Yamazaki et al. (1991) examined early Miocene siliceous sediments from similar depths in the central equatorial Pacific Ocean. Rock magnetic measurements indicated that SD magnetite was the dominant stable magnetic component of the sediments, and

Table 2: Magnetofossil reports from pre-Pleistocene localities with stratigraphic context

| PQ | SD | S | C | ChP | CrP | Age | Locality | Setting | Lithology | Depth | Lithified | Sed Rate (m/My) | Source |
|-----|----|---|----|-----|-----|----------------------|--|---------------------|---------------------------------|------------------------|-----------|-----------------|--|
| 4 | + | 2 | 2½ | nd | nd | Pliocene | North Pacific | pelagic basinal | clay | > 5000 m | N | 0.4-2.7 | (Yamazaki and Ioka, 1997) |
| 5 | + | 3 | 2 | nd | nd | Pliocene | San Salvador, Bahamas | carbonate platform | limestone and dolostone | supratidal to euphotic | Y | 11-33 | (McNeill et al., 1988) |
| 5 | + | 3 | 0 | nd | nd | Pliocene | Mururoa Atoll, French Polynesia | carbonate atoll | limestone and dolostone | euphotic | Y | 12-66 | (Aissaoui et al., 1990) |
| 5 | + | 3 | 0 | nd | nd | Miocene | Potamida Clay, Crete | hemipelagic basinal | claystone | ~600-900 m | Y | ~40 | (Chang and Kirschvink, 1985) |
| 5 | + | ½ | 0 | nd | nd | Miocene | Calcare di Base, Sicily | hemipelagic shelf | limestone and evaporite | supratidal to euphotic | Y | ~30 | (Butler et al., 1999) |
| 4 | + | 4 | 0 | nd | nd | Miocene | Central Equatorial Pacific | pelagic basinal | siliceous ooze and clay | 5200-5600 m | N | 2-6 | (Yamazaki et al., 1991) |
| 5/* | + | 4 | 4 | + | + | Eocene to Quaternary | Angola Basin, South Atlantic (DSDP Leg 73) | pelagic basinal | clay, marl, and calcareous ooze | 3800-4600 m | N | 2-9 | (Kirschvink and Chang, 1984; Petersen et al., 1986; Vali and Kirschvink, 1989) |
| nd | + | 4 | 3 | + | nd | Eocene (PETM) | Vincentown Fm., Atlantic Coastal Plain, New Jersey | hemipelagic shelf | claystone | euphotic | Y | ~25-60 | (Kent et al., 2003; Kopp et al., 2007; Lippert and Zachos, 2007) |
| 5 | + | 2 | 4 | nd | nd | Cretaceous | Southern England | pelagic shelf | limestone (chalk) | sub-euphotic shelf | Y | 30-40 | (Hounslow and Maher, 1996; Montgomery et al., 1998) |
| 5 | + | 2 | 0 | + | nd | Jurassic | Paris Basin, France | carbonate platform | limestone | euphotic | Y | ~30 | (Belkaaloul and Aissaoui, 1997) |
| 5 | + | 2 | 2 | nd | nd | Cambrian | Pestrotsvet Formation, Labaia Lena River, Siberia | carbonate platform | limestone | euphotic | Y | 5-50 | (Chang et al., 1987) |

TEM examination revealed crystals with cuboidal, prismatic, and bullet shapes characteristic of magnetofossils.

Several studies have examined magnetofossils in sediments of the Angola Basin, South Atlantic Ocean, collected during Deep Sea Drilling Project (DSDP) Leg 73 at Sites 519, 521, 522, and 523 (Figure 6b) (Chang and Kirschvink, 1984; Kopp et al., 2006b; Petersen et al., 1986; Vali and Kirschvink, 1989). The sediments range in age from Eocene to Quaternary and in composition from nearly pure carbonate ooze to carbonate-poor clays. Magnetic properties indicate that some sediments have a significant amount of MD titanomagnetite, whereas others are dominated by SD magnetite (Petersen et al., 1986), often partially oxidized (Kirschvink and Chang, 1984). Magnetic mineralogy does not correlate with lithology (Petersen et al., 1986). TEM images indicate that SD magnetite occurs in cuboidal, prismatic, and bullet shapes and is arranged in small and long chains, clumps, and meshes (Petersen et al., 1986; Vali and Kirschvink, 1989). Ferromagnetic resonance spectroscopy of Oligocene-Miocene sediments bearing SD magnetite reveals magnetic properties that are dominated by elongate magnetite particles or magnetite aligned in situ in chains (Kopp et al., 2006b). While most of these sediments carry stable remanent magnetizations (Tauxe et al., 1984), some clay-rich Miocene sediments do not, an observation Vali and Kirschvink (1989) linked to TEM observations of aggregation and partial dissolution of magnetofossils.

The first reported identifications of magnetofossils in consolidated sediments came from the Miocene (Tortonian-Messinian) Potamida clays of Crete, which were deposited in the Kastelli sub-basin at depths of ~600-900 m (Meulenkamp, 1979; van Hinsbergen and Meulenkamp, 2006). Initial paleomagnetic

work on the Potamida clays found that the intensity of remanent magnetization decreases in sediments deposited during magnetic reversals (Valet and Laj, 1981). This led Kirschvink (1982) to speculate that magnetofossils carry the magnetization in these sediments and that the decreased magnetization might result from conditions during a reversal that disfavor large populations of magnetotactic bacteria. Chang and Kirschvink (1985) examined magnetic extracts from the clay under TEM and found cuboidal and prismatic SD magnetite, which they interpreted as magnetofossils, as well octahedral magnetite that they interpreted as byproducts of bacterial metabolism.

Miocene marls from Łąka, Poland, deposited under brackish conditions in the foredeep of the Western Carpathians, contain greigite particles with a Gaussian size distribution resembling that of crystals produced by multicellular magnetotactic prokaryotes, which led Pósfai et al. (2001) to speculate that these particles were produced by magnetotactic bacteria. Though inconclusive, this is the only report of possible greigite magnetofossils.

Continental shelf sediments. Continental shelf deposits have been less frequently investigated than carbonate platform or basinal deposits but are the source of the two most robust identifications of magnetofossils in lithified sediments.

Kent et al. (2003) examined cores through Atlantic Coastal Plain sediments of New Jersey that record the Paleocene-Eocene Thermal Maximum (PETM), the ~220 ky initial Eocene global warming event (Rohl et al., 2000). Sediments that precede and follow the PETM in the cores are glauconitic silts and have hysteresis properties suggesting a dominant magnetic contribution from lithogenic input. In contrast, PETM sediments

are kaolinite-rich clays, ~3-10 times more magnetic than underlying and overlying sediments, and have hysteresis properties suggesting that their magnetic mineralogy is dominated by single domain magnetite. The anomalous magnetic properties do not appear to be lithologically controlled, because they persist for the duration of the PETM despite kaolinite concentrations that range in the most proximal core between ~8% and ~50%. Kent et al.'s TEM examination of clay suspensions found only isolated, equidimensional particles of single domain magnetite. They therefore concluded that magnetotactic bacteria had not produced the particles and instead proposed that the particles might have been produced as condensates from an impact ejecta plume.

Kopp et al. (2007) re-examined one of the cores through PETM sediments with FMR to check Kent et al.'s observation that the magnetite occurred as isolated, equidimensional particles. Whereas FMR properties of silty clays deposited above and below the PETM clay indicate a predominantly detrital magnetic mineralogy, the properties of the PETM clay indicate elongate and/or chain magnetite of biogenic origin. Contrary to Kent et al.'s TEM imaging of clay suspensions, TEM imaging of magnetic extracts reveals the presence of abundant cuboidal, prismatic, and bullet-shaped SD magnetite particles, occasionally in chains. An independent rock magnetic and TEM study of another core by Lippert and Zachos (2007) confirms this result. The findings undermine the evidence for an initial Eocene cometary impact but indicate that the Atlantic margin PETM sediments are a rich magnetofossil deposit. The Kopp et al. result is the first FMR-driven discovery of magnetofossils and confirms the utility of FMR as a technique for detecting magnetofossils in ancient sediments.

The oldest robust magnetofossils yet found come from Cretaceous (Coniacian-Campanian) chalk deposits of southern England (Hounslow and Maher, 1996; Maher et al., 1999; Montgomery et al., 1998). These sediments have been the subject of paleomagnetic, rock magnetic, SEM, and TEM studies. Rock magnetic properties indicate that sediment magnetization is dominated by SD magnetite, occasionally with some hematite. The most abundant magnetite particles are prismatic, but cuboidal and bullet shapes, as well as other elongate irregular morphologies, are also present. The crystals often occur in long chains, which have been imaged both in magnetic extracts examined under TEM and in situ adhering to clay particles under SEM (Figure 6, c-d).

Though not a robust magnetofossil identification, Butler et al. (1999) found that the magnetization in the microbial limestones and evaporites of the Miocene (Messinian) Calcare di Base, Sicily, was carried by cubic sub-micron magnetite crystals. They interpreted these particles as magnetosome crystals but did not provide detailed descriptions or images.

4.2. Putative Precambrian Magnetofossils

All putative Precambrian magnetofossils come from carbonate platform sediments, mostly stromatolitic limestones and cherts. This bias is a product of sample selection and does not necessarily reflect the distribution of magnetofossils. The samples studied are all hand samples from outcrops, and the findings are reported with limited contextual information. No Precambrian magnetofossils meet our robustness criteria.

Chang and Kirschvink (1989) found that limestones from the Ediacaran Nama

Table 3: Magnetofossil reports from pre-Pleistocene localities with limited or no stratigraphic context

| SD | S | C | ChP | CrP | Age | Locality | Setting | Lithology | Source |
|----|-----|----|-----|-----|---------------------|-------------------------------------|--------------------|------------------------------|------------------------------|
| + | 2 | 2 | nd | nd | Jurassic | Northern Calcareous Alps, Austria | carbonate platform | limestone | (Vali et al., 1987) |
| + | 1 | 2 | nd | nd | Ediacaran | Nama Group, Namibia | carbonate platform | limestone | (Chang and Kirschvink, 1989) |
| + | 2 | 2 | nd | nd | Neoproterozoic | Bitter Springs Fm., South Australia | carbonate platform | stromatolitic chert | (Chang et al., 1989) |
| + | 2 | 0 | nd | nd | Mesoproterozoic | Vempalle Fm., India | carbonate platform | stromatolitic chert | (Chang et al., 1989) |
| + | 1 | 2 | nd | nd | Paleoproterozoic | Gunflint Fm., Canada | carbonate platform | stromatolitic chert | (Chang et al., 1989) |
| nd | 1 | nd | nd | nd | Late Archean | Tumbiana Fm., Western Australia | carbonate platform | stromatolitic limestone | (Akai et al., 1997) |
| + | 2.5 | 1 | + | + | Noachian? Holocene? | ALH84001 | Mars? Antarctica? | carbonate globules in basalt | many authors (see text) |

Group, Namibia, had coercivity spectra dominated by SD magnetite. TEM images of magnetic extracts show cuboidal magnetite that is sometimes arranged in short chains. As with all rocks bearing putative Precambrian magnetofossils, no paleomagnetic data was collected from the Nama Group samples, but Meert et al. (1997) found that some parts of the Nama Group had been largely remagnetized in the Paleozoic.

Chang et al. (1989) searched for magnetofossils in a number of silicified Proterozoic stromatolites. The magnetic properties of samples from the Neoproterozoic Bitter Springs Formation, Adelaide Basin, South Australia, indicate a mixture of SD and MD magnetite. TEM investigation shows that SD magnetite occurred in octahedral and cuboidal shapes; no chains were found. Samples from the Mesoproterozoic Vempalle Formation, Cuddapah Basin, India, contain predominantly SD magnetite, which occurred in elongate prismatic shape, but again no chains were found. Samples from the

Paleoproterozoic Gunflint Formation, Canada, contain a mixture of SD and MD magnetite, which appears in somewhat corroded cuboidal shapes, sometimes in short chains (Figure 6e).

Akai et al. (1997) conducted no rock magnetic investigations but, based on TEM images alone, identified ~30-50 nm long, elongated, irregular magnetite particles in the acid-insoluble residue of recrystallized and partially silicified stromatolites from the late Archean Meentheena Member, Tumbiana Formation, Fortescue Group, Western Australia. They suggested that these particles were produced by magnetotactic bacteria, although they did not identify chains, examine crystal morphology closely, or report population statistics. Irregular elongate crystals might alternatively be produced by metamorphic alteration of siderite, as has been observed in drill core from lower greenschist grade late Archean siderite of the Ghaap Group, Transvaal Supergroup, South Africa (Tikoo et al., in prep.).

4.3. Putative extraterrestrial magnetofossils

The oldest and most controversial putative magnetofossils come from what is almost certainly the most intensively studied hand sample in the history of the geological sciences, the ~4.5 Ga Martian meteorite ALH84001 (Buseck et al., 2001; Friedmann et al., 2001; Golden et al., 2004; McKay et al., 1996; Thomas-Keprta et al., 2000; Thomas-Keprta et al., 2001; Thomas-Keprta et al., 2002; Weiss et al., 2004b and many others). A complete treatment of the debate over the biogenicity of magnetite particles in ALH84001 requires its own, full-length review and is therefore beyond the scope of this article. Briefly, the magnetic minerals associated with carbonate globules in the basaltic meteorite include stoichiometric SP and SD magnetite, as well as pyrrhotite. There are several different morphological populations of magnetite crystals. ~27% of the magnetite crystals appear chemically pure and assume elongate prismatic shape, ~7% are whiskers with typical inorganic trace impurities, and the remainder take a variety of other shapes. The arguments about biogenicity focus on the prismatic crystals, which Thomas-Keprta et al. (2000) compare to crystals from marine magnetotactic vibrio strain MV-1. Golden et al. (2004) argue that the elongate prismatic crystals from ALH84001 are distinct from those produced by MV-1 and more closely resemble those produced by thermal decomposition of Fe-rich carbonate, a claim disputed by Thomas-Keprta et al. (2004). Friedmann et al. (2001) attempted to identify in situ magnetite chains using SEM with limited success, while Weiss et al. (2004b) used low-temperature magnetometry and FMR spectroscopy to constrain the abundance of any such chains to <~10% of the volume of magnetite. In addition, Kopp and Humayun

(2003) have raised concerns that, even if magnetofossils are present in association with the carbonate globules, they could have been deposited during the period the meteorite was exposed to surface conditions in Antarctica. However, magnetotactic bacteria have not yet been identified in endolithic or psychrophilic communities, either in Antarctica or on Mars.

According to the robustness criteria proposed in this article, the ALH84001 magnetofossils are not robust, and it is unlikely that they will ever be accepted as robust by most researchers. The challenges posed by attempting to identify magnetofossils in a sample that has been stripped of geological context and is not analogous to any known magnetofossil-bearing sample are great. To overcome them would require unambiguous identification of populations of single domain particles with distinctive bacterial morphologies and narrow size and shape distributions, the identification with TEM of long chains of particles in magnetic extracts with biogenic morphologies, and an extensive search for potentially contaminating magnetotactic bacteria populations in Antarctica. The controversy will most likely be resolved only with study of fresh samples collected in context on Mars.

5. Magnetofossil Taphonomy

5.1. Taphonomy of Magnetite Magnetofossils

After a magnetotactic bacterium dies, magnetite particles it produced can suffer three fates during early diagenesis that affect their utility as fossils: oxidation, chain breakup, and reductive dissolution (Figure 1). Due to changes in redox conditions during diagenesis, particles can also experience a combination of these processes. Partial oxidation to

maghemite, driven by the oxidation and subsequent diffusive loss of Fe^{+2} from the crystal structure (Xu et al., 1997), is the least destructive fate, as it does not affect the general morphology of the crystals. While it suppresses the Verwey transition (Özdemir et al., 1993), thereby rendering the Moskowitz chain test (Moskowitz et al., 1993) ineffective, it does not greatly alter ferromagnetic resonance spectra (Weiss et al., 2004a). Although complete oxidation to hematite or goethite destroys magnetofossils, the process is thermodynamically disfavored or kinetically inhibited in many common depositional and early diagenetic settings.

The breakdown of the proteins and lipids that hold the magnetosome crystals within a cell can affect the arrangement of the particles in sediments and potentially destroy the characteristic chain structure. Chains of equidimensional particles, however, will tend to collapse into closed loops that leave the general head-to-tail ($\rightarrow\rightarrow$) dipole arrangement intact (Kobayashi et al., 2006; Kopp et al., 2006b). Elongate particles are more susceptible to the loss of linearity and tend to collapse into side-by-side dipole arrangement (\rightleftharpoons) (Kopp et al., 2006a), but can still be recognized by their distinctive morphologies. At high concentrations, both equidimensional and elongate particles collapse into clumps.

Reductive dissolution is a common fate for fine magnetite particles (e.g., Hilgenfeldt, 2000; Housen and Moskowitz, 2006; Maloof et al., 2007; Tarduno, 1994; Vali and Kirschvink, 1989). Fe(III) is a lower potential electron acceptor than nitrate but a higher potential electron acceptor than sulfate, so once oxygen and nitrate are consumed, organisms turn to Fe(III) , including Fe(III) in magnetite (Dong et al., 2000; Kostka and Nealson, 1995), as an electron acceptor. If sufficient organic matter is available to fuel microbial metabolism, iron-

reducing bacteria will dissolve fine magnetite particles, including magnetofossils. The long-term preservation of magnetofossils thus depends on the race between lithification, which should protect magnetofossils, and the metabolic activities of bacteria living in porewaters. Although little work has been done investigating the mechanisms and rates of processes that protect magnetofossils from dissolution, increased supply of organic carbon does shift the balance toward the iron-reducing bacteria and against preservation.

5.2. *Preservation Potential of Greigite*

Greigite is a metastable mineral and will transform into pyrrhotite or pyrite (Berner, 1967; Morse et al., 1987). Nonetheless, greigite can persist for geologically relevant periods of time in sulfide-limited environments. Greigite was first discovered in Miocene lacustrine sediments of the Tropic Group, Kramers-Four Corner area, California (Skinner et al., 1964), while the oldest greigite described in a published report was formed during early diagenesis in late Cretaceous sediments of the North Slope Basin, Alaska (Reynolds et al., 1994). In a meeting abstract, Niitsuma et al. (2004) described thermomagnetic evidence for greigite from the 2.77 Ga Archean Mt. Roe shale, recovered in an Archean Biosphere Drilling Project core from Western Australia, but Niitsuma et al. (2005) found no unambiguous evidence of greigite under TEM.

6. Magnetofossils as an archive of environmental change

6.1. *Glacial-Interglacial Variations in Magnetofossil Abundance*

Coincident with the discovery of the first sedimentary magnetofossils, Chang and Kirschvink (1984) proposed that magnetofossils might serve as a paleoxygen indicator. At the time, all known magnetotactic bacteria were microaerophiles, so magnetosome magnetite was interpreted as a tracer of the presence of at least small quantities of oxygen. The discovery of the strictly anaerobic, sulfate-reducing, magnetite-producing strain RS-1 (Sakaguchi et al., 1993) provided a counter-example, but subsequent work has nonetheless demonstrated a linkage between magnetofossil abundance and paleoenvironmental conditions.

Several studies have found evidence for a climatic influence on magnetofossil populations. In sediment cores from ~4500 m depth in the Tasman Sea, spanning the last ~780 ky, Hesse (1994) found that the abundance of SD magnetite decreased during discrete events coincident with glacial stages. TEM images indicated the magnetite was of bacterial origin. The change in abundance was not controlled by dilution with carbonate but rather reflected a true change in magnetic mineralogy. During the reduced magnetization events, the ratio of equidimensional magnetofossils to elongate magnetofossils also decreased. Because elongate particles have larger surface area-to-volume ratios than equidimensional particles and therefore should be more subject to reductive dissolution, Hesse speculated that the morphological change reflected differences in growth rather than in preservation. A co-occurring reduction in degree of bioturbation and dulling of sediment color indicated that sediment pore waters were more reduced during glacial intervals. Hesse therefore inferred that pore water oxygen depletion, driven either by a drop in bottom water oxygen levels or an increase in organic carbon flux, disfavored magnetotactic bacterial

growth and that the bacteria producing elongate crystals favored lower oxygen levels than did bacteria producing equidimensional particles.

Based on TEM imaging of deep-sea surface sediments and sediment trap measurements of organic carbon flux at eight sites in the Pacific Ocean, Yamazaki and Kawahata (1998) similarly found that the ratio of equidimensional to elongate magnetofossils was higher in areas with lower organic carbon flux. They observed a parallel relationship between organic carbon and magnetofossil morphology in a core through hemipelagic mud in the West Caroline Basin that extended to the Last Glacial Maximum. In the core, the proportion of magnetofossils with equidimensional shapes increased from ~10% to ~50% during the onset of the present interglacial stage, coincident with a decrease in weight percent organic carbon from ~1.4% to ~0.6%.

In a sediment core from 3556 m depth at Chatham Rise, southwest Pacific Ocean, extending from Oxygen Isotope Stage 6 to the present, Lean and McCave (1998) again identified a decrease in total magnetofossil abundance correlated with increased organic carbon levels during glacial intervals but, in contrast to Hesse (1994) and Yamazaki and Kawahata (1998), observed an increase in the proportion of equidimensional magnetofossils during glacial stages. In a core from 488 m depth through hemipelagic sediments of the Sicily Strait, spanning the last ~1 My, Dinares-Turell et al. (2003) likewise found that the total contribution of magnetofossils to sedimentary magnetism was higher in interglacial stages and lower in glacial stages.

Work on Quaternary sediments thus demonstrates an empirical linkage between redox conditions and magnetofossils, with limited evidence suggesting a greater degree of

control by ecological factors than by taphonomic factors. Because most magnetite producers live in the upper OATZ, redox changes that expand the OATZ should lead to larger populations of magnetotactic bacteria. In sediments, the size and depth of the OATZ is controlled by a balance between the diffusive supply of oxygen from bottom waters and the consumption of oxygen for organic carbon oxidation (van der Loeff, 1990). Assuming the organic carbon supply remains sufficient to deplete oxygen, both increased oxygen supply and decreased organic carbon supply to sediments lead to OATZ expansion. Increased sedimentation rate can also dilute a constant organic carbon supply and similarly expand the OATZ. The relationship between magnetofossil populations and organic carbon content of sediments observed by Hesse (1994) and Lean and McCave (1998) is consistent with this model. Taphonomic processes could produce a similar correlation, because although some magnetite producers live in the lower OATZ and under sulfidic conditions, such conditions promote the reductive dissolution of fine magnetite particles. Comparative microbiological, geochemical, and magnetic studies of marine sediments with different bottom water oxygen levels and organic carbon supplies would further elucidate and help quantify the magnetofossil paleoredox proxy.

6.2. Magnetofossils as a tracer of global oxygen levels

The linkage between paleo-redox conditions and magnetofossil patterns keeps alive Chang and Kirschvink (1984)'s hope that a rich Precambrian magnetofossil record might serve as a tracer of global changes in oxygen level. Canfield (1998) proposed that global ocean redox chemistry went through

three phases: an anoxic phase in the Archean and earliest Proterozoic, an euxinic phase in the middle Proterozoic, and an oxic phase in the late Proterozoic and the Phanerozoic. Magnetofossil populations and preservation would likely differ among the three regimes.

Studies on Quaternary sediments suggest that, in a predominantly oxic ocean, magnetofossil abundance is inversely correlated with organic carbon burial (Hesse, 1994; Lean and McCave, 1998; Yamazaki and Kawahata, 1998). Such studies have been confined to sediments with $\geq \sim 0.4$ wt% organic carbon; under conditions so organic poor that oxygen does not become depleted in the sediments, no significant magnetotactic bacteria population should grow. Greigite magnetofossils might be expected to be more abundant in higher productivity sediments but are in need of study.

Modern stratified water bodies like the Pettaquamscutt River Estuary, Rhode Island (Bazylnski et al., 1995), Salt Pond, Massachusetts (Simmons et al., 2004), and Lake Ely, Pennsylvania (Kim et al., 2005), provide analog environments for a possible ancient euxinic ocean. Whereas in an oxic water body, the OATZ and thus the highest density of magnetotactic bacteria occur in the sediments, in a euxinic water body, the OATZ occurs in the water column. Kim et al. (2005) studied the magnetic properties of sediments from Lake Ely and found that magnetite magnetofossils play a dominant role, with concentrations higher in organic-rich sediments than in organic-poor sediments. However, a steady decline in saturation remanent magnetization from sediments deposited in ~ 1700 CE to sediments deposited in ~ 1300 CE suggests that most of the magnetite may dissolve during diagenesis. Kim et al. did not find signatures of greigite magnetofossils, but cautioned that sulfide

levels in Lake Ely peak at $\sim 60 \mu\text{M}$. In settings like Salt Pond (Simmons et al., 2004), where microbiological studies have found greigite bacteria living in the water column, peak sulfide concentrations exceed $350 \mu\text{M}$. It therefore remains unclear whether marine sediments from a euxinic environment would have magnetofossil populations significantly different from oxic environments, although poor preservation might be expected due to higher organic carbon concentrations and consequent diagenetic dissolution.

Understanding the ecology of magnetotactic bacteria in an anoxic ocean where sulfide concentrations are low and iron cycling drives the biosphere (Walker, 1987) requires a better understanding of the evolution of magnetotaxis than currently exists. In such an ocean, the narrow, suboxic redox environment present in the OATZ today would fill most of the ocean. The navigational value of magnetotaxis for bacteria like the magnetite producers who dwell preferentially at the top of the OATZ would therefore be limited, though the niche occupied by some greigite bacteria at the bottom of the OATZ would still be present where high-sulfur water masses came in contact with high-iron water masses.

Thus, one might expect that the ability to produce magnetite crystals evolved after the advent of oxygenic photosynthesis and that magnetite magnetofossils trace locally oxic environments. RS-1 appears to provide a counterargument; whether it is a valid counterargument depends upon whether RS-1 independently evolved the ability to produce magnetite after it evolved into a strictly anaerobic sulfate reducer. Alternatively, the ability could have evolved in an ancestor with a different metabolism or have been laterally acquired.

The magnetosome battery hypothesis suggests the possibility that the magnetosome

arose first as an iron sulfide-based energy storage mechanism that was later exapted for magnetotaxis and still later adapted for the use of magnetite. Even more speculatively, the primitive, iron sulfide-based magnetosome could be a relict of a protobiotic iron-sulfur world (Wächtershäuser, 1990). Testing these hypotheses requires the construction of a rich magnetofossil record for all of Earth history, as well as a fuller understanding of the diversity of magnetic microbes alive today and the genetic mechanisms underlying biological controlled magnetic mineralization.

7. Summary

The existence of magnetotactic bacteria is testimony to the power of evolution, as the intracellular magnetic particles they produce reflect the optimization processes of natural selection. Magnetofossils, the remains of these particles, are therefore distinguishable in sediments from magnetic particles produced by other means and leave a record that extends firmly into the Mesozoic and more ambiguously into the Precambrian.

Most magnetotactic bacteria favor particular redox conditions, and their preservation as fossils also depends upon redox parameters. Thus, the magnetofossil record can serve as a proxy of climate-driven changes in organic productivity and bottom water oxygen and might have utility deep in Earth history as a tracer of ancient oxygen levels. The pre-Quaternary magnetofossil record is, however, currently sparse. Fully utilizing the magnetofossil proxy will require studies of the mechanisms and evolution of biomineralization in magnetotactic bacteria, investigations of the relationship between magnetotactic bacteria growth, magnetofossil population, oxygen supply, and biological

productivity, and the development of a richer magnetofossil record.

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References

- Aissaoui, D.M., McNeill, D.F. and Kirschvink, J.L., 1990. Magnetostratigraphic dating of shallow-water carbonates from Mururoa Atoll, French Polynesia - implications for global eustasy. *Earth and Planetary Science Letters*, 97: 102-112.
- Akai, J., Iida, A., Akai, K. and Chiba, A., 1997. Mn and Fe minerals of possible biogenic origin from two Precambrian stromatolites in western Australia. *Journal of the Geological Society of Japan*, 103: 484-488.
- Arató, B., Szányi, Z., Flies, C., Schüler, D., Frankel, R.B., Buseck, P.R. and Pósfai, M., 2005. Crystal-size and shape distributions of magnetite from uncultured magnetotactic bacteria as a potential biomarker. *American Mineralogist*, 90: 1233-1241.
- Bazylinski, D.A. and Frankel, R.B., 2004. Magnetosome formation in prokaryotes. *Nature Reviews Microbiology*, 2: 217-230.
- Bazylinski, D.A., Frankel, R.B., Heywood, B.R., Mann, S., King, J.W., Donaghay, P.L. and Hanson, A.K., 1995. Controlled Biomineralization of Magnetite (Fe₃O₄) and Greigite (Fe₃S₄) in a Magnetotactic Bacterium. *Applied and Environmental Microbiology*, 61: 3232-3239.
- Bazylinski, D.A., Garratt-Reed, A.J., Abedi, A. and Frankel, R.B., 1993. Copper association with iron sulfide magnetosomes in a magnetotactic bacterium. *Archives of Microbiology*, 160: 35-42.
- Bazylinski, D.A., Garratt-Reed, A.J. and Frankel, R.B., 1994. Electron-Microscopic Studies of Magnetosomes in Magnetotactic Bacteria. *Microscopy Research and Technique*, 27: 389-401.
- Bazylinski, D.A. and Moskowitz, B.M., 1997. Microbial biomineralization of magnetic iron minerals: Microbiology, magnetism and environmental significance, *Geomicrobiology: Interactions Between Microbes And Minerals. Reviews In Mineralogy*, pp. 181-223.
- Belkaoul, N.K. and Aissaoui, D.M., 1997. Nature and origin of magnetic minerals within the Middle Jurassic shallow-water carbonate rocks of the Paris Basin, France: implications for magnetostratigraphic dating. *Geophysical Journal International*, 130: 411-421.
- Berner, R.A., 1967. Thermodynamic stability of sedimentary iron sulfides. *American Journal of Science*, 265: 773-785.
- Blakemore, R., 1975. Magnetotactic Bacteria. *Science*, 190: 377-379.
- Buseck, P.R., Dunin-Borkowski, R.E., Devouard, B., Frankel, R.B., McCartney, M.R., Midgley, P.A., Pósfai, M. and Weyland, M., 2001. Magnetite morphology and life on Mars. *Proceedings Of The National Academy Of Sciences Of The United States Of America*, 98: 13490-13495.
- Butler, R.F. and Banerjee, S.K., 1975. Theoretical single-domain grain size range in magnetite and titanomagnetite. *Journal of Geophysical Research*, 80: 4049-4058.
- Butler, R.W.H., McClelland, E. and Jones, R.E., 1999. Calibrating the duration and timing of the Messinian salinity crisis in the Mediterranean: Linked tectonoclimatic signals in thrust-top basins of Sicily. *Journal of the Geological Society*, 156: 827-835.
- Canfield, D.E., 1998. A new model for Proterozoic ocean chemistry. *Nature*, 396: 450-453.
- Carter-Stiglitz, B., Jackson, M. and Moskowitz, B., 2002. Low-temperature remanence in stable single domain magnetite. *Geophysical Research Letters*, 29: 1129.
- Carter-Stiglitz, B., Moskowitz, B. and Jackson, M., 2004. More on the low-temperature magnetism of stable single domain magnetite: Reversibility and non-stoichiometry. *Geophysical Research Letters*, 31: L06606.
- Chang, S.B.R., 1988. Bacterial magnetite in sedimentary deposits and its geophysical and paleological implication. Ph.D. Thesis, California Institute of Technology, Pasadena, CA.
- Chang, S.B.R. and Kirschvink, J.L., 1984. Bacterial magnetofossils as probes of Precambrian ecological and biochemical evolutionary events, 97th annual meeting, Geological Society of America.
- Chang, S.B.R. and Kirschvink, J.L., 1985. Possible Biogenic Magnetite Fossils from the Miocene Marine Clay of Crete. In: J.L. Kirschvink, D.S. Jones and B. McFadden (Editors), *Magnetite Biomineralization and Magnetoreception in Organisms: A New Biomagnetism*. Plenum Press, New York, NY, pp. 647-669.
- Chang, S.B.R. and Kirschvink, J.L., 1989. Magnetofossils, the magnetization of sediments, and the evolution of magnetite

- biomineralization. *Annual Review of Earth and Planetary Sciences*, 17: 169-195.
- Chang, S.B.R., Kirschvink, J.L. and Stolz, J.F., 1987. Biogenic Magnetite As A Primary Remanence Carrier In Limestone Deposits. *Physics Of The Earth And Planetary Interiors*, 46: 289-303.
- Chang, S.B.R., Stolz, J.F., Kirschvink, J.L. and Awramik, S.M., 1989. Biogenic magnetite in stromatolites. 2. Occurrence In ancient sedimentary environments. *Precambrian Research*, 43: 305-315.
- Cox, B., 2002. Organization and Elemental Analysis of P-, S-, and Fe-rich Inclusions in a Population of Freshwater Magnetococci. *Geomicrobiology Journal*, 19: 387-406.
- Dearing, J.A., Boyle, J.F., Appleby, P.G., Mackay, A.W. and Flower, R.J., 1998. Magnetic properties of recent sediments in Lake Baikal, Siberia. *Journal Of Paleolimnology*, 20: 163-173.
- DeLong, E.F., Frankel, R.B. and Bazylinski, D.A., 1993. Multiple evolutionary origins of magnetotaxis in bacteria. *Science*, 259: 803-806.
- Devouard, B., Posfai, M., Hua, X., Bazylinski, D.A., Frankel, R.B. and Buseck, P.R., 1998. Magnetite from magnetotactic bacteria: Size distributions and twinning. *American Mineralogist*, 83: 1387-1398.
- Diaz-Ricci, J.C. and Kirschvink, J.L., 1992. Magnetic Domain State And Coercivity Predictions For Biogenic Greigite (Fe₃S₄) - A Comparison Of Theory With Magnetosome Observations. *Journal Of Geophysical Research-Solid Earth*, 97: 17309-17315.
- Dinares-Turell, J., Hoogakker, B.A.A., Roberts, A.P., Rohling, E.J. and Sagnotti, L., 2003. Quaternary climatic control of biogenic magnetite production and eolian dust input in cores from the Mediterranean Sea. *Palaeogeography Palaeoclimatology Palaeoecology*, 190: 195-209.
- Dong, H., Fredrickson, J.K., Kennedy, D.W., Zachara, J.M., Kukkadapu, R.K. and Onstott, T.C., 2000. Mineral transformation associated with the microbial reduction of magnetite. *Chem. Geol*, 169: 299-318.
- Dunin-Borkowski, R.E., McCartney, M.R., Posfai, M., Frankel, R.B., Bazylinski, D.A. and Buseck, P.R., 2001. Off-axis electron holography of magnetotactic bacteria: magnetic microstructure of strains MV-1 and MS-1. *European Journal of Mineralogy*, 13: 671-684.
- Egli, R., 2004. Characterization of individual rock magnetic components by analysis of remanence curves, 1. Unmixing natural sediments. *Studia Geophysica Et Geodaetica*, 48: 391-446.
- Farina, M., Kachar, B., Lins, U., Broderick, R. and Debarros, H.L., 1994. The Observation of Large Magnetite (Fe₃O₄) Crystals from Magnetotactic Bacteria by Electron and Atomic-Force Microscopy. *Journal of Microscopy-Oxford*, 173: 1-8.
- Frankel, R.B. and Blakemore, R.P., 1989. Magnetite and magnetotaxis in microorganisms. *Bioelectromagnetics*, 10: 223-237.
- Friedmann, E.I., Wierzchos, J., Ascaso, C. and Winklhofer, M., 2001. Chains of magnetite crystals in the meteorite ALH84001: Evidence of biological origin. *Proceedings Of The National Academy Of Sciences Of The United States Of America*, 98: 2176-2181.
- Glasauer, S., Langley, S. and Beveridge, T.J., 2002. Intracellular Iron Minerals in a Dissimilatory Iron-Reducing Bacterium. *Science*, 295: 117-119.
- Golden, D.C., Ming, D.W., Morris, R.V., Brearley, A., Lauer, H.V., Treiman, A.H., Zolensky, M.E., Schwandt, C.S., Lofgren, G.E. and McKay, G.A., 2004. Evidence for exclusively inorganic formation of magnetite in Martian meteorite ALH84001. *American Mineralogist*, 89: 681-695.
- Gorby, Y.A., Beveridge, T.J. and Blakemore, R.P., 1988. Characterization of the Bacterial Magnetosome Membrane. *Journal of Bacteriology*, 170: 834-841.
- Hesse, P.P., 1994. Evidence for Bacterial Paleocological Origin of Mineral Magnetic Cycles in Oxidic and Sub-Oxidic Tasman Sea Sediments. *Marine Geology*, 117: 1-17.
- Heywood, B.R., Bazylinski, D.A., Garrattred, A., Mann, S. and Frankel, R.B., 1990. Controlled Biosynthesis Of Greigite (Fe₃S₄) In Magnetotactic Bacteria. *Naturwissenschaften*, 77: 536-538.
- Hilgenfeldt, K., 2000. Diagenetic dissolution of biogenic magnetite in surface sediments of the Benguela upwelling system. *International Journal Of Earth Sciences*, 88: 630-640.
- Hounslow, M.W. and Maher, B.A., 1996. Quantitative extraction and analysis of carriers of magnetization in sediments. *Geophysical Journal International*, 124: 57-74.
- Housen, B.A. and Moskowitz, B.M., 2006. Depth distribution of magnetofossils in near-surface sediments from the Blake/Bahama Outer Ridge, western North Atlantic Ocean, determined by low-temperature magnetism. *Journal of Geophysical Research*, 111: G01005.
- Jørgensen, B.B. and Gallardo, V.A., 1999. Thioploca spp.: filamentous sulfur bacteria with nitrate vacuoles. *FEMS Microbiology Ecology*, 28: 301-313.
- Keim, C.N., Solórzano, G., Farina, M. and Lins, U., 2005. Intracellular inclusions of uncultured magnetotactic bacteria. *International Microbiology*, 8: 111-117.
- Kent, D.V., Cramer, B.S., Lanci, L., Wang, D., Wright, J.D. and Van der Voo, R., 2003. A case for a

- comet impact trigger for the Paleocene/Eocene thermal maximum and carbon isotope excursion. *Earth and Planetary Science Letters*, 211: 13-26.
- Kim, B.Y., Kodama, K.P. and Moeller, R.E., 2005. Bacterial magnetite produced in water column dominates lake sediment mineral magnetism: Lake Ely, USA. *Geophysical Journal International*, 163: 26-37.
- Kirschvink, J.L., 1980. South-seeking magnetic bacteria. *Journal of Experimental Biology*, 86: 345-347.
- Kirschvink, J.L., 1982. Paleomagnetic Evidence For Fossil Biogenic Magnetite In Western Crete. *Earth And Planetary Science Letters*, 59: 388-392.
- Kirschvink, J.L., 2001. A seventh criterion for the identification of bacterial magnetofossils. *Eos Trans. AGU*, 82: S131.
- Kirschvink, J.L. and Chang, S.B.R., 1984. Ultrafine-Grained Magnetite in Deep-Sea Sediments - Possible Bacterial Magnetofossils. *Geology*, 12: 559-562.
- Kirschvink, J.L. and Lowenstam, H.A., 1979. Mineralization and magnetization of chiton teeth: paleomagnetic, sedimentologic, and biologic implications of organic magnetite. *Earth and Planetary Science Letters*, 44: 193-204.
- Kirschvink, J.L. and Rozanov, A.Y., 1984. Magnetostratigraphy of lower Cambrian strata from the Siberian Platform: a paleomagnetic pole and a preliminary polarity time-scale. *Geol. Mag.*, 121: 189-203 .
- Kobayashi, A., Kirschvink, J.L., Nash, C.Z., Kopp, R.E., Sauer, D.A., Bertani, L.E., Voorhout, W.F. and Taguchi, T., 2006. Experimental observation of magnetosome chain collapse in magnetotactic bacteria: sedimentological, paleomagnetic, and evolutionary implications. *Earth And Planetary Science Letters*, 245: 538-550.
- Komeili, A., Li, Z., Newman, D.K. and Jensen, G.J., 2006. Magnetosomes are cell membrane invaginations organized by the actin-like protein MamK. *Science*, 311: 242-245.
- Komeili, A., Vali, H., Beveridge, T.J. and Newman, D.K., 2004. Magnetosome vesicles are present before magnetite formation, and MamA is required for their activation. *Proceedings of the National Academy of Sciences*, 101: 3839-3844.
- Kopp, R.E., 2007. The identification and interpretation of microbial biogeomagnetism. Ph.D. Thesis, California Institute of Technology, Pasadena, California, 190 pp.
- Kopp, R.E. and Humayun, M., 2003. Kinetic model of carbonate dissolution in Martian meteorite ALH84001. *Geochimica et Cosmochimica Acta*, 67: 3247-3256.
- Kopp, R.E., Nash, C.Z., Kobayashi, A., Weiss, B.P., Bazylinski, D.A. and Kirschvink, J.L., 2006a. Ferromagnetic resonance spectroscopy for assessment of magnetic anisotropy and magnetostatic interactions: A case study of mutant magnetotactic bacteria. *J. Geophys. Res.*, 111: B12S25.
- Kopp, R.E., Raub, T.D., Schumann, D., Vali, H., Smirnov, A.V. and Kirschvink, J.L., 2007. Magnetofossil Spike at the Paleocene-Eocene Thermal Maximum: Ferromagnetic resonance, rock magnetic, and electron microscopy evidence from Ancora, New Jersey, USA. *Paleoceanography*, 22, PA4103, doi: 10.1029/2007PA001473.
- Kopp, R.E., Weiss, B.P., Maloof, A.C., Vali, H., Nash, C.Z. and Kirschvink, J.L., 2006b. Chains, clumps, and strings: Magnetofossil taphonomy with ferromagnetic resonance spectroscopy. *Earth and Planetary Science Letters*, 247: 10-25.
- Kostka, J.E. and Nealson, K.H., 1995. Dissolution and Reduction of Magnetite by Bacteria. *Environmental Science & Technology*, 29: 2535-2540.
- Lean, C.M.B. and McCave, I.N., 1998. Glacial to interglacial mineral magnetic and palaeoceanographic changes at Chatham Rise, SW Pacific Ocean. *Earth and Planetary Science Letters*, 163: 247-260.
- Lippert, P.C. and Zachos, J.C., 2007. A biogenic origin for anomalous fine-grained magnetic material at the Paleocene-Eocene boundary at Wilson Lake, New Jersey. *Paleoceanography*, 22, PA4104, doi:10.1029/2007PA001471.
- Lowenstam, H.A., 1981. Minerals formed by organisms. *Science*, 211: 1126.
- Maher, B.A., Thompson, R. and Hounslow, M.W., 1999. Introduction. In: B.A. Maher and R. Thompson (Editors), *Quaternary Climates, Environments, and Magnetism*. Cambridge University Press, Cambridge, pp. 1-48.
- Maloof, A.C., Kopp, R.E., Grotzinger, J.P., Fike, D.A., Bosak, T., Vali, H., Poussart, P.M., Weiss, B.P. and Kirschvink, J.L., 2007. Sedimentary Iron Cycling and the Origin and Preservation of Magnetization in Platform Carbonate Muds, Andros Island, Bahamas. *Earth and Planetary Science Letters*, 259: 581-598.
- Mann, S., Sparks, N.H.C. and Blakemore, R., 1987. Structure, morphology, and crystal growth of anisotropic magnetite crystals in magnetotactic bacteria. *Proc. R. Soc. Lond. B*, 231: 477-487.
- Maratea, D. and Blakemore, R.P., 1981. *Aquaspirillum magnetotacticum* sp. nov., a magnetic spirillum. *International Journal of Systematic Bacteriology*, 31: 452-455.
- Matsunaga, T. and Okamura, Y., 2003. Genes and proteins involved in bacterial magnetite particle

- formation. *Trends in Microbiology*, 11: 536-541.
- McKay, D.S., Gibson, E.K., Thomas-Keprta, K.L., Vali, H., Romanek, C.S., Clemett, S.J., Chillier, X.D.F., Maechling, C.R. and Zare, R.N., 1996. Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001. *Science*, 273: 924-930.
- McNeill, D.F., 1990. Biogenic magnetite from surface Holocene carbonate sediments, Great Bahama Bank. *Journal Of Geophysical Research-Solid Earth And Planets*, 95: 4363-4371.
- McNeill, D.F., Ginsburg, R.N., Chang, S.B.R. and Kirschvink, J.L., 1988. Magnetostratigraphic Dating Of Shallow-Water Carbonates From San-Salvador, Bahamas. *Geology*, 16: 8-12.
- Meert, J.G., Eide, E.A. and Torsvik, T.H., 1997. The Nama Group revisited. *Geophys. J. Int.*, 129: 637-650.
- Meldrum, F.C., Mann, S., Heywood, B.R., Frankel, R.B. and Bazylinski, D.A., 1993a. Electron-Microscopy Study of Magnetosomes in 2 Cultured Vibrioid Magnetotactic Bacteria. *Proceedings of the Royal Society of London Series B-Biological Sciences*, 251: 237-242.
- Meldrum, F.C., Mann, S., Heywood, B.R., Frankel, R.B. and Bazylinski, D.A., 1993b. Electron-Microscopy Study of Magnetosomes in a Cultured Coccioid Magnetotactic Bacterium. *Proceedings of the Royal Society of London Series B-Biological Sciences*, 251: 231-236.
- Meulenkamp, J.E., 1979. Lithostratigraphy and relative chronostratigraphic position of the sections Apostoli and Potamidha 1 and 2. *Utrecht Micropaleontol. Bull.*, 21: 9-21.
- Moench, T.T., 1988. *Bilophococcus magnetotacticus* gen. nov. sp. nov., a motile, magnetic coccus. *Antonie van Leeuwenhoek, International Journal of General and Molecular Microbiology*, 54: 483-496.
- Montgomery, P., Hailwood, E.A., Gale, A.S. and Burnett, J.A., 1998. The magnetostratigraphy of Coniacian late Campanian chalk sequences in southern England. *Earth And Planetary Science Letters*, 156: 209-224.
- Morse, J.W., Millero, F.J., Cornwell, J.C. and Rickard, D., 1987. The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. *Earth-Science Reviews*, 24: 1-42.
- Moskowitz, B.M., Frankel, R.B. and Bazylinski, D.A., 1993. Rock magnetic criteria for the detection of biogenic magnetite. *Earth And Planetary Science Letters*, 120: 283-300.
- Niitsuma, S., Kakegawa, T., Nagasu, T. and Nedachi, M., 2005. Discovery of greigite from Archean rock?, Japan Earth and Planetary Science Joint Meeting. Japan Geoscience Union, Makuhari, Japan.
- Niitsuma, S., Nedachi, M., Hoashi, M., Suganuma, Y., Sugita, T., Ohno, K., Hisamitsu, T., Kodama, K. and Niitsuma, N., 2004. Rock magnetism of the black shale in the Mt. Roe Basalt, Pilbara Craton, Western Australia. Japan Earth and Planetary Science Joint Meeting. Japan Geoscience Union, Makuhari, Japan.
- Oldfield, F., Wake, R., Boyle, J., Jones, R., Nolan, S., Gibbs, Z., Appleby, P., Fisher, E. and Wolff, G., 2003. The late-Holocene history of Gormire Lake (NE England) and its catchment: a multiproxy reconstruction of past human impact. *Holocene*, 13: 677-690.
- Özdemir, Ö., Dunlop, D.J. and Moskowitz, B.M., 1993. The effect of oxidation on the Verwey transition in magnetite. *Geophysical Research Letters*, 20: 1671-1674.
- Pan, Y.X., Petersen, N., Davila, A.F., Zhang, L.M., Winklhofer, M., Liu, Q.S., Hanzlik, M. and Zhu, R.X., 2005. The detection of bacterial magnetite in recent sediments of Lake Chiemsee (southern Germany). *Earth And Planetary Science Letters*, 232: 109-123.
- Peck, J.A. and King, J.W., 1996. Magnetofossils in the sediment of Lake Baikal, Siberia. *Earth and Planetary Science Letters*, 140: 159-172.
- Petersen, N., Vondobeneck, T. and Vali, H., 1986. Fossil Bacterial Magnetite In Deep-Sea Sediments From The South-Atlantic Ocean. *Nature*, 320: 611-615.
- Pósfai, M., Buseck, P.R., Bazylinski, D.A. and Frankel, R.B., 1998. Iron sulfides from magnetotactic bacteria: Structure, composition, and phase transitions. *American Mineralogist*, 83: 1469-1481.
- Pósfai, M., Cziner, K., Marton, E., Marton, P., Buseck, P.R., Frankel, R.B. and Bazylinski, D.A., 2001. Crystal-size distributions and possible biogenic origin of Fe sulfides. *European Journal Of Mineralogy*, 13: 691-703.
- Pósfai, M., Moskowitz, B.M., Arato, B., Schüler, D., Flies, C., Bazylinski, D.A. and Frankel, R.B., 2006. Properties of intracellular magnetite crystals produced by *Desulfovibrio magneticus* strain RS-1. *Earth and Planetary Science Letters*, 249: 444-455.
- Reitner, J., Peckmann, J., Blumenberg, M., Michaelis, W., Reimer, A. and Thiel, V., 2005. Concretionary methane-seep carbonates and associated microbial communities in Black Sea sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 227: 18-30.
- Reynolds, R.L., Tuttle, M.L., Rice, C.A., Fishman, N.S., Karachewski, J.A. and Sherman, D.M., 1994. Magnetization and geochemistry of greigite-bearing Cretaceous strata, North Slope basin, Alaska. *Am J Sci*, 294: 485-528.
- Rohl, U., Bralower, T.J., Norris, R.D. and Wefer, G., 2000. New chronology for the late Paleocene

- thermal maximum and its environmental implications. *Geology*, 28: 927-930.
- Sakaguchi, T., Arakaki, A. and Matsunaga, T., 2002. *Desulfovibrio magneticus* sp. nov., a novel sulfate-reducing bacterium that produces intracellular single-domain-sized magnetite particles. *International Journal of Systematic and Evolutionary Microbiology*, 52: 215-221.
- Sakaguchi, T., Burgess, J.G. and Matsunaga, T., 1993. Magnetite formation by a sulphate-reducing bacterium. *Nature*, 365: 47-49.
- Sakai, S. and Jige, M., 2006. Characterization of magnetic particles and magnetostratigraphic dating of shallow-water carbonates in the Ryukyu Islands, northwestern Pacific. *The Island Arc*, 15: 468-475.
- Scheffel, A., Gruska, M., Faivre, D., Linaroudis, A., Plitzko, J.M. and Schuler, D., 2006. An acidic protein aligns magnetosomes along a filamentous structure in magnetotactic bacteria. *Nature*, 440: 110-114.
- Schüler, D. and Bauerlein, E., 1998. Dynamics of iron uptake and Fe₃O₄ biomineralization during aerobic and microaerobic growth of *Magnetospirillum gryphiswaldense*. *Journal of Bacteriology*, 180: 159-162.
- Schulz, H.N. and Jørgensen, B.B., 2001. Big bacteria. *Annual Review of Microbiology*, 55: 105-137.
- Simmons, S.L., Sievert, S.M., Frankel, R.B., Bazylinski, D.A. and Edwards, K.J., 2004. Spatiotemporal distribution of marine magnetotactic bacteria in a seasonally stratified coastal salt pond. *Applied and Environmental Microbiology*, 70: 6230-6239.
- Skinner, B.J., Grimaldi, F.S. and Erd, R.C., 1964. Greigite Thio-Spinel of Iron - New Mineral. *American Mineralogist*, 49: 543-&.
- Snowball, I.F., 1994. Bacterial magnetite and the magnetic properties of sediments in a Swedish lake. *Earth And Planetary Science Letters*, 126: 129-142.
- Spring, S., Amann, R., Ludwig, W., Schleifer, K.H., Van Gemerden, H. and Petersen, N., 1993. Dominating role of an unusual magnetotactic bacterium in the microaerobic zone of a freshwater sediment. *Applied and Environmental Microbiology*, 59: 2397-2403.
- Spring, S. and Schleifer, K.H., 1995. Diversity of magnetotactic bacteria. *Systematic and Applied Microbiology*, 18: 147-153.
- Stolz, J.F., Chang, S.B.R. and Kirschvink, J.L., 1986. Magnetotactic Bacteria And Single-Domain Magnetite In Hemipelagic Sediments. *Nature*, 321: 849-851.
- Stolz, J.F., Chang, S.B.R. and Kirschvink, J.L., 1989. Biogenic Magnetite In Stromatolites .1. Occurrence In Modern Sedimentary Environments. *Precambrian Research*, 43: 295-304.
- Tarduno, J.A., 1994. Temporal Trends of Magnetic Dissolution in the Pelagic Realm - Gauging Paleoproductivity. *Earth and Planetary Science Letters*, 123: 39-48.
- Tauxe, L., Tucker, P., Petersen, N.P. and LaBrecque, J.L., 1984. Magnetostratigraphy of Leg 73 Sediments. In: K.J. Hsü and J.L. LaBrecque (Editors), *Initial Reports of the Deep Sea Drilling Project*. U.S. Govt. Printing Office, Washington, pp. 609-622.
- Taylor, A.P. and Barry, J.C., 2004. Magnetosomal matrix: ultrafine structure may template biomineralization of magnetosomes. *Journal of Microscopy*, 213: 180-197.
- Taylor, A.P., Barry, J.C. and Webb, R.I., 2001. Structural and morphological anomalies in magnetosomes: possible biogenic origin for magnetite in ALH84001. *Journal of Microscopy*, 201: 84-106.
- Thomas-Keprta, K.L., Bazylinski, D.A., Kirschvink, J.L., Clemett, S.J., McKay, D.S., Wentworth, S.J., Vali, H., Gibson, E.K. and Romanek, C.S., 2000. Elongated prismatic magnetite crystals in ALH84001 carbonate globules: Potential Martian magnetofossils. *Geochimica Et Cosmochimica Acta*, 64: 4049-4081.
- Thomas-Keprta, K.L., Clemett, S.J., Bazylinski, D.A., Kirschvink, J.L., McKay, D.S., Wentworth, S.J., Vali, H., Gibson, E.K., McKay, M.F. and Romanek, C.S., 2001. Truncated hexa-octahedral magnetite crystals in ALH84001: Presumptive biosignatures. *Proceedings Of The National Academy Of Sciences Of The United States Of America*, 98: 2164-2169.
- Thomas-Keprta, K.L., Clemett, S.J., Bazylinski, D.A., Kirschvink, J.L., McKay, D.S., Wentworth, S.J., Vali, H., Gibson, E.K. and Romanek, C.S., 2002. Magnetofossils from ancient Mars: a robust biosignature in the Martian meteorite ALH84001. *Applied And Environmental Microbiology*, 68: 3663-3672.
- Thomas-Keprta, K.L., Clemett, S.J., Schwartz, C., Morphey, M., McIntosh, J.R., Bazylinski, D.A., Kirschvink, J.L., Wentworth, S.J., McKay, D.S., Vali, H., Gibson, E.K. and Romanek, C.S., 2004. Determination of the three-dimensional morphology of ALH84001 and biogenic MV-1 magnetite: comparison of results from electron tomography and classical transmission electron microscopy (abstract), *Lunar and Planetary Science XXXV*, pp. 2030.
- Thornhill, R.H., Burgess, J.G., Sakaguchi, T. and Matsunaga, T., 1994. A morphological classification of bacteria containing bullet-shaped magnetic particles. *FEMS Microbiology Letters*, 115: 169-176.
- Tikoo, S.M., Kopp, R. E., Vali, H., and Kirschvink, J.L., in prep. Rock magnetic characterization of the late Archean Ghaap Group, Transvaal

- Supergroup, from Agouon drill core GKP01: No signs of life, but a magnetic paleothermometer for siderite metamorphism. *Precambrian Research*.
- Valet, J.-P. and Laj, C., 1981. Paleomagnetic record of two successive Miocene geomagnetic reversals in western Crete. *Earth and Planetary Science Letters*, 54: 53-63.
- Vali, H., Forster, O., Amarantidis, G. and Petersen, N., 1987. Magnetotactic Bacteria And Their Magnetofossils In Sediments. *Earth And Planetary Science Letters*, 86: 389-400.
- Vali, H. and Kirschvink, J.L., 1989. Magnetofossil dissolution in a paleomagnetically unstable deep-sea sediment. *Nature*, 339: 203-206.
- Vali, H. and Kirschvink, J.L., 1991. Observations of Magnetosome Organization, Surface Structure, and Iron Biomineralization of Undescribed Magnetic Bacteria: Evolutionary Speculations. In: R.B. Frankel and R.P. Blakemore (Editors), *Iron biominerals*. Plenum Press, New York, pp. 97-116.
- van der Loeff, M.M.R., 1990. Oxygen in Pore Waters of Deep-Sea Sediments. *Philosophical Transactions of the Royal Society of London Series A*, 331: 69-84.
- van der Voo, R., 1990. The reliability of paleomagnetic data. *Tectonophysics*, 184: 1-9.
- van Hinsbergen, D.J.J. and Meulenkamp, J.E., 2006. Neogene supradatchment basin development on Crete (Greece) during exhumation of the South Aegean core complex. *Basin Research*, 18: 103-124.
- Wachtershauser, G., 1990. The Case for the Chemoautotrophic Origin of Life in an Iron-Sulfur World. *Origins of Life and Evolution of the Biosphere*, 20: 173-176.
- Walker, J.C.G., 1987. Was the Archaean biosphere upside down? *Nature*, 329: 710-712.
- Weiss, B.P., Kim, S.S., Kirschvink, J.L., Kopp, R.E., Sankaran, M., Kobayashi, A. and Komeili, A., 2004a. Ferromagnetic resonance and low temperature magnetic tests for biogenic magnetite. *Earth and Planetary Science Letters*, 224: 73-89.
- Weiss, B.P., Kim, S.S., Kirschvink, J.L., Kopp, R.E., Sankaran, M., Kobayashi, A. and Komeili, A., 2004b. Magnetic tests for magnetosome chains in Martian meteorite ALH84001. *Proceedings Of The National Academy Of Sciences Of The United States Of America*, 101: 8281-8284.
- Witt, A., Fabian, K. and Bleil, U., 2005. Three-dimensional micromagnetic calculations for naturally shaped magnetite: Octahedra and magnetosomes. *Earth And Planetary Science Letters*, 233: 311-324.
- Xu, W.X., Peacor, D.R., Dollase, W.A., Van Der Voo, R. and Beaubouef, R., 1997. Transformation of titanomagnetite to titanomaghemite: A slow, two-step, oxidation-ordering process in MORB. *American Mineralogist*, 82: 1101-1110.
- Yamazaki, T. and Ioka, N., 1997. Environmental rock-magnetism of pelagic clay: Implications for Asian eolian input to the North Pacific since the Pliocene. *Paleoceanography*, 12: 111-124.
- Yamazaki, T., Katsura, I. and Marumo, K., 1991. Origin Of Stable Remanent Magnetization Of Siliceous Sediments In The Central Equatorial Pacific. *Earth And Planetary Science Letters*, 105: 81-93.
- Yamazaki, T. and Kawahata, H., 1998. Organic carbon flux controls the morphology of magnetofossils in marine sediments. *Geology*, 26: 1064-1066.