

# MAGNETOFOSSILS, THE MAGNETIZATION OF SEDIMENTS, AND THE EVOLUTION OF MAGNETITE BIOMINERALIZATION

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## 1. INTRODUCTION

Magnetite  $\text{Fe}_3\text{O}_4$  is one of the most stable carriers of natural remanent magnetization (NRM) in sedimentary rocks, and paleomagnetic studies of magnetite-bearing sediments, such as deep-sea cores and pelagic limestones, have provided a detailed calibration between the biostratigraphic and magnetic polarity time scales. Despite this important role, there is as yet a very poor understanding of how ultrafine-grained ( $< 0.1 \mu\text{m}$ ) magnetite is formed, transported, and preserved in marine environments. A major conceptual advance in our understanding of these processes is the recent discovery that biogenic magnetite, formed by magnetotactic bacteria and/or other magnetite-precipitating organisms, is responsible for much of the stable magnetic remanence in many marine sediments and sedimentary rocks. Since these magnetite particles are of biogenic origin, they are termed properly magnetofossils (Kirschvink & Chang 1984).

Magnetite biomineralization is now known in three of the five kingdoms of living organisms [Monera (Bacteria), Proctista (Protozoa), and Animalia]. To date, the known functions of biogenic magnetite and its min

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eral precursors include the hardening of teeth, geomagnetic navigation, and perhaps the storage of iron. In the radular teeth of chitons, magnetite acts to harden the surface, allowing them to feed on endolithic algae (Lowenstam 1962). In magnetotactic bacteria, protozoists, and oceanic fish, the magnetite is of single-domain size and usually held together in a chainlike structure called a magnetosome; in the microorganism this is implicated clearly in their magnetotaxis, and in the fish it may form the basis of a geomagnetic sensory organelle. In other higher animals, including cetaceans and turtles, studies of magnetic extracts from macerated tissue often reveal framboidal particles up to 50  $\mu\text{m}$  in diameter of unknown function. In addition, ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ), known to be the precursor of magnetite biomineralization in the bacteria and chitons (Iowa & Lowenstam 1967, Kirschvink & Lowenstam 1979, Frankel et al 1985), forms the core component (micelle) of the iron storage protein, ferritin, in both bacteria (Sriefer & Watt 1979, Yariv et al 1981) and higher organisms (Hyde et al 1963, David & Easterbrook 1971, Ford et al 1984).

This wide phyletic distribution of magnetite and its precursors reflects the fundamental role that iron plays in biological processes. In the oxidizing atmosphere and oceans of the modern Earth, the concentration of dissolved iron is low; most of the iron which is there is transported as some form of organically bound Fe<sup>3+</sup> colloidal particles. Hence, organisms have evolved a variety of mechanisms to gather iron for metabolic use and have developed internal storage sites to provide a constant supply despite fluctuating availability. On the other hand, life probably evolved under moderately to strongly reducing conditions in the early Archean, where ferrous iron in solution would have been far more abundant. Evidence for this is largely biochemical, as most metabolic and catabolic pathways known in anaerobic organisms are also present in aerobes but not vice versa; hence, anaerobes came first. The use of ferrous iron as an electron donor for photosynthesis (rather than  $\text{H}_2\text{S}$  or  $\text{H}_2\text{O}$ ) may well have been one of the earliest biochemical processes to induce extracellular iron oxide mineralization (Lowenstam & Kirschvink 1985). It is clear from the widespread presence of iron-containing proteins in both anaerobic and aerobic organisms that they evolved prior to the widespread oxidation of the world oceans, which probably occurred around 2 Ga (signaled by the widespread deposition of banded iron formations). In the final section of this review, we consider the possibility that intracellular magnetite biomineralization evolved as an iron storage response for microaerophilic bacteria faced with the problem of decreasing Fe<sup>2+</sup> concentrations in the water. Therefore, finding the earliest occurrence of biogenic magnetite in the Precambrian fossil record might yield information concerning the past concentration of oxygen, at least in the local environment.

## 2. MAGNETITE BIOMINERALIZATION

### *Chiton Teeth*

Magnetite was first identified in chiton teeth (Molluscan class Polyplacophora) by Lowenstam (1962), who along with his students and colleagues have since taken the leading role in the investigation of its biomineralization process. They discovered that iron passes through at least three consecutive stages in the process of chiton magnetite formation (Towe & Lowenstam 1967, Kirschvink & Lowenstam 1979, Nesson & Lowenstam 1985): (a) the transport of ferric iron in the cores of ferritin molecules in the hemolymph, (b) the deposition of a mineral precursor, ferrihydrite, within an organic matrix network, and (c) the partial reduction and recrystallization of the ferric iron to form magnetite. Recent work by Kim (1987) has also demonstrated the presence of the mineral goethite within the iron biomineralizing zone of the Australian chiton *Clavarizona hirtosa*, although it is not yet known how widespread this process is within the Polyplacophora. Biogenic magnetite produced by chitons has not yet been identified in marine sediments, although many equatorial carbonate-rich environments look promising for such a search.

### *Magnetotactic Bacteria*

Blakemore's (1975) report of magnetotactic bacteria in Cape Cod Marsh, Massachusetts, was a major step in the understanding of magnetite biomineralization. Subsequent studies, which include X-ray and electron diffraction, Mössbauer spectroscopy, and direct lattice imaging, have shown that the intracellular iron particles of the bacteria are made invariably of magnetite despite a wide range of biologically unique crystal morphologies and sizes (Frankel et al 1979, Towe & Moench 1981, Matsuda et al 1983, Mann et al 1984a,b, 1987a,b, Mann 1985). The existence of an additional micellelike intracellular substance in the magnetotactic bacteria has been shown recently by the low-temperature Mössbauer spectroscopy studies of Frankel et al (1985). Hence, these bacteria may use a biochemical pathway similar to that of the chitons in magnetite formation. Magnetite crystals in these bacteria are held aligned in a parallel chain, termed the magnetosome by Balkwill et al (1980), with particles separated from each other and bound together by proper lipid bilayer membranes (Gorby et al 1988). The magnetosome acts to hold the magnetite crystals aligned such that all of their magnetic moments add vectorially along its length, thereby producing a larger net magnetic moment (Frankel & Blakemore 1980, Blakemore 1982). Furthermore, the crystals in the magnetosome tend to have similar orientations of their crystallographic axes, either along the [111] or [112] directions (Mann et al 1987b), which

happen to be at or very close to the "easy" direction of magnetization for magnetite. This structure is clearly a sophisticated, highly evolved biological "bar magnet".

#### *Other Organisms*

In addition to the chitons and bacteria, several other organisms are known to precipitate magnetite. These organisms include honeybees, pigeons, turtles, protoctists, and a variety of pelagic fish (Gould et al 1978, Walcott et al 1979, Kirschvink & Gould 1981, Walker et al 1984, 1988, Kirschvink et al 1985a,b, Mann et al 1988). In terms of phyletic diversity, magnetite may soon rank as the fourth-most abundant biogenic mineral after calcite, aragonite, and opal. Studies using superconducting magnetometry also indicate the presence of ferromagnetic minerals in tissues of butterflies, shrimps, barnacles, bats, rodents, and humans (Kirschvink 1981, MacFadden & Jones 1985, Buskirk & O'Brien 1985, Perry et al 1985, Buchler & Wasilewski 1985, Bauer et al 1985, Mather 1985). Recent discoveries have shown that magnetosomes or magnetosomelike structures are not confined only to the bacteria, but are also present in magnetotactic protoctists (Torres de Araujo et al 1986, Vali et al 1987) and in higher animals such as pelagic fish (Mann et al 1988). As in the bacteria, the magnetophysical properties of these structures are consistent with their roles as biological "bar magnets" and probably have a geomagnetic sensory function.

#### *Characteristics of Biogenic Magnetite*

With the exception of one species of chiton and framboidal spheres in some turtles and cetaceans, all of the biogenic magnetite particles that have been characterized with transmission electron microscopy (TEM) to date have dimensions that fall in the relatively narrow single-domain stability field of magnetite (Figure 1). This is a fundamentally important observation for the fields of rock magnetism and paleomagnetism, as single-domain magnetite particles are the most desirable carriers of NRM in rocks. This average grain size has been interpreted as the result of natural selection on the magnetic properties of the crystals by organisms that use their internally formed magnetite for geomagnetic sensitivity of some sort (Kirschvink & Lowenstam 1979, Kirschvink 1983).

The crystal morphology of biogenic magnetite crystals formed by magnetotactic bacteria, chitons, and pelagic fish has been studied in most detail at present, as illustrated in Figure 2. In the bacteria, three distinctive particle morphologies have been reported: subrounded cubes and rectangles (Balkwill et al 1980); hexagonal prisms with flat ends (Towe & Moench 1981, Matsuda et al 1983); and "teardrop," "bullet," or irregular

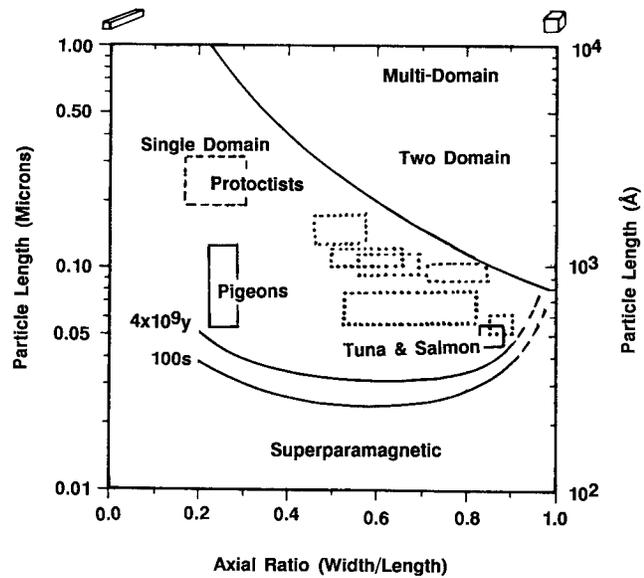
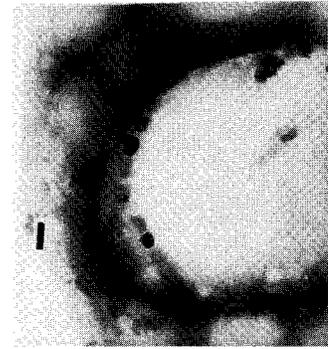
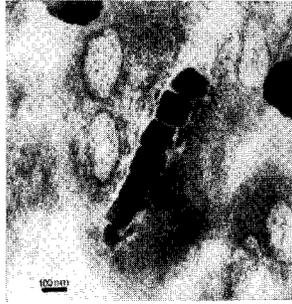


Figure 1 Size and shape distribution of magnetite particles formed by magnetotactic protists, pigeons, pelagic fish, and bacteria as plotted into the domain stability field diagram for magnetite (Butler & Banerjee 1975). Dotted outlines show the shapes and sizes for various types of magnetic bacteria as compiled by McNeill et al (1988).

shapes (Blakemore et al 1981). All of these forms clearly are distinct from the octahedral, spherical, and framboidal magnetite particles that commonly form through igneous, cosmic, and authigenic processes in nature. Some of the bacterial particles may even have small inclusions of organic material trapped within the lattice, forming a distinctive "halo" structure (Towe & Moench 1981). Similarly, Walker et al (1984, 1985) and Mann et al (1988) found that the magnetite particles extracted from pelagic fishes have shapes and sizes resembling those of magnetotactic bacteria (Figure 3). Finally, magnetite particles in the chiton teeth appear to grow until they are flush with the organic matrix wall and have no euhedral crystal faces expressed at all (Figure 4). In summary, all of the ultrafine-grained biogenic magnetite crystals examined to date appear to be easily distinguishable on simple morphological grounds from their inorganic counterparts. Of course, the membrane-bound linear arrangement within a magnetosome is an unequivocal result of biological activity.

Lowenstam (1981) noted that mineral-forming mechanisms used by organisms range from biologically induced to matrix mediated. Biologically induced minerals have crystal habits and chemical signatures

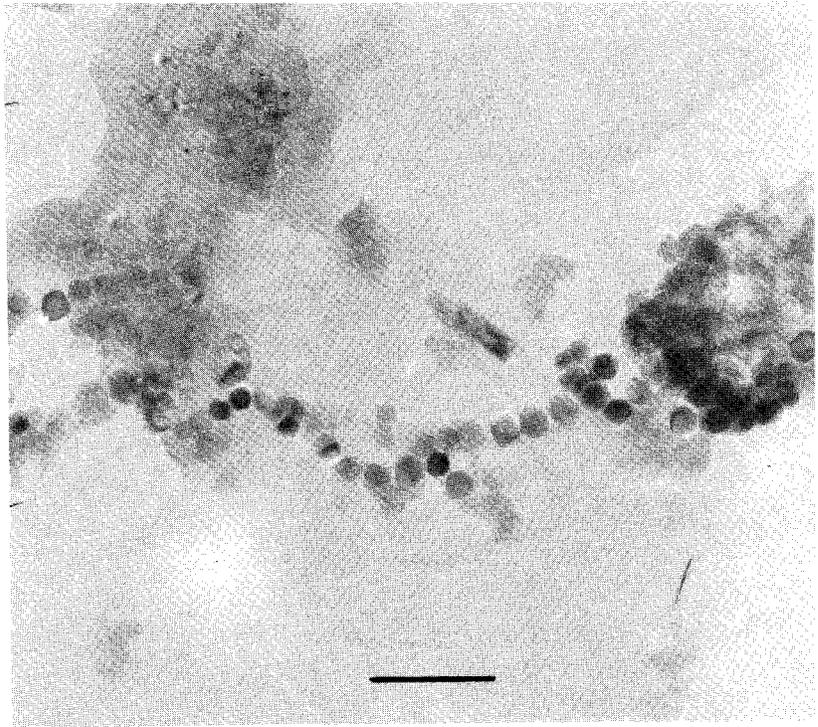


(C)



Figure 2 (A) Magnetotactic bacteria collected from Laguna Figueroa, Baja California, Mexico, showing internal chain of cuboidal magnetite crystals; (B) magnetotactic bacteria collected from the intertidal zone of Sugarloaf Key, Florida, showing internal chain of magnetite crystals with hexagonal parallelepiped in shape; (C) magnetovibrio from Santa Barbara Basin, California, showing internal chain of irregular-shaped magnetite crystals. All bars are 100 nm; micrographs courtesy of J. Stolz.

that are governed by the same equilibrium principles that control the crystallization of their inorganic counterparts. Organic activity aids the crystallization of these minerals, but the level of biochemical control for their formation is relatively low. On the other hand, matrix-mediated minerals are grown in a preformed organic framework (the matrix). A high level of biochemical control makes their sizes, shapes, and chemical signatures distinguishable from their inorganic counterparts. As a result of their unique shapes, biologically formed magnetite particles are clear examples of matrix-mediated biogenic minerals. Studies of the isotopes of oxygen on the magnetite particles formed by magnetotactic bacteria show no biological fractionation from the in situ water (J. R. O'Neil, personal communication). On the other hand, the isotopic ratio for chiton teeth



*Figure 3* Chain of cuboidal magnetite particles extracted from sockeye salmon, *Oncorhynchus nerka* (Walker et al 1988, Mann et al 1988). Scale bar is 100 nm; micrograph courtesy of S. Mann.

has been reported to be about 7‰ more positive (O'Neil & Clayton 1964) than the theoretically derived equilibrium value for magnetite formed at low temperatures (Becker & Clayton 1976); this difference, however, may be a result of the difficulty in separating the magnetite in the teeth from other iron-oxide minerals (such as goethite and lepidocrocite) that were also present in the sample analyzed (H. Lowenstam, personal communication).

### 3. THE SEARCH FOR MAGNETIC MINERALS IN MARINE SEDIMENTS

#### *Early Extraction and Scanning Electron Microscopy Studies*

Although magnetite is a common phase in igneous and metamorphic rocks, in most fine-grained sediments it is only present in very small

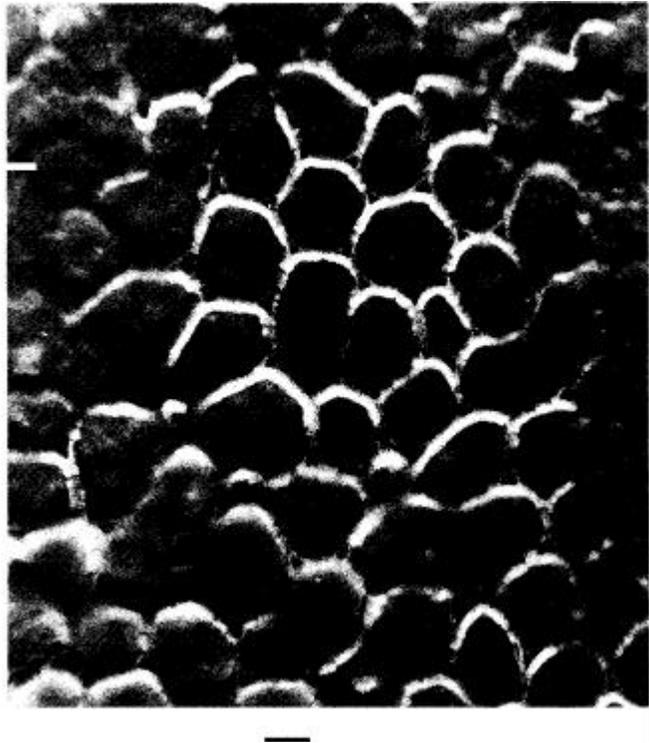


Figure 4 Magnetite crystals formed by the chiton, *Cryptochiton stelleri* (Towe & Lowenstam 1967, with permission). Scale bar is 100 nm.

concentrations (typically < 0.01 %). Despite these low concentrations, its high saturation magnetization (48 mT) makes it an important carrier of natural remanent magnetization. Although the typical size range of the particles may vary from 0.05 to 100  $\mu\text{m}$  in fine-grained sediments, only the particles at the smallest end (about 0.05-0.15  $\mu\text{m}$  across) are suitable for producing a stable magnetic remanence. These particles fall within the size range for single-domain behavior, which means that individual particles are magnetized uniformly and capable of preserving the direction of their magnetic moment for long periods of geologic time (Neel 1955, Butler & Banerjee 1975). With the possible exception of slightly larger pseudosingle-domain grains, other particles with sizes falling in the multidomain field are far less stable magnetically and often have a much lower net magnetization.

The fine grain size and small concentration of single-domain magnetite particles in rocks make them impossible to identify with petrographic

techniques. Paleomagnetists, therefore, have tried a variety of techniques to separate and purify magnetic particles from sediments for observation with electron microscopy. However, most attempts to extract magnetic particles have been plagued with low efficiencies in the fine to ultrafine size range and incomplete separation of magnetic minerals from other components of the sample. In some cases, only a small fraction of the total magnetic material has been isolated, and the particles that are removed fall at the large end of the grain size distribution. Compounding these extraction problems, several workers have used scanning electron microscopy (SEM) rather than TEM to characterize these extracted particles. With SEM it is easy to identify particles larger than 0.5  $\mu\text{m}$  in size (i.e. the pseudo-single-domain to multidomain range for magnetite), and it is no surprise that all such studies reveal objects of either terrigenous, volcanic, or authigenic origin (Lowrie et al 1971, Lowrie & Heller 1982, McCabe et al 1983). However, only SEM studies of exceptional quality have the ability to resolve the shape of particles in the single-domain size range (e.g. Matsunaga 1986).

#### *Fine-Grained Magnetite in Deep-Sea Sediments*

Rock magnetists have devised a variety of indirect techniques, based on magnetic properties, to recognize the presence of single-domain magnetite particles (e.g. Cisowski 1981, Collinson 1983). The presence of single-domain magnetite in deep-sea sediments and limestones detected this way has been documented extensively by Lowrie & Heller (1982) and Petersen et al (1986). However, the origin of this single-domain magnetite has not been determined until recently.

Several cases of inorganically formed, single-domain magnetite have been discovered by direct TEM examination of ionization-thinned sections of igneous rocks and meteorites. These include (a) ellipsoidal magnetite inclusions in the clouded plagioclase of a Precambrian Greenland metadolerite (Morgan & Smith 1981), (b) octahedral titanomagnetite particles found in Mid-Atlantic Ridge basalt glass (Smith 1979), and (c) octahedral magnetite crystals in a C2M carbonaceous meteorite named Code Bokkeveld (Barber 1981). However, none of these inorganic sources is likely to provide a significant contribution of ultrafine-grained magnetite to marine sediments for at least three reasons. First, meteoritic material is scarce, even in deep-sea sediments with slow sedimentation rates. Second, magnetite of single-domain size probably will be kept in suspension by the slow motion of oceanic bottom water. By applying the experimentally determined relationships between deposition, transportation, erosion, and current velocity for sediment particles ranging from 100  $\mu\text{m}$  to 8 mm and extrapolating down to particles in the 10- $\mu\text{m}$  size range, Amerigian (1974)

was able to obtain a grain-size distribution diagram of magnetite particles that would be deposited under various bottom current velocities. According to these calculations, current velocities on the order of 0.1-0.2 cm s<sup>-1</sup> would tend to inhibit deposition of magnetic particles less than 0.5 μm across. Only under extremely calm conditions (e.g. bottom current velocity < 0.01 cm s<sup>-1</sup>) should magnetite particles as small as 0.05 μm be deposited. Third, the chemical alteration of continentally derived single-domain magnetite crystals during settling might prevent the crystals from reaching the seafloor. Magnetite reacts in oxygenic waters to form maghemite and/or hematite. Studies of the magnetization of red beds show that this alteration process could occur in intervals as short as 500 to 5000 yr (Walker et al 1981), and a simple Stokes' law calculation indicates that it would require up to 10,000 yr for a 0.05 μm magnetite particle to settle through the water column to the deep-sea floor (although biological processes could act to sequester it on a faster time scale). Moreover, ferrous ions generally are released more easily from their mineral states and oxidized to form ferric ions in aqueous aerobic environments (Murray 1979). Given their large surface/volume ratios and long settling times, it is probable that single-domain magnetite particles will be altered completely during the settling process. It seems doubtful that igneous single-domain magnetite particles brought out to sea by wind or river transport would survive alteration unless their vertical settling through the water column is aided by incorporation into organic materials or anaerobic conditions prevail throughout the water column.

Authigenesis is another possible source of ultrafine-grained magnetite in marine sediments. Sugimoto & Matijevic (1980) have been able to precipitate successfully single-domain octahedral magnetite from aqueous solution. However, the conditions required for this artificial synthesis (> 90°C with excess OH<sup>-</sup>) of single-domain magnetite are rarely encountered in nature.

#### *Estimates for the Contribution of Biogenic Magnetite to NRM*

Summarizing the above arguments, we see that inorganically formed single-domain magnetite is not likely to be a major source of ultrafine-grained magnetite in marine sediments. On the other hand, magnetite crystals precipitated biochemically by the magnetotactic bacteria and protoctists are a potential source of this ultrafine-grained fraction in deep-sea sediments. Extant bacteria have been found living in both marine and freshwater environments, principally in the poorly oxygenated zone near the mud-water interface (Blakemore 1975, 1982, Moench & Konetzka 1978). They exist in both the Northern and Southern Hemispheres and at the geomagnetic equator (Kirschvink 1980, Blakemore et al 1980, Frankel et

al 1981), and they have been found in open marine environments (Stolz et al 1986).

Using a simple calculation based on typical sedimentation rates, bacterial cell abundance, growth rates, and estimates for the average volume of magnetite per cell, Kirschvink & Lowenstam (1979) have estimated the bacterial contribution to remanence in sediments to be about  $10^{-5}$ - $10^{-4}$  A m<sup>-1</sup>. Lowrie & Heller (1982) cautioned that these values might be overestimated because the sedimentation rates in most depositional environments are higher than the rate (10<sup>-3</sup> cm yr<sup>-1</sup>) assumed by Kirschvink & Lowenstam (1979). However, the revised values (10<sup>-6</sup>-10<sup>-5</sup> A m<sup>-1</sup>) in Lowrie & Heller's (1982) estimations are still comparable to the magnetic remanence generally found in sediments, and local environmental variation could alter greatly the bacterially contributed remanence value.

#### *Discovery and Distribution of Bacterial Magnetofossils*

Shortly after the discovery of magnetotactic bacteria by Blakemore (1975), Kirschvink & Lowenstam (1979) proposed that the unique crystals these bacteria produce could be preserved in sediments and contribute to the depositional magnetic remanence. However, the active search for fossil bacterial magnetite in sediments was first stimulated by studies of geomagnetic field behavior during transitions as recorded in sediments. The ability of sediments to record accurately the geomagnetic field depends on the constant influx of suitable magnetic carriers; consequently, the magnetic mineralogy of sediments deposited during transitions has been studied carefully. In one of the geomagnetic field transition studies conducted by Valet & Laj (1981) on the marine clays of the Potamida section in northwestern Crete, a decrease of the ultrafine-grained magnetite flux during the transition was revealed by detailed rock magnetic measurements. Kirschvink (1982) proposed that the remanence carrier of the Potamida clay was produced bacterially, and that the reduced geomagnetic field intensity during the transition leads to a temporary decrease in the population density of magnetotactic bacteria. To test this hypothesis, Chang & Kirschvink (1985) developed various extraction techniques and employed TEM to study the magnetic mineralogy of the Potamida section. Although many types of magnetite particles with widely varying sizes and shapes were present, they found abundant single-domain prismatic crystals with hexagonal cross sections in sediments deposited during nontransitional periods. Even though these single-domain particles were not aligned in chains, as are the crystals in magnetosomes, their crystal morphologies were characteristic of a biogenic origin.

Kirschvink & Chang (1984) then applied their extraction techniques to study the magnetic mineralogy of Deep-Sea Drilling Project (DSDP) Leg

73 cores and a variety of other marine sediments. Single-domain cuboidal magnetite crystals, presumably having a bacterial origin, were found to be particularly abundant in calcareous ooze. Petersen et al (1986) and von Dobeneck et al (1987) extended this work, developing a milder magnetic extraction technique, and were able to recover intact "teardrop" or "bullet" shape and hexagonal parallelepiped single-domain magnetite crystals from DSDP Leg 73 cores. Some of the magnetite crystals they extracted were still aligned in a chain, as in the original bacterial magnetosome, which provided unambiguous confirmation of their biogenic origin. Meanwhile, Stolz et al (1986, 1988) discovered magnetotactic bacterial magnetite in three recent marine environments, including (a) organic-rich muds from an open marine basin off the California coast (Santa Barbara Basin); (b) carbonate oozes from Sugarloaf Key, Florida, a "typical" carbonatedepositing environment; and (c) laminated algal mats from a hypersaline lagoon (Laguna Figueroa) in Baja California, Mexico, a well-known and well-studied present-day analog of a Precambrian stromatolite-forming environment. They also conducted surveys on the occurrence of bacterial magnetite in a variety of other recent aquatic environments and were able to recover intact magnetosomes from the muds.

Table 1 summarizes the known occurrences of bacterial magnetite in

**Table 1** Occurrences of bacterial magnetite in modern sediments

Locality <sup>a</sup>	Sediment type	Bacteria	Extract	Magne- tometry <sup>b</sup>
Laguna Figueroa, Mexico (1)	Laminated, microbial mat	Cocoid, rod "mulberry"	Prismatic	SD, MD
Sugarloaf Key, Florida (1)	Stromatolitic nodules	Cocoid, rod "mulberry"	Hexagonal	SD
Santa Barbara Basin, California (2)	Open ocean sediments	Vibrio, rod cocoid	Prismatic cuboidal	SD
Palma Solo Pond, Bahamas (3)	Carbonaceous sediments	N.D. <sup>c</sup>	Prismatic euhedral	SD
Shark Bay, Australia (4)	Laminated, microbial mat	N.D.	Prismatic	SD
Walker Lake, Nevada (4)	Stromatolite, lacustrine	N.D.	Prismatic	SD

<sup>a</sup>References (in parentheses):

1. Stolz et al 1988, Chang et al 1987.

2. Stolz et al 1986.

3. R. Ginsburg, University of Miami, Florida.

4. S. Awramik, University of California, Santa Barbara.

<sup>b</sup>SD, single-domain magnetite; MD, multidomain magnetite.

<sup>c</sup>N.D., not determined.

recent sedimentary environments, and Table 2 lists the reported occurrences of bacterial magnetite in many ancient sediments. Similarly, Figures 5 and 6 show single-domain bacterial magnetite crystals extracted from some of these recent and ancient sediments, respectively. To date, the oldest clear occurrence of magnetofossils yet found is a chain of single domain cuboidal magnetite particles extracted from limestone of the ~ 700 Ma Nama Group of South Africa (Figure 6C). Chains of single-domain magnetite particles with less regular outlines and dimensions have also been identified in the magnetic extracts of limestone from within the ~ 2.0 Ga Gunflint Iron Formation of Canada, but the origin of these particles is less clear (Figure 6D). One possibility, however, is that these more irregular crystals date from a time when the biological control of the mineralization process had not yet evolved the ability to make more regular particles.

### *Preservation of Bacterial Magnetite in Marine Sediments*

It is clear from the preceding discussion that bacterial magnetite has a widespread distribution among recent and ancient sediments. However,

**Table 2** Occurrences of fossil bacterial magnetite particles

Formation and location <sup>a</sup>	Age	Description	Extract	Magnetometry <sup>b</sup>
Ocean sediment, Bahamas (1)	Pliocene	Carbonate sediments	Cuboidal, teardrop	SD
Potamida Clay, Crete (2)	Miocene	Marine clays	Prismatic, hexagonal	SD, MD
DSDP 522 core, South Atlantic (3)	Oligocene	Deep-ocean sediments	Cuboidal, euhedral	SD, MD
DSDP 523 core, South Atlantic (4)	Eocene	Deep-ocean sediments	Prismatic, teardrop	SD, MD
Sinskian, Siberia, USSR (5)	Cambrian	Black marine limestone	Cuboidal	SD
Nama, South Africa (6)	700 Ma	Black limestone	Cuboidal	SD
Gunflint, Canada (7)	2000 Ma	Stromatolitic chert	Cuboidal, octahedral	SD, MD

<sup>a</sup>References (in parentheses):

1. McNeill et al 1988.
2. Chang & Kirschvink 1985.
3. Kirschvink & Chang 1984.
4. Petersen et al 1986.
5. Chang et al 1987.
6. S. Grant, Harvard University, Cambridge, Massachusetts.
7. S. Awramik, University of California, Santa Barbara.

<sup>b</sup>SD, single-domain magnetite; MD, multidomain magnetite.

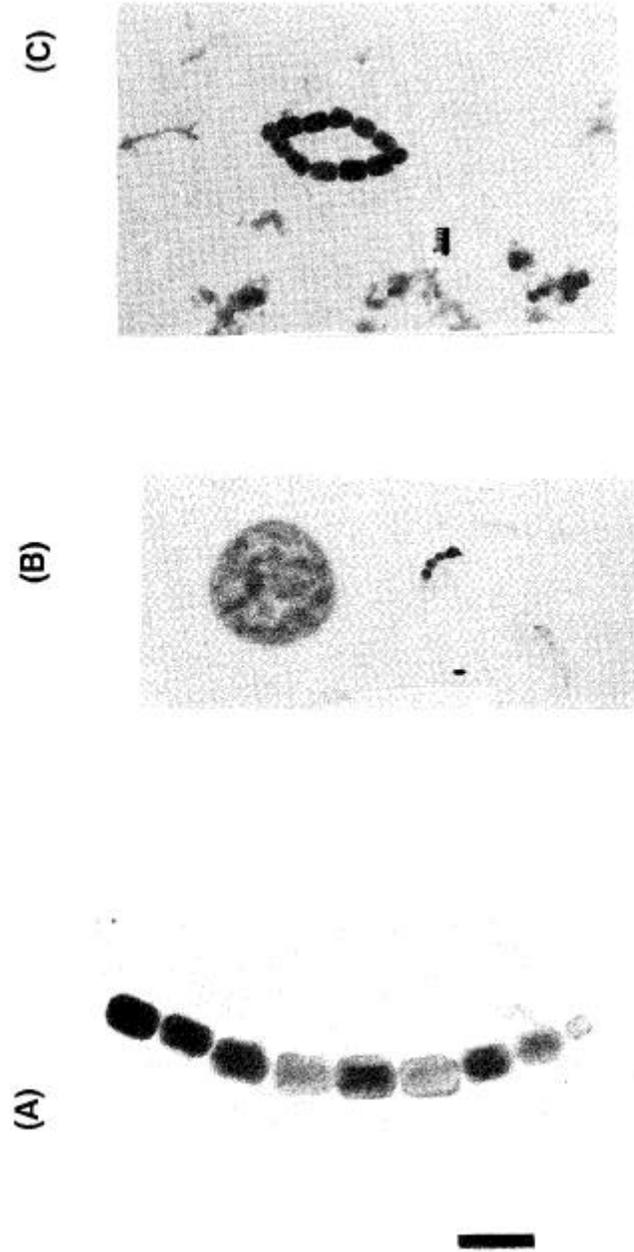
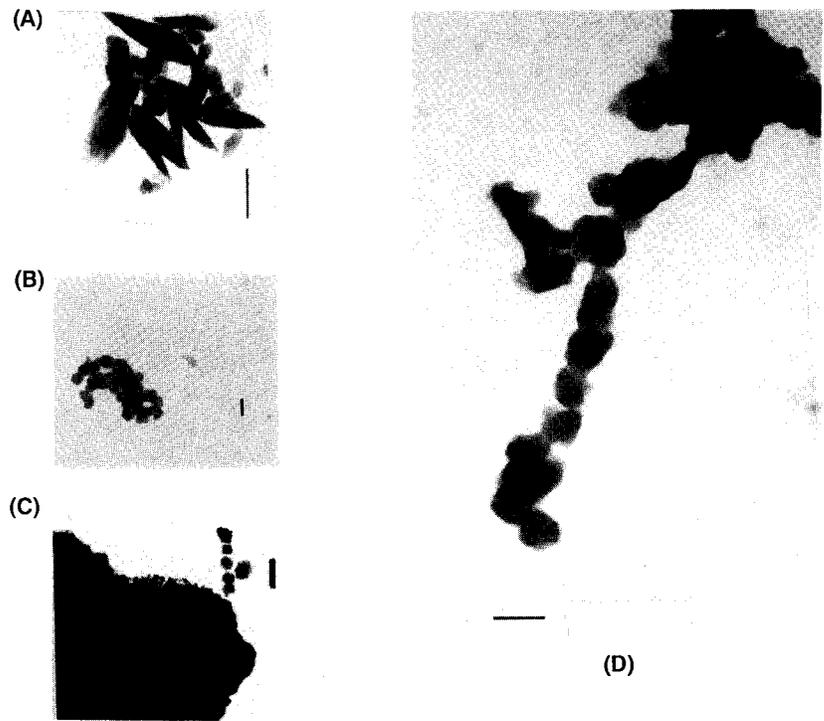


Figure 5 Bacterial magnetite from modern marine environments. (A) Chain of crystals, which appears to be an intact magnetosome, extracted from Santa Barbara Basin, California; (B) extracted magnetosome from sediments in Sugarloaf Key, Florida; (C) bacterial magnetite crystals extracted from the surface sediments of Laguna Figueroa, Mexico. All scale bars are 100 nm.



*Figure 6* Selected ultrafine-grained magnetite occurrences in ancient sediments. (A) Carbonate core sample from San Salvador Island, Bahamas; (B) core sample from DSDP site 522, Section 1, 80-82 cm; (C) limestone from Nama Group, South Africa; (D) limestone from Gunflint Iron Formation, Canada. All scale bars are 100 nm.

the chemical instability of fine-grained magnetite should reduce the potential for its preservation in certain environments. In an aerobic environment, for example, bacterial magnetite could alter easily to maghemite or hematite; and in a 142S-rich environment, it might react to form greigite ( $\text{Fe}_3\text{S}_4$ ) or a variety of Fe-sulfides (Canfield & Berner 1987). In some deep-sea sediments, the surface layer of bacterial magnetite particles appears to have altered to form maghemite (Kirschvink & Chang 1984). On the other hand, Demitrack (1985) observed that the greigite grains preserved in Eel Marsh, Massachusetts, have the same size and shape distributions as those

of the bacterial magnetite particles. She interpreted these grains to be chemically altered pseudomorphs of the original bacterial magnetite crystals. Ghiorse (cited in Blakemore 1982) has also found as yet unidentified mineral particles with shapes similar to those of bacterial magnetite particles both inside and outside bacterial cells associated with manganese nodules in Oneida Lake, New York. However, partial conversion of singledomain magnetite to maghemite does not influence the direction of the particle moment because there is a complete electronic spin-coupling between the lattices. Indeed, if the geometry of the crystals is still preserved, they can still be recognized as magnetofossils that preserve a stable NRM. On the other hand, the formation of hematite and perhaps greigite might lead to the acquisition of secondary or viscous magnetic components.

Under reducing conditions, the ferric ions in bacterial magnetite crystals might be reduced to form ferrous ions and released away from sediments. Karlin & Levi (1983, 1985) and Lund et al (1983) have found a dramatic decrease in the ultrafine-grained portion of magnetite with depth in sediments from the California Continental Borderlands and the Gulf of California. They explained this disappearance as the result of iron oxide reduction coupled with the decay of organic materials. If this is the case, there should be an inverse correlation between the abundance of ultrafine-grained magnetite and the original total organic carbon (TOC) content of the sediments. One way of testing this idea is to compare those sediments known to preserve magnetofossils with some measure of the original TOC level. Johnson-Ibach (1982) has compiled analyses of TOC in numerous **DSDP** core samples and has obtained a semiquantitative relationship between TOC and the sedimentation rate. Generally speaking, TOC decreases with increasing sedimentation rate as a result of the clastic dilution of an otherwise fairly constant organic input. In the same study, Johnson-Ibach found that at a given sedimentation rate the TOC by weight percent increases from calcareous sediments to calcareous-siliceous sediments to siliceous sediments to black shales. If one then assumes a relatively constant supply of ultrafine-grained magnetite from magnetotactic bacteria through time (as might be expected from a constant flux of nutrients), the bacterially produced particles should appear to be most abundant and best preserved in calcareous sediments with high sedimentation rate. This is consistent with results from studies on the bacterial magnetite occurrences in deep-sea sediments (Kirschvink & Chang 1984, Petersen et al 1986).

In summary, bacterial magnetite crystals should be preserved in some depositional environments. In turn, the presence of bacterial magnetite in sediments might be of use as a paleoenvironmental indicator, as well as in providing the sediments with a depositional remanent magnetization.

### *A Paleomagnetic Stability Test*

If magnetofossils are capable of providing a depositional remanent magnetization to sediments, then they must preserve somehow their spatial orientations relative to the rock matrix. On the other hand, if thermal, chemical, or physically disruptive events are strong enough to alter or destroy the bacterial magnetite crystals, the simple presence or absence of magnetofossils could serve as a useful guide to test for the presence of depositional remanent magnetization in samples used for paleomagnetic study. Interestingly, all samples and formations from which clear magnetofossils have been extracted to date appear to preserve a primary, depositional magnetization. Conversely, no unit that clearly flunks one of the **standard paleomagnetic field** tests has yet produced anything resembling a magnetofossil. Of course, we know of many sedimentary rock units that appear to have a stable, primary NRM but that do not contain magnetofossils; hence, the presence of abundant magnetofossils may indicate a primary NRM, whereas their absence is not conclusive.

### *Magnetotactic Bacteria, the Geomagnetic Equator, and Geomagnetic Reversals*

Two interesting questions concerning the role of magnetofossils in producing the NRM of sediments relate to the relative viability of magnetotactic organisms on the geomagnetic equator and during geomagnetic reversals. Frankel et al (1981) were the first to report the presence of the magnetotactic bacteria in localities close to the geomagnetic equator (inclination  $< 4^\circ$ ). They found that populations of these bacteria contained roughly equal numbers of north-seeking and south-seeking organisms, with a variety of morphological types. However, it was not possible for them to compare the relative population *densities* of magnetotactic organisms between sites of varying magnetic inclination, as the sites were separated by large distances and did not have homogeneous sediment compositions. Although magnetotactic bacteria clearly survive in areas with low magnetic inclination, this does not imply that their contribution of magnetofossils to sediments will continue at the same level.

To answer this question, one of us (JLK) recently studied the magnetotactic bacteria in a shallow saltwater pond used for fish aquaculture experimentation at the Micronesian Mariculture Demonstration Center (MMDC) on the island of Koror, Republic of Palau, West Caroline Islands. This locality is very close to the geomagnetic equator, with a nearly horizontal magnetic inclination of only  $-2.1^\circ$  (magnetic north is slightly upward, as in the Southern Hemisphere). Although the bottom of this 14 m x 16 m rectangular earthen pond is flat over most of its area, it

slopes appreciably along the margins, with dips of up to  $30^\circ$ . Relative to the bottom, therefore, the local magnetic field intersects at angles ranging between about  $+30^\circ$  and  $-30^\circ$ . The pond is supplied continuously with fresh seawater, and the bottom is covered nearly everywhere with a thin layer of black organic-rich mud. In a single, homogeneous pond we therefore have an ideal environment for determining how the population of magnetotactic bacteria varies with the inclination angle of the local magnetic field.

As expected, north-seeking magnetic bacteria dominated the population in samples collected from the sloping northern margin of the pond by a ratio greater than 10 (north vs. south seeking), whereas south-seeking bacteria displayed a similar preference for the southern margin. Mud samples from the flat, central area of the pond and from the eastward west-sloping margins (where the magnetic field was also nearly tangent to the mud surface) had roughly equal numbers of north- and south-seeking organisms. However, samples from both the northern and southern margins had far higher concentrations of bacteria, by factors estimated to be on the order of 100-1000, than did those from elsewhere within the pond. Surface mud from these localities produced visible bacterial concentrations when separated from the mud by a pair of small bar magnets (e.g. Moench & Konetzka 1978), whereas otherwise indistinguishable samples from the other localities produced no visible aggregation and required microscopic observation to verify the presence of magnetotactic organisms. Inclination angles with a magnitude of  $5^\circ$  or more between the field and the mud surface were sufficient to bias the swimming preference of the bacteria, as well as to yield much higher population densities.

These observations have clear implications for the paleomagnetism of sediments deposited in low latitudes, as well as those deposited during a geomagnetic reversal. During the course of the normal secular variation in the geomagnetic field, the passage of the magnetic equator across a site should produce an abrupt drop in the relative concentration of magnetic bacteria in the sediments and hence a drop in the concentration of magnetofossils. If the remanent magnetization is preserved faithfully at the time of deposition, samples with low NRM inclinations should also have relatively lower NRM intensity. On the other hand, postdepositional recording of the field would cause the inclination low to appear slightly before the intensity drop. A geomagnetic reversal should produce a similar effect because at any point at the Earth's surface, the field must rotate through horizontal sometime during the transition process. In addition, the associated drop in overall intensity of the field during reversals should also reduce the selective advantages of magnetotaxis (Kirschvink 1982) and may yield an additional decline in magnetofossil concentra

tion. Valet & Laj (1981) discovered a decrease of this sort in the concentration of fine-grained magnetite during a geomagnetic reversal in Crete, in sediments that were later found to contain biogenic magnetite (Chang & Kirschvink 1985). Similar studies obviously should be conducted on low-latitude deposits.

#### 4. EVOLUTIONARY IMPLICATIONS OF MAGNETITE BIOMINERALIZATION

From the preceding discussions, it is clear that magnetite is unique among biogenic materials. It is found as a biochemical precipitate in three of the five kingdoms of living organisms (Monera, Proctista, and Animalia) but has not yet been recorded in the higher plants and fungi. As can be seen by comparing the magnetosomes in Figures 2 and 3, the ultrastructure of the magnetite can be remarkably similar in widely divergent groups. In addition, several unique crystal forms are present in more than one kingdom, including pseudo-hexagonal prisms, "teardrop" or "bullet" shaped blobs, and truncated octahedra (cuboidal). In bacteria and fish, the crystallographic axes are often aligned along either the [111] or [112] directions, orientations that yield slightly higher magnetic moments per unit volume of the magnetite (Matsuda et al 1983, Mann et al 1984a,b, 1987b, 1988, Mann 1985). Our growing knowledge of the record of fossil magnetite, although still sketchy, indicates that the biochemical ability arose during the Precambrian and therefore may have been possessed by the last common ancestor of the magnetotactic bacteria, protoctists, and animals.

At the risk of engaging in undue speculation, we think it worthwhile to develop an evolutionary hypothesis that might aid in understanding how such divergent groups of organisms came to possess morphologically similar structures. Coupled with this are questions such as how magnetite biomineralization evolved originally, and what relationship this biochemical system has, if any, to the numerous other matrix-mediated biominerals that are found in living organisms today. Our first-order model, outlined in the following discussion, is an attempt to place these events within the framework of Earth history.

Figure 7 is a summary of this scenario. Geologic time is shown along the vertical axis in units of 10<sup>9</sup> years, along with some of the major events in Earth history that may have influenced magnetite biomineralization. These include (a) the origin of the Earth at 4.5 Ga; (b) the oldest sedimentary rocks from the Isua complex of Greenland at 3.8 Ga; (c) the major deposition of the banded iron formations at 2.5-2.0 Ga, which presumably

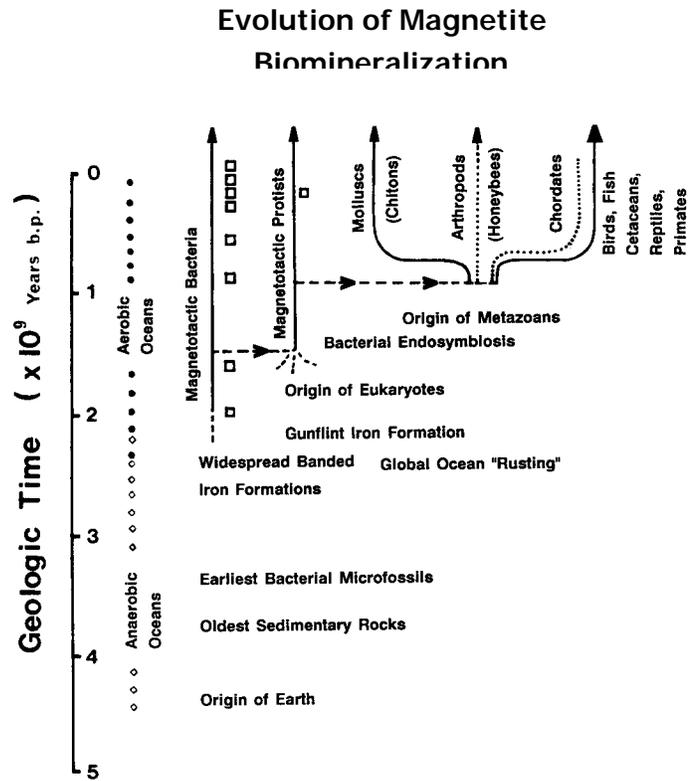


Figure 7 Proposed evolutionary scenario of magnetite biomineralization.

corresponds to the time in which the bulk of the deep oceanic water mass changed from anaerobic to more aerobic conditions; (d) the endosymbiotic origin of eukaryotic cells at about 1.6 Ga; (e) the diversification of metazoan phyla at - 0.9 Ga; and (f) the widespread appearance of diverse biomineralization at the Precambrian-Cambrian boundary at - 0.6 Ga. Along with this summary, the fossil record of biogenic magnetite is shown by the small squares along the evolutionary line of the magnetotactic bacteria. As discussed earlier, numerous magnetofossils have been found in Recent, Tertiary, and Mesozoic marine sediments. The oldest, clearly bacterial assemblage yet found is in sediments from the Nama Group (-700 Ma; Figure 6), although less regular chains of magnetite have been recovered from rocks as old as the Gunflint Iron Formation (- 2 Ga; Figure 6).

We think that the initial evolution of magnetite biomineralization may

have been triggered as a consequence of the gradual increase in the oxidation state of the Earth's surface. Although anaerobic organisms may under some restricted conditions catalyze the *extracellular* formation of magnetite (Lovley et al 1987), all known magnetotactic bacteria are microaerophilic, or at least facultative aerobes, and in *Aquaspirillum magnetotacticum* trace quantities of O<sub>2</sub> are required for magnetite formation (Blakemore et al 1985). Why is this so? Most plausible schemes for the origin of life assume that the early Earth possessed a highly reducing environment (e.g. Walker et al 1983, Chang et al 1983) that would be suitable for the abiotic synthesis of a variety of organic molecules. Life would therefore evolve in an environment where ferrous iron was highly soluble, and organisms could incorporate it easily into a variety of essential biochemical functions, as indeed they have. However, the gradual increase of oxygenic conditions with time on the surface would lead to a drastic decrease in the availability of dissolved iron, and the newly evolving aerobic and microaerophilic organisms would be forced to gather their metabolic iron against increasingly stringent concentration gradients. Microaerophilic and aerobic bacteria have, in fact, developed an array of highly efficient iron-gathering agents (siderophores) that are excreted into the surrounding medium for the purpose of chelating iron (Neilands 1977, Raymond & Carrano 1979). The molecules with their bound iron are then reabsorbed by the bacteria. Competition among different strains of bacteria is so intense, however, that some strains have developed compounds to inhibit the action of siderophores generated by their competitors!

In this environment, a motile bacterium with the ability to store iron when it could find it for use when it was scarce would have a clear competitive advantage over those organisms with no such ability. Hence, we would expect natural selection for iron storage among the microaerophilic bacteria. At this point three things are worth noting: First, bacterial storage vacuoles have a wide range of sizes, some of which overlap with the single-domain stability field of magnetite (0.04-0.1  $\mu\text{m}$ , as shown in Figure 1). Within these vacuoles, the iron probably would be stored in a cryptocrystalline ferric form like ferrihydrite, similar to that found in the core of the iron storage protein, ferritin, a protein that is known from both prokaryotes and eukaryotes (Stiefel & Watt 1979) but that has not yet been identified in magnetotactic bacteria. Second, in a closed, organic-rich environment of this sort it should be easy to produce conditions that favor the spontaneous crystallization of magnetite (e.g. Mann 1985, Couling & Mann 1985), or else it can be converted from the ferric iron by use as a terminal electron acceptor (Lovley et al 1987). Thus, it is possible that the early attempts at bacterial iron storage resulted in

the accidental formation of intracellular magnetite crystals, which provided the cell with a small but stable magnetic moment. Although these crystals would be far less soluble than the cryptocrystalline ferrihydritelike material, and hence not as useful for iron storage, the subsequent natural selection for magnetotaxis eventually should yield single-domain crystals. Cells with larger moments would have better orientation characteristics, so further selection would favor larger crystals or linear strings of these magnetite particles such that their individual magnetic moments would add together vectorially and make a large net magnetic moment. However, crystals larger than about 0.1  $\mu\text{m}$  in diameter will break down spontaneously into two or more magnetic domains with a much smaller magnetic moment, as indicated in Figure 1, so selection pressure to increase the cellular moment should favor the chainlike organization and eventually lead to something like a magnetosome. Finally, studies of the organic matrix of the bacterial magnetosomes have shown that the material is a membrane with characteristics of a protein-containing lipid bilayer (Balkwill et al 1980, Gorby et al 1988). Although this is at present the only organelle known from a prokaryote that is bound by a lipid-bilayer membrane, such structures are used commonly as storage vacuoles in eukaryotes.

The next major evolutionary step in the natural history of magnetite biomineralization concerns how this ability was obtained by the protoctists and higher animals. This distinction between the prokaryotes (bacteria and other organisms lacking nuclei) and eukaryotes (those with nuclei) is the largest discontinuity known in biology (e.g. Margulis & Bermudes 1985). It is agreed generally that the eukaryotes are related to the prokaryotes by descent, based on the detailed biochemical similarity of all life on Earth. Furthermore, ribosomal RNA nucleotide sequencing studies have shown clearly that two subcellular organelles in eukaryotes, mitochondria and plastids, originated as free-living bacteria (Grey 1983), even though many of their original genes are now found with the nuclear DNA. This and other evidence strongly supports the Serial Endosymbiotic Theory (SET), which holds that the eukaryotic cell formed through the association of aerobic respirers, oxygenic phototropic bacteria, and possibly spirochetes with a Thermoplasma-like host (Margulis 1981, pp. 233313; Margulis & Bermudes 1985).

Fossil evidence for the first eukaryotic planktonic organisms (acritarchs) begins in rocks of mid-Proterozoic age ( $\sim 1.6$  Ga; Vidal & Ford 1985), roughly 400 m.y. after the earliest known putative magnetofossils discussed earlier. It is therefore probable that magnetotactic bacteria were present during the formation of the first eukaryotic cells, and hence that they could have participated in the endosymbiosis. The recently discovered

magnetotactic prototists (Torres de Araujo et al 1986, Vali et al 1987) would then be the extant codescendants of these early eukaryotes. Similarly, at least three major animal phyla known to biomineralize magnetite (mollusks, arthropods, and chordates) could retain this early biochemical ability.

Finally, the sudden and widespread appearance of matrix-mediated biomineralization in many animal groups at or near the Precambrian-Cambrian boundary no longer demands the separate evolution of these matrix-mediated processes; rather, it would be simpler for organisms to combine existing structural genes that control the formation of the magnetosome with the calcium, phosphate, and carbonate systems to yield other mineral phases within a matrix-mediated framework. If this were so, the magnetite biochemical system may have been yet another evolutionary prerequisite for the onset of widespread Ca-based biomineralization, supplementing the calcium and microtubule regulatory systems as proposed originally by Lowenstam & Margulis (1980).

Although this evolutionary scenario is obviously speculative, at this stage it offers a simple framework for understanding a large variety of information concerning magnetite biomineralization. Furthermore, it leads to a variety of testable predictions, some of which are briefly worth mentioning. First, we should not find magnetotaxis in strictly anaerobic bacteria, as our model predicts that this should have arisen gradually in response to the increasing oxidation state of the oceans. An exception to this might arise if the information for producing magnetosomes were present on a plasmid that could be transferred from one bacterial species to another; however, there is as yet no evidence for this, and no strictly anaerobic magnetotactic bacteria have been reported to date. Second, magnetotactic bacteria depend on the presence of a magnetic field to maintain their alignment (e.g. Kirschvink 1982), so we would not expect them to have evolved prior to the time when the Earth developed a strong magnetic field. If the paleointensity data compiled by Hale (1987) are correct, the geomagnetic field might not have been strong enough to support magnetotaxis prior to about 2.8 Ga, and thus magnetofossils should not be present in older sediments. Third, our model predicts a common origin for the magnetite biomineralization system in three separate kingdoms; it should be possible to test this through studies of molecular homology. The presence of structurally similar magnetosomes in bacteria, prototists, and fish lends credibility to the idea that the magnetite system may have been conserved strongly, despite divergence times in the mid-Proterozoic. Should suitably homologous proteins or genes be found, it might be possible to use the molecular clock to constrain the time of origin of the eukaryotic cell, in a fashion analogous to that of Runnegar

(1982, 1986), who used the globin system to infer the divergence time of the animal phyla. Finally, our scheme suggests that magnetite could have been one of the earliest minerals to be formed within a membrane-bound vacuole, perhaps with matrix-mediated control. This raises the possibility that this component of other matrix-mediated biogenic minerals may have been adapted from the magnetite system. Again, studies of molecular homology could test this idea eventually by determining whether or not components of such other systems are indeed related, and whether or not magnetite lies at the common base of their evolutionary tree.

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