

BACTERIAL MAGNETITE IN SEDIMENTARY DEPOSITS AND ITS  
GEOPHYSICAL AND PALEOECOLOGICAL IMPLICATION

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This work is dedicated to

Mom and Dad;

My dear wife Jean;

and

Jeffrey and Kenneth

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Abstract

In the past two decades, natural remanent magnetization carried by marine sediments and sedimentary rocks has been used extensively to monitor the history of the geomagnetic field and to constrain motion of crustal plates. But the origin of the magnetic minerals contributing to observed remanent magnetization is only now being resolved. The main reason behind that is that representative magnetic extracts are hard to obtain from marine sediments for direct observation. Previous attempts to separate the magnetic carriers in sediments and to examine their granulometry under the scanning electron microscope (SEM) have revealed the existence of large detrital, diagenetic, and meteoritic magnetite particles. These studies, however, have been limited in their ability to recognize the more magnetically stable and smaller single-domain fraction (<0.1 micron in size) of magnetite particles. Meanwhile, the existence of single-domain magnetite grains as a major remanence carrier in a variety of marine sedimentary deposits has been shown by various rock magnetic methods, but the origin of these grains was not revealed. The major part of this thesis is devoted to the development of better extraction techniques, employing the higher resolution transmission electron microscope (TEM) to identify the presence and to study the origin of these ultrafine-grained magnetite particles in marine sediments. Special emphasis is paid to search for the existence of magnetite precipitated by magnetotactic bacteria and to determine its role as the remanence carrier in certain sediments.

Several new occurrences of living magnetotactic bacteria have been discovered and investigated. Among them, the organic-rich mud from a shallow marine basin off the California coast (the Santa Barbara Basin)

and the carbonate ooze from Sugarloaf Key, Florida are of particular interest. The former demonstrates that magnetotactic bacteria are able to live and flourish at depth in an open marine environment similar to that present over most of the world ocean floors; if the local marine sediments are able to preserve the bacterial magnetite particles, then they have an excellent chance for recording a stable remanent magnetization. The latter implies that there is a good chance for using magnetostratigraphy study on shallow water carbonates to unravel the history of their formation. In addition, the occurrences of magnetotactic bacteria and bacterial magnetite at a hypersaline lagoon (Laguna Figueroa) in Baja California, Mexico, a well-known and well-studied present-day analog of Precambrian stromatolites, suggest that stromatolites would be a good place to search for bacterial magnetofossils in Precambrian.

The magnetotactic organisms from all the newly studied occurrences have been isolated and examined. The magnetite crystals in them are similar in size and morphology to those previously found in magnetotactic bacteria from other environments. Three basic shapes of bacterial magnetite are cuboid, hexagonal prism, and tear-drop, which are all quite distinguishable from that (typical octahedra) of inorganically formed magnetite. In addition, all of the measured sizes of bacterial magnetite crystals fall well within the single-domain stability field of magnetite. It is this characteristic size and shape distribution of bacterial magnetite particles that enables the search for their occurrences in modern and fossil sedimentary records.

A set of calcite, aragonite, and recrystallized dolomite samples from Bahama Bank and a core sample from Laguna Figueroa that displays

interlayers of flood derived sediments and laminated mats are studied to determine the possible diagenetic effects on bacterial magnetite. Euhedral bacterial magnetite crystals have been found in all three types of sediments from Bahama Bank. Apparently, the recrystallization process does not change or alter the identity of bacterial magnetite. In Laguna Figueroa core samples, the bacterial magnetite has only been observed in the surface layer (where the living magnetotactic bacteria were found) and flood derived sediments. No bacterial magnetite was detected from laminated mat samples, and rock magnetic study shows the disappearance of a significant portion of ultrafine-grained magnetite through depth in them. Iron reduction coupled with the oxidation of organic materials, which are rich in laminated mats and relatively scarce in flood derived sediments, is one possible explanation for these observations.

Numerous deep sea core samples have been examined to identify the presence of bacterial magnetite particles. To date, the oldest undoubtedly bacterial magnetite assemblage detected in deep sea core materials is from Miocene ODP Leg 101 sample 633A-023X-03. Some bacterial magnetite-like crystals have also been isolated from Oligocene DSDP Leg 73 samples, but they are not aligned in a chain or clumped together like bacterial magnetite particles extracted from modern environments are. Among varieties of deep sea sediments being studied, bacterially formed single-domain magnetite grains are found to be most abundant in calcareous sediments with high sedimentation rate, which might reflect the enhancement of preservation potential of ultrafine-grained magnetite during the period when massive carbonate deposition diluted the concentration of organic materials.

Some possible implications of surveying the fossil occurrences of bacterial magnetite were explored. One of them is using the presence of bacterial magnetite as an independent magnetic stability indicator. It seems clear that bacterial magnetite crystals should preserve their spatial orientations and magnetic remanence directions relative to the rock matrix, unless they are disrupted by major events of thermal, chemical, or physical alteration, which would result in producing a strong secondary component in the sample. Several sets of samples that have been shown by conventional paleomagnetic or rock magnetic techniques to contain either one single primary component or one main primary component plus a weak secondary component are analyzed to test this possibility. Bacterial magnetite has been found well preserved in some of them (e.g., Neogene carbonate samples from the Bahamas, Miocene Potamida Clay of Crete, Cambrian Sinskian Formation of Siberian Platform, etc.). On the other hand, no bacterial magnetite was detected from samples with well-documented overprinting records (e.g., materials from the Great Basin, Morocco, and Newfoundland).

Because bacterial magnetite formation requires iron-mediating enzymes and certain amounts of free oxygen, to trace back the earliest occurrence of bacterial magnetite in Precambrian would support constraints on some important biochemical evolutionary sequences. Stromatolitic carbonate and chert samples with ages ranging from middle Archaean to late Proterozoic are studied. Euhedral bacterial magnetite chain has been found from Nama sedimentary rocks of South Africa (approximately 700-600 My) which represents the oldest bacterial magnetofossils reported to date. A chain composed of single-domain magnetite particles with fuzzy outlines has also been detected from the 2000 My Gunflint deposit. These findings

support the currently accepted hypothesis about the timing of abrupt Precambrian atmospheric oxygen buildup. They also reflect the necessity for organisms to develop mechanisms for acquiring and storing extracellular iron after the Global Ocean "Rusting" event drastically reduced the availability of dissolved iron (normally in the ferrous state) in the hydrosphere. The geologic record shows this event probably occurred around Early Proterozoic as represented by worldwide-spread Banded Iron Formation deposition at that time.



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CHAPTER ONE

INTRODUCTION



## Organization

This thesis is composed of four separate chapters, an introduction, and appendices. Each chapter appears here with its own abstract, introduction paragraph, and references. Most of the works presented here have been either published or submitted for publication. During my stay at Caltech as a graduate student, hundreds of samples have been studied and thousands of magnetic analyses and TEM pictures have been conducted or taken. Only works of broad enough interest to be formally published are included here.

The introduction summarizes our current knowledge about magnetite biomineralization processes and documents evidence for the presence of ultrafine-grained magnetite as remanence carrier in certain sedimentary deposits. It concludes with a discussion on the possible role of biogenic magnetite (especially bacterial magnetite) as a major source of ultrafine-grained magnetite in sediments, which supports the basic motivation of this thesis study. Some potential implications of searching for the fossil bacterial magnetite which have or have not been thoroughly assessed in this study are discussed. Chapter 2 describes the study on the examination of ultrafine-grained magnetite extracts from the Miocene Potamida Clay of Crete, in which the possible occurrence of bacterial magnetite particles was suggested by rock magnetic and paleomagnetic records. The basic methodology for extracting pure magnetite from sediments and the discussion on other possible sources of magnetite in sediments are included. The conclusion is some of the ultrafine-grained magnetite particles from this unit might indeed be bacterially formed. Chapter 2 has been published as a chapter in the book "Magnetite Biomineralization and Magnetoreception in Organisms". Chapter 3 is

composed of three short papers. The first one reports the occurrences of magnetotactic bacteria and bacterial magnetite in recent Santa Barbara Basin sediments and has been published in NATURE. The second and the third papers, which have separately been published in GEOLOGY and the book ORIGIN, EVOLUTION, AND MODERN ASPECTS OF BIOMINERALIZATION IN PLANTS AND ANIMALS, appear here with their own abstracts, introductions, and conclusions. The former reports the distribution of ultrafine-grained magnetite with possible bacterial origin in ancient deep-sea core samples. The latter summarizes the effect of magnetotactic bacteria on the magnetic properties of marine sediments and emphasizes the significance of bacterial magnetite particles as remanence carriers in them. Chapter 4, which has been published in PHYSICS OF EARTH AND PLANETARY INTERIORS, describes the occurrences of magnetotactic bacteria in varieties of modern carbonate-depositing environments and the findings of bacterial magnetite particles in limestones through time. The hypothesis, using the presence of bacterial magnetite in ancient sedimentary deposits as a stability indicator, is proposed and tested. Chapter 5 is composed of two papers, which have been submitted to PRECAMBRIAN RESEARCH, describing the occurrences of bacterial magnetite in modern and ancient stromatolite deposits. Discussion on using the existence of bacterial magnetite in fossil records as a monitor of paleoenvironmental changes is included. One important implication following this line of study is trying to constrain the evolution sequence of Precambrian atmospheric oxygen level by the earliest occurrence of bacterial magnetite identified through extensive survey on Precambrian sediments. Some preliminary results are presented in this chapter.

The appendices include four papers, published or submitted for publication, which report results of various studies I collaborated on with my colleagues. The first two are reports of studies on the presence of magnetite particles in some other marine organisms and speculations of their physiological functions. The last two present the results of magnetostratigraphy studies of a detrital unit outcropping near the San Andreas fault in southern California (Appendix 3) and abyssal core samples from the Bahamas (Appendix 4).

#### Magnetite Biomineralization

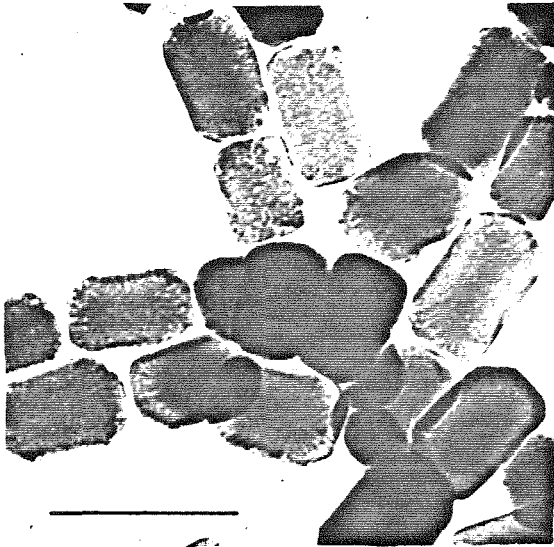
Magnetite was first identified in chiton teeth (class Polyplacophora) by Lowenstam (1962), who along with his students and colleagues have since taken the leading role in the investigation of chiton magnetite biomineralization mechanism (Towe and Lowenstam, 1969; Nesson, 1969; Kirschvink and Lowenstam, 1979). They discovered that iron passes through at least three consecutive stages in the process of chiton magnetite formation, including (1) ferritin micelles (an storage protein), (2) a mineral precursor, ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ), and (3) final reduction to magnetite ( $\text{Fe}_3\text{O}_4$ ). The next major discovery was Blakemore's report of the magnetotactic bacteria in Cape Code Marsh, Massachusetts. Subsequent work has shown that the iron particles formed intracellularly by them are also made of magnetite (Frankel et al., 1979; Towe and Moench, 1981). The existence of an additional micelle-like substance in the cells of magnetotactic bacteria has recently been shown by low temperature Mossbauer spectroscopy studies made by Frankel et al. (1985). Hence, these bacteria may use a biochemical pathway similar to that of the chitons in magnetite formation.

In addition to the chitons and bacteria, several other organisms are able to precipitate magnetite. To briefly summarize, these organisms include honey bees (Gould et al., 1978), pigeons (Walcott et al., 1979), turtles (Perry et al., 1985), green algae (Lins de Barros and Esquivel, 1985), and pelagic fish (Walker et al., 1982). With the exception of one chiton species, a probable contaminant in dolphins, and a framboidal sphere in the green turtle, all of the biogenic magnetite particles, which have been characterized with high-resolution transmission electron microscopy (TEM) to date, have sizes and shapes falling in the single-domain stability field of magnetite (Kirschvink and Gould, 1981). Kirschvink (1983) has interpreted this as a result of natural selection on organisms that use their internally-formed magnetite for directional sensitivity of some sort.

The crystal morphology of biogenic magnetite crystals formed by magnetotactic bacteria, chitons, and pelagic fish have been studied in the most detail at present (Towe and Moench, 1981; Matsuda et al., 1983; Towe and Lowenstam, 1967; Kirschvink and Lowenstam, 1979; Walker et al., 1984; Kirschvink et al., 1985; the last two references which I coauthored with my colleagues are included in this thesis as appendices). In the bacteria, the hexagonal parallelepiped shape reported by Towe and Moench (1983, Fig. 1A here) and the tear-drop and cuboidal shapes reported by Blakemore (1982, Fig. 1B and C here) easily distinguished them from the octahedral, spherical, and framboidal magnetite particles commonly formed 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 very distinctive "halo" structure (Towe and Moench, 1981). In all bacterial magnetite crystals examined to

Figure 1-1 - The magnetotactic bacteria magnetite crystals. (A) Bacterial magnetite crystal with hexagonal parallelepiped in shape (courtesy of Towe, K. L.); (B) rod-shaped cell with single chain of tear-drop shaped magnetite crystals (Blakemore, 1982); (C) Aquaspirillum magnetotacticum cell showing internal chain of cuboidal magnetite crystals (Blakemore, 1982).  
Scale bar = 0.1 micron.

(A)



(C)



(B)



date, the crystals are elongated along the (111) crystallographic axis, which also is the easy direction of magnetization and the most efficient orientation for magnetic crystals in a chain (Kirschvink, 1983; Matsuda et al., 1983; Mann et al., 1984ab). In a similar fashion, we found that the magnetite particles extracted from the ethmoid bone complex of yellowfin tuna (Walker et al., 1984; Mann, pers. comm.) have shapes and sizes resembling those of magnetotactic bacteria. 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. In summary, all of the fine-grained biogenic magnetite crystals examined to date appear to be easily distinguished on morphological grounds from their inorganic counterparts.

Lowenstam (1981) showed that mineral-forming mechanisms used by organisms range from "biologically-induced" to "matrix-mediated". "Biologically-induced" minerals have crystal habits and chemical signatures which 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 pre-formed organic framework (the matrix). A high level of biochemical control makes their size, shape, and chemical signature distinguishable from their inorganic counterparts. Due to their unique shapes, biologically-formed magnetite particles are clear examples of matrix-mediated biogenic minerals. Towe and Moench (1981) have detected trace amounts of titanium in bacterial magnetite particles, which is distinguished from high titanium contents of typical igneous magnetite but is the same with most authigenic magnetite

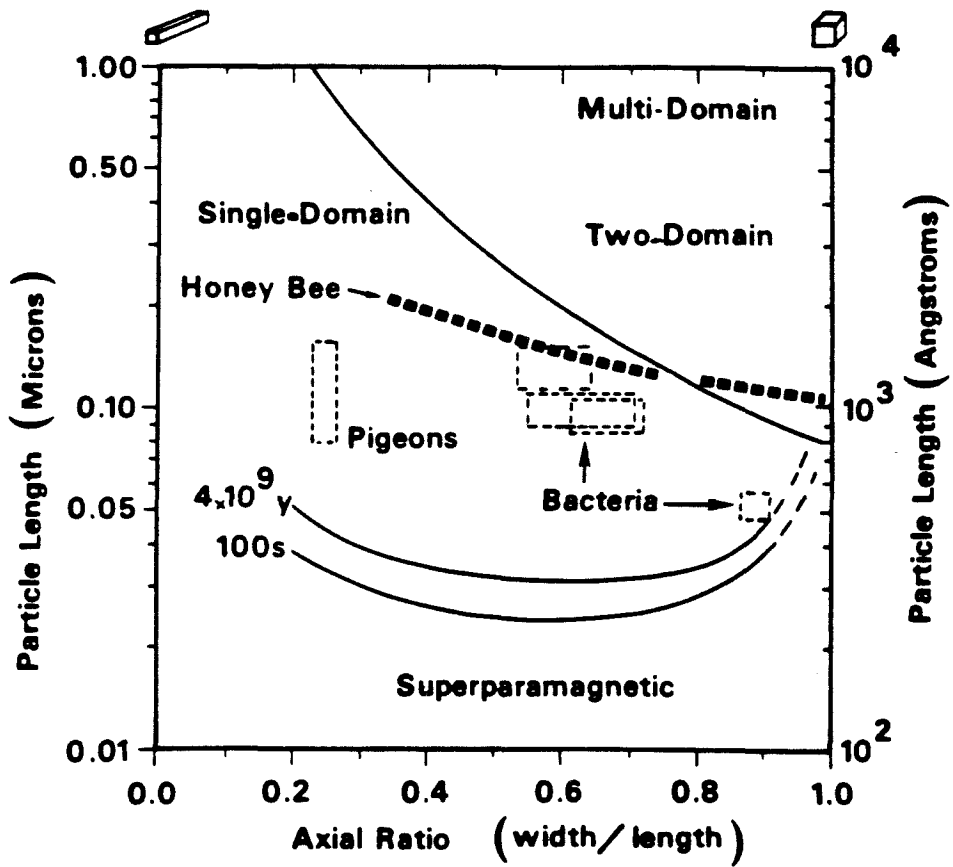
particles identified to date. Stable isotope studies on the magnetite particles formed by magnetotactic bacteria show no fractionation from the in situ water (O'Neil, pers. comm.). On the other hand, the oxygen isotope ratio of the chiton teeth (O'Neil and Clayton, 1964) is about 7% more positive (Lowenstam cautioned this measurement may be due to artifact) than the theoretically derived equilibrium value for the low temperature formed magnetite (Becker and Clayton, 1976). Unless detailed mechanisms controlling the trace element and the stable isotope fractionations of various biologically formed magnetite particles can be further demonstrated, these analyses have only limited uses for distinguishing biogenic magnetite from inorganic magnetite.

#### Ultrafine-Grained Magnetite in Sedimentary Deposits

Although magnetite is a common phase in igneous and metamorphic rocks, it is only present in a very small concentration in most fine-grained sediments ( $\ll 0.01\%$ ). Despite this, the high saturated moment (48 mT) of magnetite still makes it an important remanence carrier in many sedimentary deposits. The size range of magnetite grains in fine-grained sediments varies from 0.05 to 100 micron. Among this broad size distribution, only the particles at the smallest end (about 0.05-0.15 micron across) are best suited for producing a stable magnetic remanence. These particles fall within the size range for single-domain behavior (Fig. 2), which means that the individual particle is uniformly magnetized and capable of preserving the direction of its magnetic moment for long periods of geologic time (Neel, 1955; Butler and Banerjee, 1975). With the possible exception of slightly larger pseudo-single-domain grains, other particles with sizes falling in the multi-domain field are far less magnetically stable. The fine grain size and small concentration



Figure 1-2 - Size-shape relationships and magnetic properties of magnetite crystals (from Kirschvink and Gould, 1981). Each point on this diagram represents a rectangular magnetite crystal of specified size and shape. Points which plot in the upper right area labeled multi-domain or two domain represent crystals with two or more differently magnetized sub-regions within them; their net external magnetism is consequently reduced. Crystals which plot in the single-domain field are those in which a single electron spin direction exists across their entire volume, they are magnetized fully to magnetite's saturation value of 48 mT. The particle shape constraints the magnetic remanence to lie permanently along its length unless forced to move by a strong magnetic pulse. In small single-domain crystals, thermal activation can sometimes cause the direction of the magnetic moment to change relative to the crystal axes. The tendency for this to happen is given by an exponential time constant which depends in a complex manner on the volume and shape of each crystal. For simplicity, two lines have been drawn on the bottom of this figure showing all particles with time constants of  $4 \times 10^9$  years, and those with 100 s, respectively. Very small particles in which the magnetic moment moves quickly are termed superparamagnetic because they act like very strong paramagnets. Numerous bacterial and pigeon magnetite crystals which have been measured by electron microscopy all plot in the single-domain field as shown.



of single-domain particles in sediments makes them extremely difficult to be directly observed and identified in thin section. Therefore, rock magnetists have devised a variety of indirect techniques to recognize the presence of single-domain magnetite particles as remanence carriers in rocks based on their magnetic properties (e.g. Collinson, 1983; Cisowski, 1981). The occurrences of single-domain magnetite in deep sea sediments and limestones detected this way have been well documented by Lowrie and Heller (1982). Magnetite particles larger than 0.5 micron (pseudo-single-domain to multi-domain) extracted from these two types of sedimentary deposits have been examined with scanning electron microscopy (SEM) by Lowrie and Heller (1982), Lovlie et al. (1971), and Murray (1979). Without exception, all such particles resemble those produced by inorganic processes. The stable remanent magnetization carried by them is generally assumed to be primary in origin, with some notable exceptions where the magnetite appears to be diagenetic (McCabe et al., 1983). However, all of these workers have failed to characterize the magnetite particles of single-domain size.

Other than deep sea sediments and limestones, which are subjects of studies presented in Chapters 3 and 4, ultrafine-grained magnetite has been detected rock magnetically in several other sedimentary deposits. Noticeable examples of this kind include the following: (1) Mackereth (1971) and Thompson et al. (1980) have shown that the enhancement of magnetization in the top layer of soils might be due to the presence of non-stoichiometric magnetite; and (2) Granar's (1958) magnetic measurements of varved clay imply that magnetite may be an important remanence carrier in glacial deposits. Studies on the magnetic granulometry of soils and glacial varves have been conducted by

collaborating with Dr. Barbara Maher at University of East Anglia and Dr. Subir Banerjee at University of Minnesota, but no conclusive results regarding the existence of bacterial magnetite in these sediments have been reached. Therefore, they are not included in this thesis.

#### Bacterial Magnetite as a Source of Single-Domain Magnetite and Natural Remanent Magnetization in Sediments

The widespread distribution of magnetite-precipitating organisms implies that biogenic magnetite might be preserved in a wide variety of sediments, and the observation that most such particles are of single-domain size suggests that they could be extremely important for the preservation of natural remanent magnetization (Kirschvink and Lowenstam, 1979). Among these organisms, the magnetotactic bacterium is the most probable biologic contributor of single-domain magnetite. They have been found in virtually all unpolluted marine and freshwater habitats (Blakemore, 1975; Moench and Konetzka, 1978; Frankel et al., 1979; Kirschvink, 1980; Blakemore, 1982) and have high population densities. Using a simple calculation based on typical sedimentation rates, bacterial cell abundance, growth rates, and average volume of magnetite per cell, Kirschvink and Lowenstam (1979) have estimated the bacterial contribution to remanence in sediments to be about  $10^{-5}$  to  $10^{-4}$  A/m. Lowrie and Heller (1982) cautioned that these values might be overestimated due to the fact that the sedimentation rates in most depositional environments are higher than the rate (1cm/1000 yr.) assumed by Kirschvink and Lowenstam (1979). However, the revised values ( $10^{-6}$  -  $10^{-5}$  A/m) in Lowrie and Heller's (1982) estimations are still comparable to the magnetic remanence generally found in sediments and local environmental variation could greatly alter the bacterially contributed

remanence value.

Besides the biogenic magnetite, the reported occurrences of single-domain magnetite in nature as revealed by direct TEM examination include:

(1) ellipsoidal magnetite inclusion in the clouded plagioclase of a Precambrian Greenland metadolerite (Morgan and Smith, 1981); (2) small octahedral titanomagnetite particles found in Mid-Atlantic Ridge basalt glass (Smith, 1979); and (3) small octahedral magnetite crystals in Code, Bokkeveld, a C2M carbonaceous meteorite (Barber, 1981).

Significant contribution of meteoritic single-domain magnetite to marine sediments is unlikely due to the scarcity of meteorite falling. The contribution of igneous single-domain magnetite to marine sediments has been questioned by Amerigian (1974). Applying the experimentally determined relationships between deposition, transportation, erosion, and current velocity for sediment particles ranging from 100 microns to 8 mm with extrapolation to particles down to the 10 microns size range compiled by Heezen and Hollister (1964) to magnetite crystals, Amerigian (1974) was able to attain a grain-size distribution diagram of magnetite particles as deposited under various bottom current velocities. According to these calculations, current velocities on the order of 0.1-0.2 cm/sec would tend to inhibit deposition of magnetite particles less than 50 microns across. Only under extremely calm conditions (bottom current velocity  $< 0.01$  cm/sec) can magnetite particles less than 5 microns across be deposited.

In addition to the difficulties for physical transport and deposition of ultrafine-grained magnetite particles, chemical transformation of igneous single-domain magnetite crystals during settling is another factor which might prevent them from reaching the sea floor

intact. Magnetite is generally known to be chemically unstable in aerobic environments and tends to alter to form maghemite and/or hematite. A simple Stokes' law calculation indicates that it would require up to  $10^4$  years for the single-domain magnetite particles to settle from the surface through the water column to deep sea floor. In general, ferrous ions are more easily released from their mineral states and oxidized to form ferric ions in aqueous environments. Given their large surface/volume ratio, single-domain particles would be likely to be completely altered during the settling process. It seems doubtful that single-domain igneous 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. Ultrafine-grained iron oxides are indeed common associated phases with organic materials, but preliminary examination of them indicates most of them are ferrihydrite particles rather than magnetite crystals (J. Edmond, pers. comm.).

Authigenesis is another possible source of ultrafine-grained magnetite in marine sediments. Sugimoto and Matijevic (1980) have been able to successfully precipitate single-domain octahedral magnetite from aqueous solution. However, the condition required for this artificial synthesis ( $> 90^\circ\text{C}$  with excess  $\text{OH}^-$ ) of single-domain magnetite is hard to be simulated in nature.

Summarizing the above arguments, we can see that bacterial magnetite is a likely source of single-domain magnetite in deep sea sediments. However, the chemical instability of single-domain magnetite would likely affect the preservation potential of bacterial magnetite in sediments.

For example, in a highly aerobic environment, bacterial magnetite could easily alter to form maghemite or hematite as described above; and in a sulfide rich environment, they may alter to greigite ( $\text{Fe}_3\text{S}_4$ ) or pyrite ( $\text{FeS}_2$ ). We have found in some deep sea sediments, the surface layer of bacterial magnetite particles altered to form maghemite (see Chapter 4 for more detail). On the other hand, Demitrack (1985) has observed that the greigite grains preserved in Eel Marsh, Massachusetts, where Blakemore (1975) first discovered the occurrence of magnetotactic bacteria, have the same size and shape distribution as that of the bacterial magnetite particles. She explained these grains as chemically altered pseudomorphs of the original bacterial magnetite crystals. Ghiorse (referenced in Blakemore, 1982) has also found unidentified mineral particles with similar shapes as bacterial magnetite occurring both inside and outside bacterial cells associated with manganese nodules in Oneida Lake, New York.

Under reducing conditions, the ferric ions in bacterial magnetite crystals might be reduced to form ferrous ions and released away from sediments. Karlin and Levi (1983, 1985) and Lund and his colleagues (Lund et al., 1983; Leslie et al., 1984) have found a dramatic decrease of the ultrafine-grained portion of magnetite with depth in sediments from the California continental borderlands and the Gulf of California. They explained the disappearance of this ultrafine-grained magnetite 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. Johnson-Ibach (1982) has compiled analyses of TOC in numerous deep sea drilling project

(DSDP) core samples and obtained a quantitative relationship between the TOC and the sedimentation rate; generally speaking, TOC decreases with increasing sedimentation rate due to the clastic dilution of the organic input. In the same study, Johnson-Ibach also 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 constant supply of ultrafine-grained magnetite from magnetotactic bacteria through time, then the bacterially-produced single-domain magnetite particles should appear to be most abundant and best preserved in calcareous sediments with high sedimentation rates. Therefore, I chose deep sea sediments with high sedimentation rate and limestones as main targets when searching for fossil bacterial magnetites.

#### Other Implications

Besides identifying the role of bacterial magnetite as a remanence carrier and source of magnetization in sediments, there are other important implications of searching for the presence of bacterial magnetite in sediments. Among the implications discussed below, the first two (stability test and paleoxygen indicator) have been assessed by the results presented in Chapters 4 and 5. Providing some better extraction or dispersion techniques being advanced, the last two (paleointensity and grain-grain interaction) could also be approached in the future.

Paleomagnetic stability test. If bacterial magnetite particles are responsible for the remanence of sediments, it seems clear that they should preserve their spatial orientations and magnetic remanence directions relative to the rock matrix, unless they are disrupted by major events of thermal, chemical, or physical alteration. On the other hand, if these events are strong enough to alter or destroy the bacterial magnetite



crystals, the simple presence or absence of these particles could serve as a useful guide for interpreting the nature of the natural remanent magnetization in samples used for paleomagnetic study. To test this idea, a variety of carbonate samples which have been shown by conventional paleomagnetic techniques to contain a dominantly primary component, a primary component plus a weak secondary component, or a principally secondary component were examined for the presence of bacterial magnetite.

Constraints on oxygen abundance. Blakemore et al. (1985) reported that the optimum condition for magnetite formation in Aquaspirillum magnetotacticum (one strain of magnetotactic bacteria) is obtained with the initial oxygen concentration at about 5% of the present oxygen level (1 kPascal) with virtually no magnetite production when the oxygen concentration goes below 2.5% of present atmospheric level. To our knowledge, all natural environments in which living magnetotactic bacteria have been found are microaerobic, and a reasonable inference that can be obtained at this stage is that some form of free molecular oxygen is necessary for the bacterial magnetite biomineralization process. If this is the case, the presence of bacterial magnetite crystals in a sediment sample could imply that microaerobic conditions prevailed at the sediment-water interface, the optimum niche of magnetotactic bacteria, during deposition. The study of bacterial magnetite crystals in the fossil record could therefore provide an important constraint on the chemistry of bottom waters through the Phanerozoic, and may ultimately shed light on the evolution of free oxygen during the Precambrian.

Several stromatolitic limestone and chert samples from the Proterozoic (kindly supplied by Dr. S. Awramik at UCSB and Dr. J. W. Schopf at UCLA) were studied to examine the presence of bacterial magnetite in

them with the hope to set some constraints on the Precambrian atmospheric oxygen level evolution sequence.

Sedimentary paleointensity. Although numerous reliable techniques exist for measuring the absolute intensity of the past geomagnetic field with igneous rocks (e.g. Thellier and Thellier, 1942; Coe and Gromme, 1973; Shaw, 1974; Boyd, 1986), at present it is only possible to measure relative paleointensity variations from sedimentary deposits. Kirschvink (1982) has proposed a possible solution to this problem which involves using the orientation energy product of a magnetotactic bacterium in the geomagnetic field,  $uB/kT$ , where  $u$  is the magnetic moment of the bacterium,  $B$  is the intensity of the local magnetic field, and  $kT$  the background thermal energy. For a magnetotactic microorganism of a specified diameter, this energy ratio tends to have a constant value, ranging from as low as 3, for extremely small organisms, to several thousands for a recently reported magnetotactic eugleanid (Lins de Barros and Esquivel, 1985). Natural selection probably acts to optimize the total torque which is felt by these organisms in the geomagnetic field ( $uB$ ), and therefore bacteria growing in strong fields would eventually adapt by producing slightly smaller magnetosomes than their contemporaries in areas with weaker magnetic fields. Lins de Barros and Esquivel (1985) suggested that this might indeed be the case in comparing living populations of magnetotactic bacteria in Brazil where the geomagnetic field is virtually the weakest on Earth ( $B = 0.24$  Gauss) with those from the eastern United States. In the simplest case, therefore, one might be able to measure the paleointensity of the field by measuring the total magnetic moment of a fossil bacterial magnetosome. This can be obtained quickly from a TEM image by summing up the volume of all

magnetite crystals in the chain, providing some milder extraction technique, which will not destroy the chain structure of magnetosomes preserved in sediments, will be developed in the future.

Intergrain interactions. Biogenic magnetite offers a unique opportunity to test experimentally for a variety of magnetic interparticle interaction effects. For example, Cisowski (1981) developed several analytical procedures for measuring the strength of interactions between assemblages of single-domain magnetite crystals. Among other things, he found that chiton teeth display the strongest such effects yet observed. The study taken on the marine magnetotactic bacteria from Baja California (see Chapter 3) reveals that the linear arrangement of crystals within a magnetosome also yields measurable interaction effects, principally a relative shift in the coercivity spectra (measured by the isothermal remanent magnetization IRM acquisition and alternating fields AF demagnetization techniques [Cisowski, 1981]). This shift of the bacteria spectra is similar to that observed in spectra of magnetic tissues from oceanic fish (tuna and salmon) which also contain linear chains of magnetite (Walker et al., 1984; Kirschvink et al., 1985; S. Mann, pers. comm.). However, there seems to be a theoretical disagreement between the analysis of Cisowski (1981) and that of Jacobs and Bean (1955) concerning the measured coercivity of an interacting chain of particles. Jacob and Bean's model would attribute a large fraction of the observed coercive force for the magnetotactic bacteria to the interactions between the single-domain crystals within the chain. On the other hand, the more traditional rock-magnetic view holds that the base coercivity is determined by the shape anisotropy of the individual magnetite crystals, and the interparticle interaction merely serves to shift the observed

coercivity spectrum slightly, depending on the method to measure it (IRM or AF). Providing the method for successfully dispersing the magnetite chain isolated from magnetotactic bacteria can be developed, these models can be easily testified by measuring the coercivity spectra before and after the dispersion. Unlike the traditional rock-magnetic approach, the Jacobs and Bean's model would predict that the base coercivity would also show a measurable decrease.

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CHAPTER TWO

POSSIBLE BIOGENIC MAGNETITE FOSSILS FROM THE  
LATE-MIOCENE POTAMIDA CLAYS OF CRETE

Possible Biogenic Magnetite Fossils From the Late-Miocene Potamida Clays  
of Crete

Chang, S.R., and Kirschvink, J.L.

ABSTRACT

A very fine-grained (0.05-0.2  $\mu\text{m}$ ) magnetic mineral extract has been obtained from the Late-Miocene Potamida clays of Crete. X-ray and electron diffraction patterns taken from this material confirm that it is magnetite. Particle size and shape measurements from transmission electron microscopy indicate that most of the magnetite grains are of single-domain size. Paleomagnetic and morphologic evidence suggest that some of the magnetite in this clay might have been produced biologically. Further distinguishing characteristics of biogenic magnetite need to be identified in order to determine the concentration variations of biogenic magnetite in separate depositional environments and different geologic periods.

A. INTRODUCTION

In the 22 years since Lowenstam (1962) first discovered the mineral magnetite in chiton teeth, many other organisms have been reported to be able to form this mineral as well (Blakemore, 1975; Frankel et al., 1979; Gould et al., 1978; Walcott et al., 1979; Kirschvink, 1981a; Walker & Dizon, 1981; and Lins de Barros et al., 1981). Magnetite is now the fourth most common biogenic mineral after carbonate, opal and ferrihydrite and related ferric oxide in terms of its production by different groups of organisms (Lowenstam and Weiner, 1982). A variety of magnetite-forming organisms live in aquatic environments and hence there is the question whether magnetite formed by organisms can be preserved in sediments. In particular, one group of magnetite-

synthesizing organisms, the magnetotactic bacteria, are cosmopolitan in their aquatic distribution. Based on calculations considering their natural population density, sedimentation rates, and volume of magnetite per cell, the biologic contribution of magnetic remanence in sediments has been estimated by Kirschvink & Lowenstam (1979) to reach the  $10^{-4}$  A/m level. Towe & Moench (1981) revised this estimate upwards to  $10^{-3}$  A/m level which is more compatible with the remanence generally observed in sediments.

Recently, a variety of paleomagnetic studies have attempted to unravel the detailed behavior of the geomagnetic field during geomagnetic polarity transitions as recorded in marine and lacustrine sediments and volcanics (e.g., Valet & Laj, 1981; Bogue & Coe, 1982). The reliability of sediments to accurately record the geomagnetic field depends on the constant influx of suitable magnetic particles; consequently, many authors have carefully studied the magnetic mineralogy of sediments deposited during transitions. Of particular interest in the search for fossil, biologically-formed magnetite is the work of Langereis (1979) and Valet & Laj (1981) on the marine clays of the Potamida section in northwestern Crete. During the two geomagnetic transitions studied, they found that both the anhysteretic remanent magnetization (ARM) and the saturation isothermal remanent magnetization (sIRM) decreased, indicating that the sedimentary magnetic fraction was temporarily reduced. Closer examination of their data also reveals that the ARM/sIRM ratio decreased during the transitions. Because sIRM is proportional to the total amount of magnetic mineral and the ARM level is biased towards the extremely fine-grained (SD or PSD) fraction, a drop in the ARM/sIRM ratio suggests that the concentration of fine-grained material disappeared during the reversal. In addition, the IRM

acquisition curve argues that magnetite might be the major carrier of the stable magnetic remanence in this clay section.

The suggested decrease of fine-grained magnetic material associated with the geomagnetic transition led Kirschvink (1982) to propose that some of the magnetic material normally contributing remanence to the sediments was bacterially produced, and that the period of reduced geomagnetic intensity surrounding the transition led to a decrease in the bacterial contribution to the sediments. Several lines of evidence suggest that the selective advantage of magnetotaxis would be diminished during periods of low geomagnetic intensity (Kirschvink & Gould, 1981). This hypothesis would predict the decrease of fine-grained magnetite particles observed during the transitions preserved in the Potamida clays of Crete. This hypothesis leads to two testable predictions. First, single-domain magnetite crystals with characteristics similar to those of extant magnetotactic bacteria ought to be present in the non-transitional portions of the Potamida clays and extensive purification followed by electron microscopy will reveal their presence. Second, if such particles are indeed found, their absolute concentration should decrease during the transition. A test of this first prediction is the focus of this study; answer to the question of fluctuations in the bacterially-formed magnetite concentration requires the development of a quantitative method for assessing the absolute abundance of bacterially-formed magnetite in sediments.

Previous results with scanning electron microscopy on magnetic extracts from modern sediments and ancient sedimentary rocks (Lovlie et al., 1971; Lowrie & Heller, 1982; Demitrack, 1985) indicate that this technique does not have the ability to resolve the morphology and internal characteristics of magnetite grains in the single-domain size

region ( $0.1 \mu\text{m}$ ). The higher resolution of transmission electron microscopy (Towe, 1985) is required. Furthermore, it is necessary to eliminate all minerals except magnetite prior to electron microscopic examination; if this is not done the identity of ferromagnetic phases will remain in question.

The purpose of this study is to search for biogenic magnetite in the Potamida clays. We developed a new extraction technique which efficiently separates fine-grained magnetite from all the other ferromagnetic minerals in the sediments. The recovery and identification of bacterial fossils is an important test of the hypothesis that biochemically-formed magnetite contributes a substantial fraction of the magnetic material in marine sediments. In addition, the ability to recognize these fossils in old sediments would help unravel when the magnetotactic bacteria evolved and may ultimately shed light on the origin of iron-mediating enzymes.

## B. SAMPLES

18 samples from the Potamida clays were supplied by Drs. Zijderveld and C.G. Langereis at the State University of Utrecht. These cores span 40 meters of strata which correspond to a continuous sedimentary record of approximately 1 My and have a relatively high sedimentation rate of 4 cm/1,000 yr. Drooger et al. (1979) provide a detailed geological description of the sampling locality, and Langereis (pers. comm.) has measured the magnetic intensities of these 18 samples before and after 50 mT alternating field (AF) demagnetization (shown in Fig. 1). The NRM-intensity decrease occurs in all three transitions, which is consistent with the result of Valet & Laj (1981). The sedimentary environment of the Potamida clays has been determined by facies analyses

Figure 2-1 - Variations of magnetic intensity of bulk sample and the ratio of first extract intensity and bulk sample intensity for the Potamida and the Skouloudhina sections. Langereis's measurements (pers. comm.) have been listed for comparison.

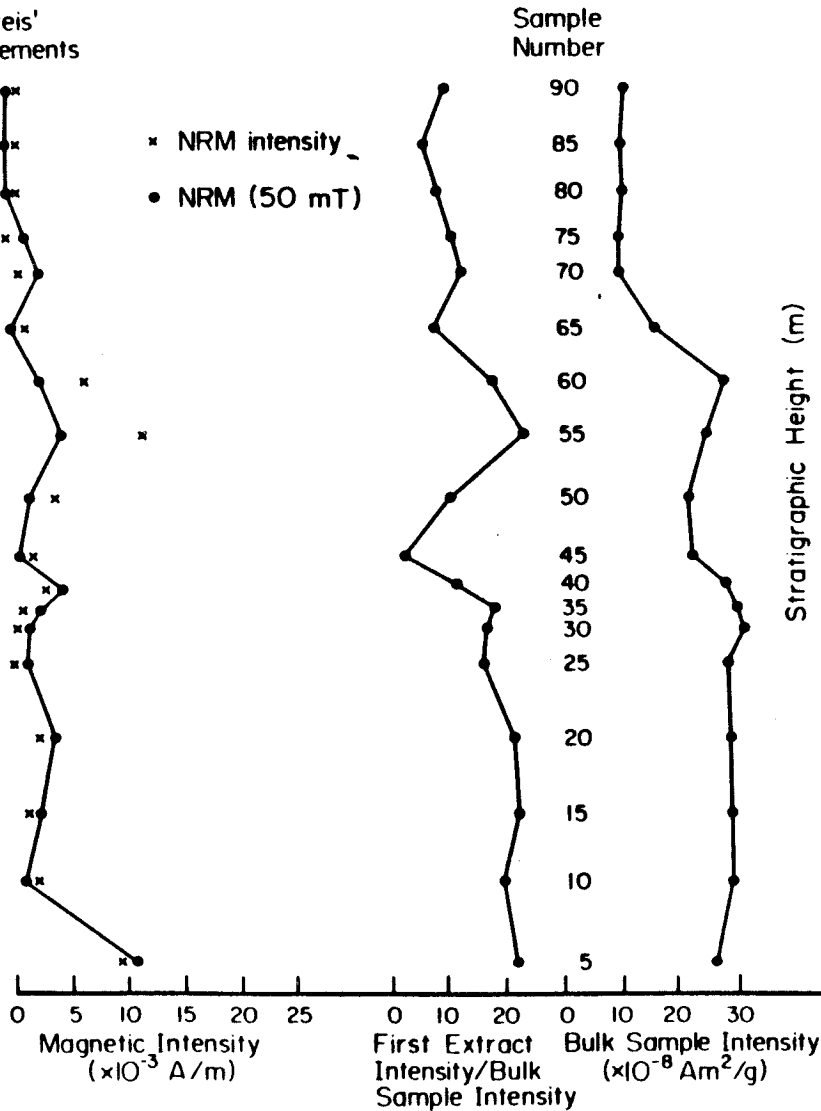
Potamida Section

Polarity

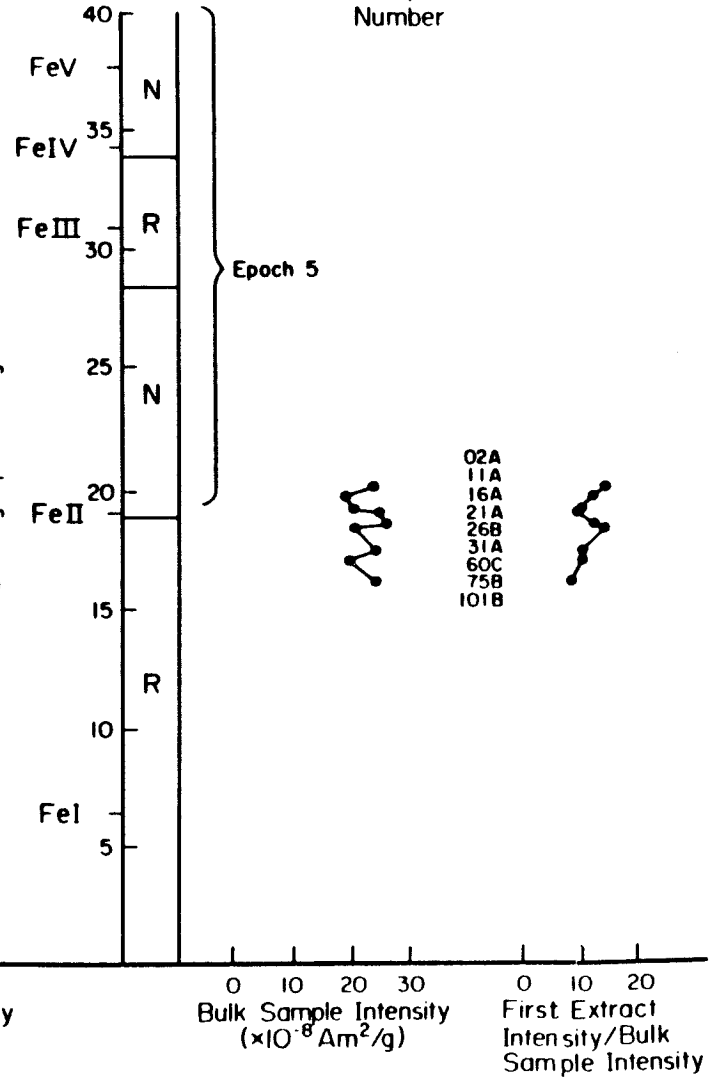
Skouloudhina Section

Langereis' Measurements

x NRM intensity  
 • NRM (50 mT)



Stratigraphic Height (m)



to be an open basin (Meulenkamp et al., 1979). Detailed biostratigraphic and magnetostratigraphic correlations indicate that this clay was deposited between 6.3 My and 5.3 My ago (Tortonian/Messinian; Langereis & Zachariasse, 1983). Small evaporite deposits have been observed near the Potamida section (Meulenkamp et al., 1979), and studies of the large-scale tectonic history of this area show that this sedimentary basin was connected to the Mediterranean during the late-Miocene Messinian salinity crisis (Meulenkamp et al., 1979; Drooger et al., 1979). The whole sequence of this section appears to be continuous. Five iron-rich layers have been found separately around sampling localities 15, 45, 70, 80, and 85. One of them (sampling locality 45) corresponds to the distant part of one turbiditic layer but represents no sedimentary hiatus (Drooger et al., 1979). An abrupt appearance of Globorotalia conomiozea (Tortonian/Messinian boundary) has been reported just above sampling locality 70 (Zachariasse, 1979).

In addition to the Potamida section, another section at Skouloudhina in northwestern Crete recorded the same R-N transition as Potamida, but did not show the same ARM drop (Laj, pers. comm.; Valet et al., 1983). Nine cores of this section have been sent by Dr. Laj in France, and the grain-size distribution and major mineral occurrences of the two sections show no obvious contrast. The upper five levels of the Potamida section samples available for this study have relatively larger grains. The average grains of the other cores are mainly below 10  $\mu$ m in size. Kaolinite, illite, calcite, and quartz are the dominant mineral phases observed in all the samples.



### C. LABORATORY EXTRACTION OF MAGNETITE

The extraction technique used in this study is based on the physical and chemical characteristics of magnetite: high magnetization, high density, and resistance to dithionite-citric acid dissolution. Although this technique may still need revision and improvement before it can be more widely applied, it is at present the most efficient way to extract pure magnetite from poorly-consolidated sedimentary samples and works well on the material from Crete.

The extraction begins by preparing a fine-grained slurry from the dry mud by adding distilled water, and stirring the resulting mixture evenly. An initial magnetic separation is made using a 60 ml manual speed-controlled separatory funnel attached to a Franz isodynamic magnetic separator with a rubber tube fitted with a clamp to allow a slow flow of water through the system. The current of the separator should be set at about 0.5 Amps. The slurry would pass through this funnel slowly and all of the magnetic grains will be held at the side of the funnel. After this step, the average magnetic intensity for the sample will increase from about  $1-2 \times 10^{-7} \text{Am}^2/\text{g}$  for bulk material to  $2-4 \times 10^{-6} \text{Am}^2/\text{g}$ .

A second magnetic separation is done by transferring the first magnetic separate into a 10 ml conical centrifuge tube with distilled water. In order to disperse the quartz and clay mineral grains which clump together with magnetite, the tube is placed in an ultrasonic shaker for about 10 minutes. The highly-magnetic grains can then be pulled to the edge of the tube by attaching a small magnet to the side and gently sloshing the fluid/sediment mixture back and forth. After discarding the supernatant liquid and washing the residue twice more, the magnetic intensity of the resulting magnetic separate is in the

range of  $5-8 \times 10^{-5} \text{Am}^2/\text{g}$ .

Next, the residual material is cleaned off of all other ferric iron oxide minerals by treating it for two days in a buffered sodium dithionite-citrate solution (Mehra & Jackson, 1960). This solution under these conditions is known to dissolve hematite, maghemite, and the other possible iron oxide minerals in the samples, but will not attack magnetite at room temperature for several months (Kirschvink, 1981b). Previous work has shown that hematite, maghemite, and goethite dissolve quickly in this solution and we have experimentally established that it works for pyrrhotite as well. A TEM control experiment on a fine-grained magnetite standard powder confirmed that there was no observable change after two days of dithionite treatment. This is the only chemical treatment used in the whole extraction procedure and it should not alter the morphology of magnetite, unless the surface has been oxidized to form a thin layer of maghemite.

After two days of chemical dissolution, the solution is centrifuged, the liquid discarded, and the sample ultrasonically resuspended and washed several times with distilled water. A final magnetic extraction is done by pipetting the solution onto a glass microscope slide and letting it form a thin film with most of the particles in the center. A small hand magnet can then be used to work the magnetic particles away from the center leaving any non-magnetic grains behind.

Samples were prepared for transmission electron microscopy using the procedures described by Towe (1985), with one minor modification. Clumps of magnetic particles were partially dispersed using a 100 mT, 400 Hz peak-to-peak oscillating magnetic field produced by our alternating-field demagnetizing unit. In theory, this procedure should

first break the clumps into mutually repelling particle chains aligned parallel to the oscillating field. As these chains settle through the liquid onto the grids, the oscillating field hits them perpendicularly to their length, and will free some of the individual crystals. This works fairly well in practice.

A check of the purity of the resulting powder was made using the standard Debye-Scherrer method. Almost all diffraction lines from our sample matched those from a pure magnetite standard (Fig. 2). Cell dimensions and mole fraction of  $\text{Fe}_2\text{TiO}_4$  of these magnetite extracts can be determined from comparing the diffraction patterns of them with those of the silicon standard as 8.39 Å and 0.02. Before surveying the final magnetic extracts of all the samples, we also examined the magnetic extract, prior to dithionite treatment under the TEM. The electron diffraction patterns (Fig. 3) of the dominating dark mineral grains in the extract confirm that most, if not all, of the material in the samples is magnetite. These two direct observations are consistent with the conclusion derived indirectly from the magnetic measurements (Langereis, 1979; Valet & Laj, 1981).

#### D. MAGNETIC STUDIES

Another measure of the concentration of fine-grained magnetite in each sample is the ratio between the IRM intensity of the first extract and that of the bulk sample. Fig. 1 shows variations in this ratio as well as those for the magnetic intensity of bulk material for each sample of both Potamida and Skouloudhina sections. Both of these parameters decreased during the lower two transitions at the Potamida section, but no such decrease is observed in the corresponding R-N transition at the Skouloudhina section. The intensity also decreases

Figure 2-2 - X-ray diffraction patterns of (a) magnetite standard and  
(b) final extract of the Potamida clays.

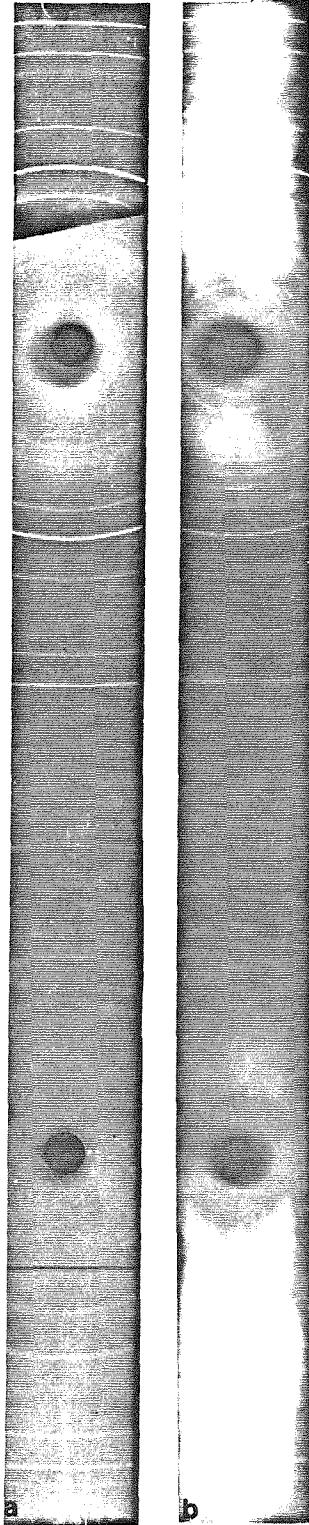
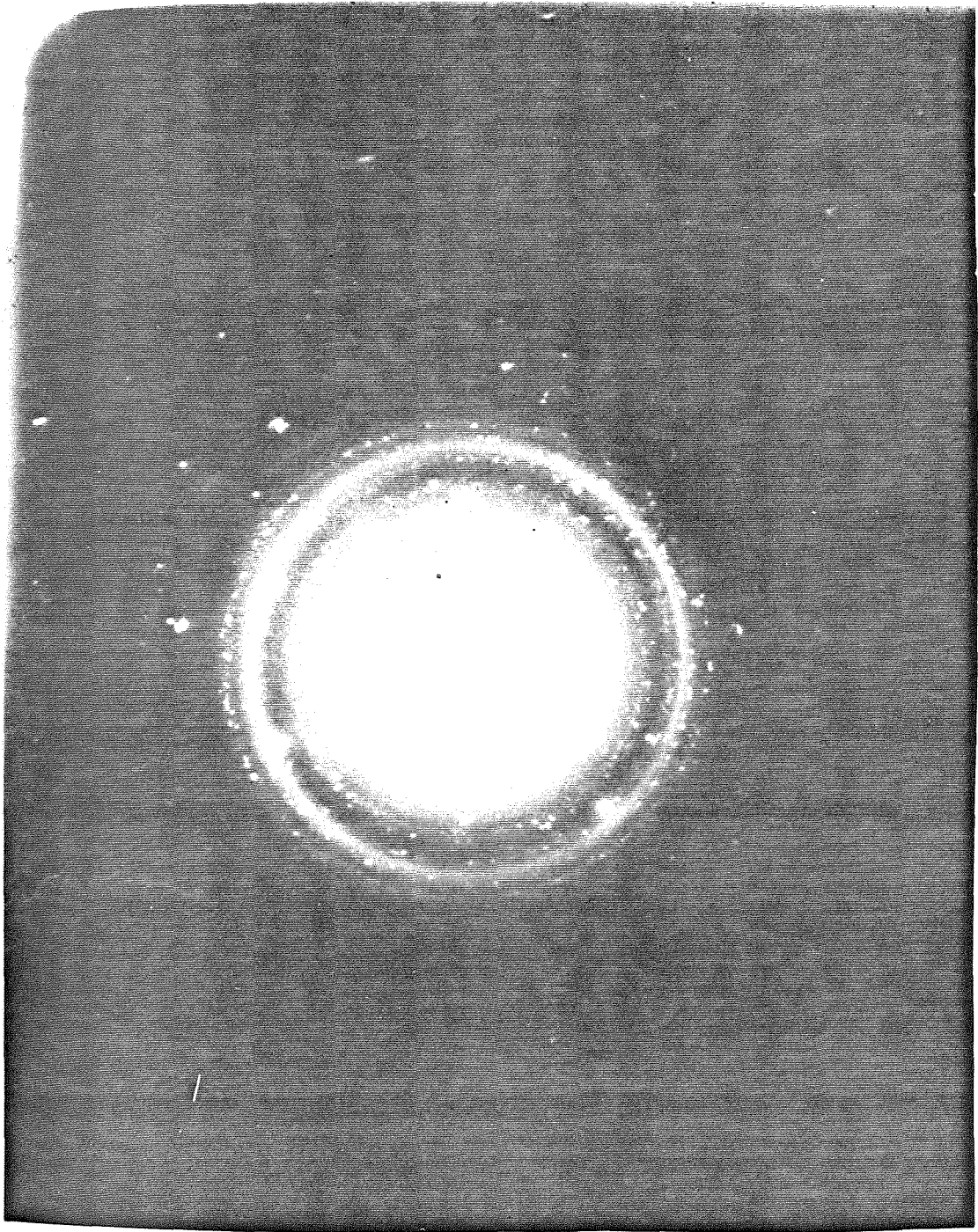


Figure 2-3 - Electron diffraction patterns of grains in the magnetic extract prior to dithionite treatment from the Potamida Clays in Crete. The wavelength of electrons is 6 pm, and the camera length is 180 mm. Positive was enlarged 7 times.



during the upper transition of the Potamida section (Langereis, written comm.). These data are consistent with the disappearance of large amounts of single-domain magnetite in some parts of the formation.

We also ran a progressive AF demagnetization of the sIRM on the final extract from the lower portion of the Potamida section (Fig. 4). Two magnetic fractions are clearly present, a relatively soft one with coercivity less than 10 mT, which probably is a result of multi-domain grains, and a magnetically harder portion corresponding to smaller, presumably single-domain grains.

A summary of all the data obtained from Valet & Laj's (1981) previous work and this study gives us an overview of the magnetic mineral phase variations in these sections:

1. Magnetite is the major remanence carrier in both sections.
2. A large amount of the fine-grained (probably single-domain) magnetite disappears during the lower two transitions of the Potamida section.
3. The remanence of the upper third of the Potamida section and most of the Skouloudhina section is probably mainly due to large-grained (pseudo-single-domain or multi-domain) magnetite or other magnetic minerals.

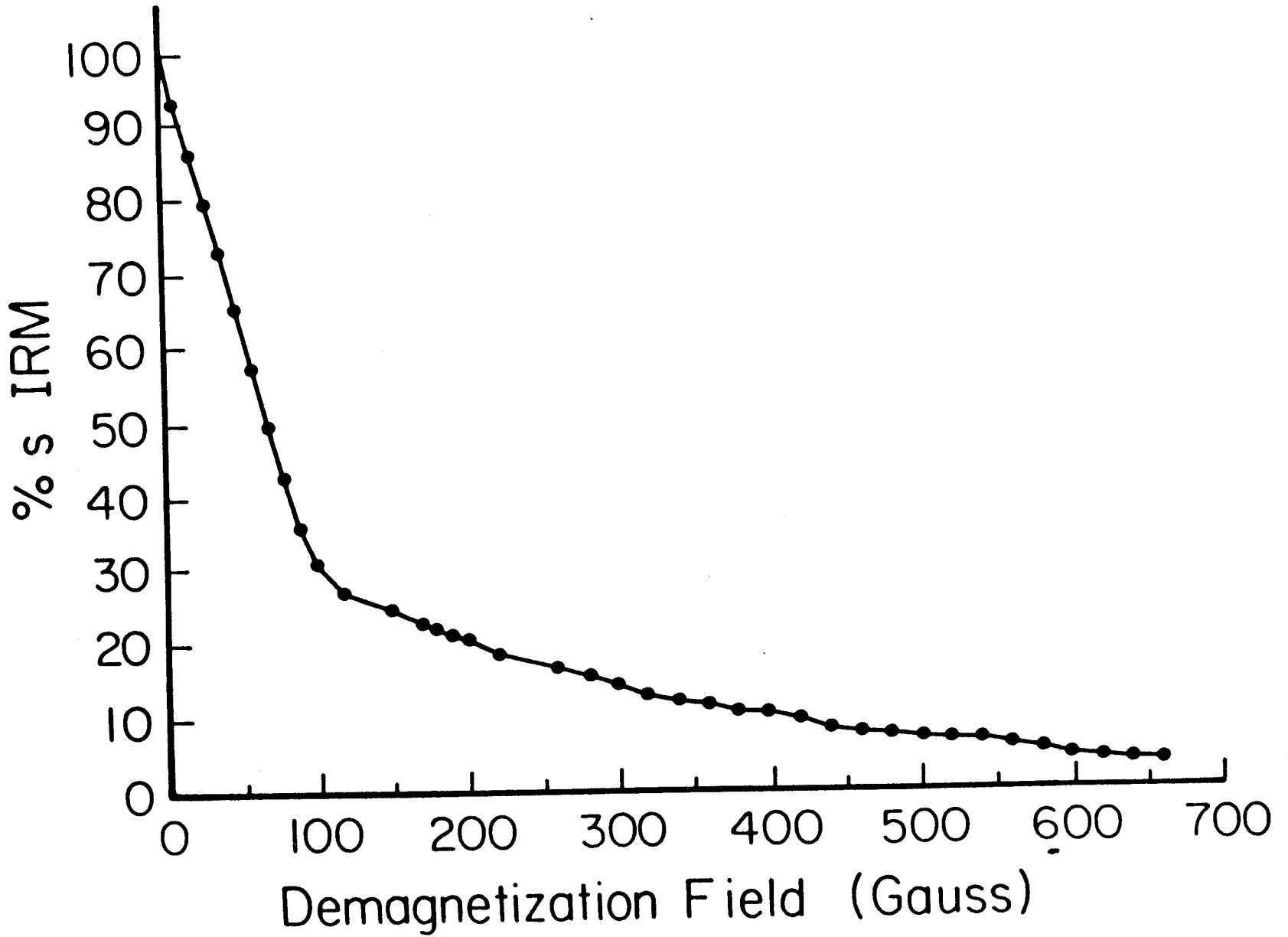
These phenomena do not unambiguously constrain the origin of the magnetite in these clays. However, the other possible sources (e.g. volcanic eruptions, weathering, falling of cosmic dust, etc.) would not lead to a drop in concentration of magnetite during magnetic reversal as would the biogenic hypothesis.

#### E. SIZE AND SHAPE DISTRIBUTION OF MAGNETITE

The detailed size and shape distribution of the final magnetite



Figure 2-4 - AF demagnetization curve for final extract from the Potamida Clays. Due to low demagnetization resistance of MD magnetite and strong interacting field of dense-packed SD magnetite, sIRM demagnetization normalized remanence for both MD and interacting SD magnetite grains will increase abruptly (Cisowski, 1981). The soft part of this final extract, which corresponds to the abrupt decrease of % sIRM during < 100-G demagnetization, can be characterized as MD or interacting SD magnetite. The smooth decrease of % sIRM at demagnetization level > 100 G is a characteristic of SD magnetite.



extract from samples 5, 15, 25, 35, 45, and 60 of the Potamida section and sample 21B of the Skouloudhina section have been studied with the TEM. The majority of the extract grains in the first 5 samples are of single-domain size. The latter 2 samples are primarily composed of two-domain or multi-domain magnetite. These direct magnetic phase variation observations reinforce arguments based on magnetic measurements in these formations. A plot of the general size and shape distribution of the grains from the final extract of the first 5 samples on the magnetite domain stability diagram of Butler & Banerjee (1975) shows that the range of grain size from these extracts overlaps with the size and shape distribution of bacterial magnetite (Fig. 5).

Another characteristic feature used to distinguish biogenic magnetite from inorganic magnetite is the morphology. Both the hexagonal shape reported by Towe & Moench (1981) and the tear-drop shape found by Blakemore et al. (1980) are diagnostic.

Surveying the grains in the final magnetic extract of the sample, we found that they can be grouped into four modes of occurrence. The first is composed of rounded or elongate grains with frothy surfaces (A; Fig. 6, 7). The modal size distribution is from 0.1-0.2  $\mu\text{m}$ , but occasionally, large grains up to 1  $\mu\text{m}$  in size have been found. Euhedral crystals with typical octahedral (B) or hexagonal (C) shapes in their microscopic image are also frequently observed (Fig. 8). The smooth surfaces of these two types of grains suggest amazingly good preservation of magnetite in the Potamida Clay. The size of the octahedral grains varies from 0.05-0.2  $\mu\text{m}$ . In addition to their shape, a narrow range of size distributions ( $0.1 \pm 0.02 \mu\text{m}$ ) is another intriguing feature of the hexagonal grains. A very small number of the fourth type of grains consisting of crystals with prismatic or oval

Figure 2-5 - Plotted on this domain stability field diagram for magnetite (Butler and Banerjee, 1975), the size and shape distribution of fine-grained magnetite in the final extract of samples from the lower half of the Potamida section shows overlapping with the reported size and shape distribution of bacterially formed magnetite.

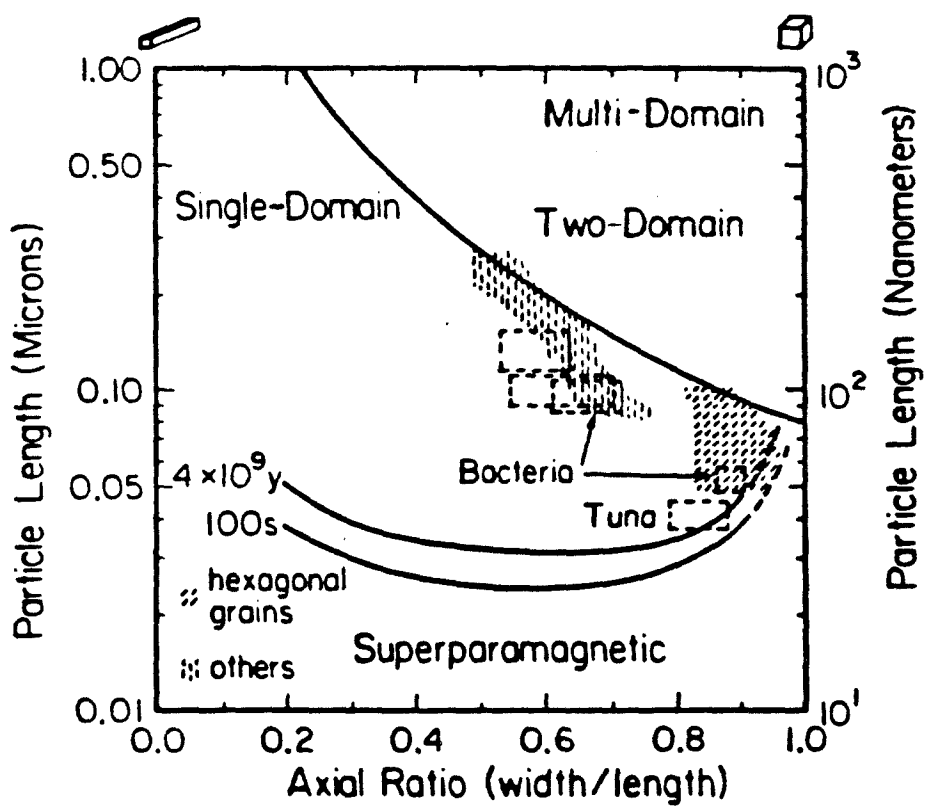


Figure 2-6-17 - Transmission electron micrographs of the final extract from samples of the Potamida section in Crete (6-10, 12-17) and magnetite standard (11). Scales are variable. Arrow in Fig. 13 indicates a possible characteristic feature--an uneven crystal face.

Figure 2-6

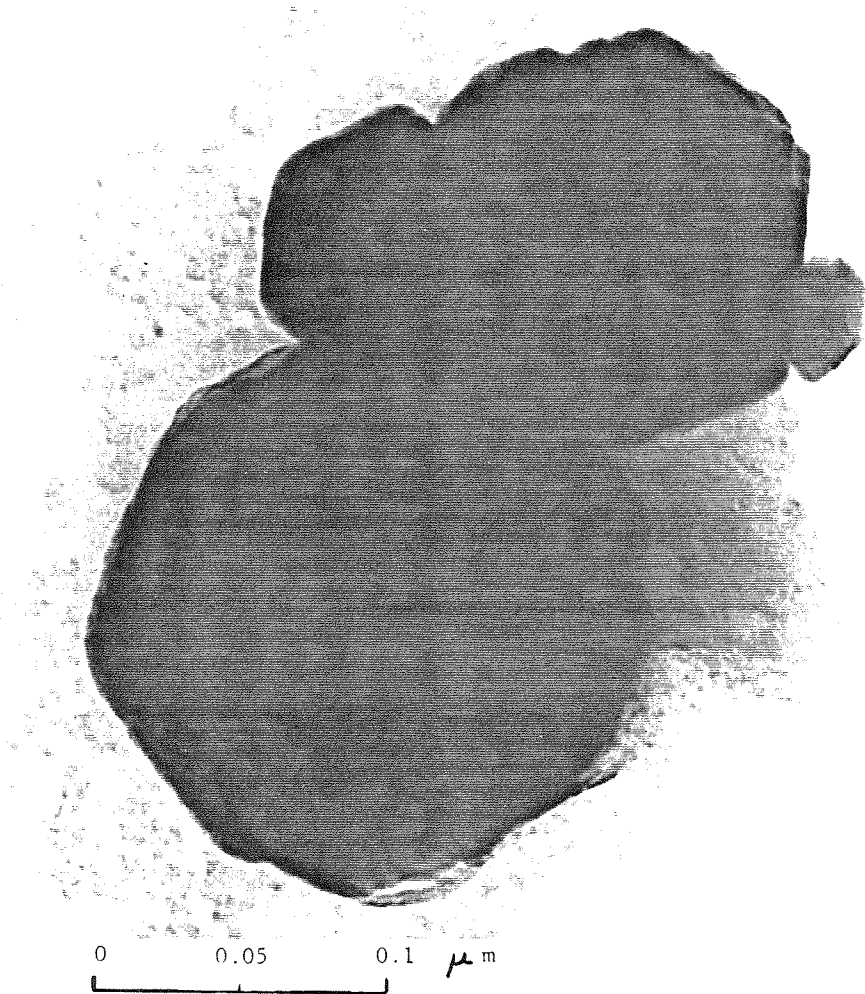


Figure 2-7





Figure 2-8

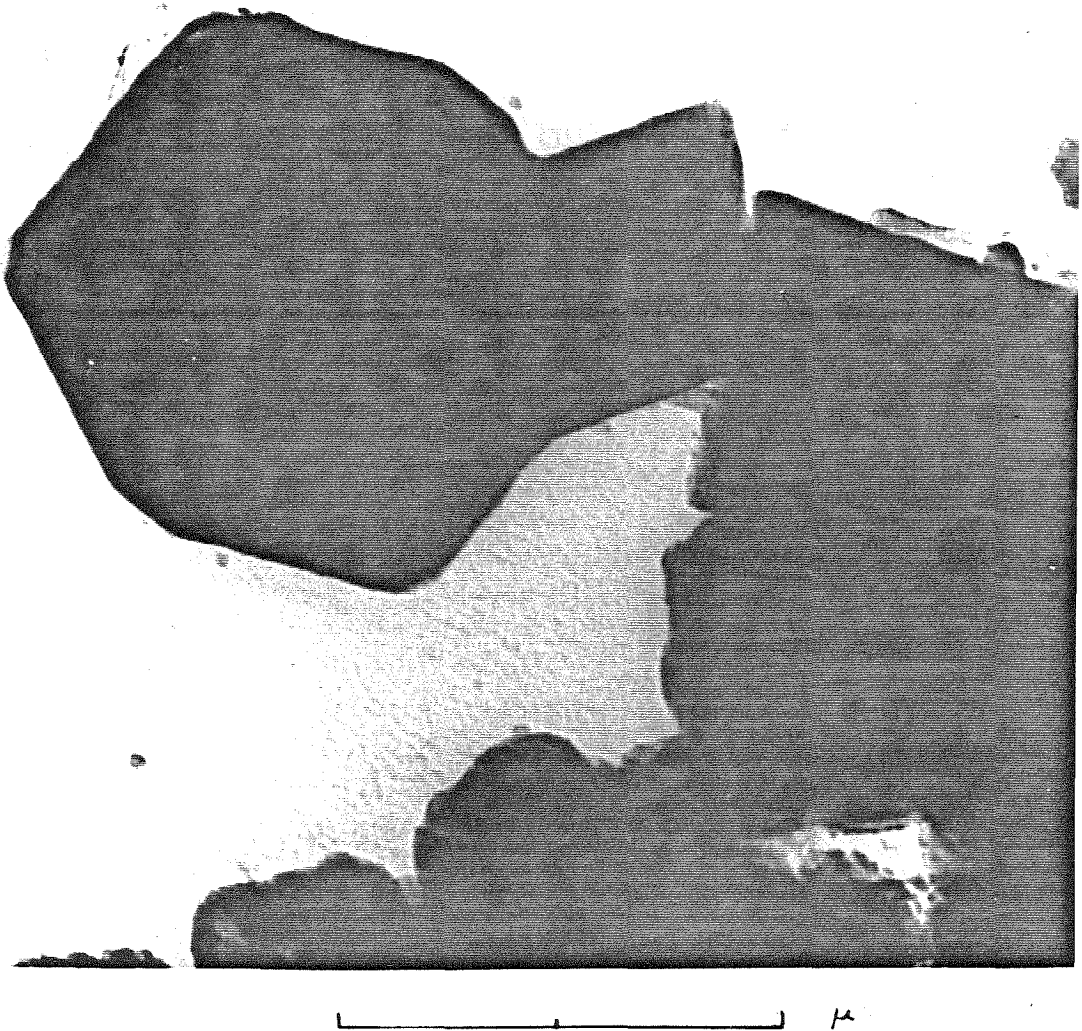
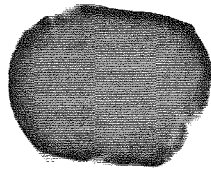


Figure 2-9.



0 0.1 0.2  $\mu$ m

Figure 2-10

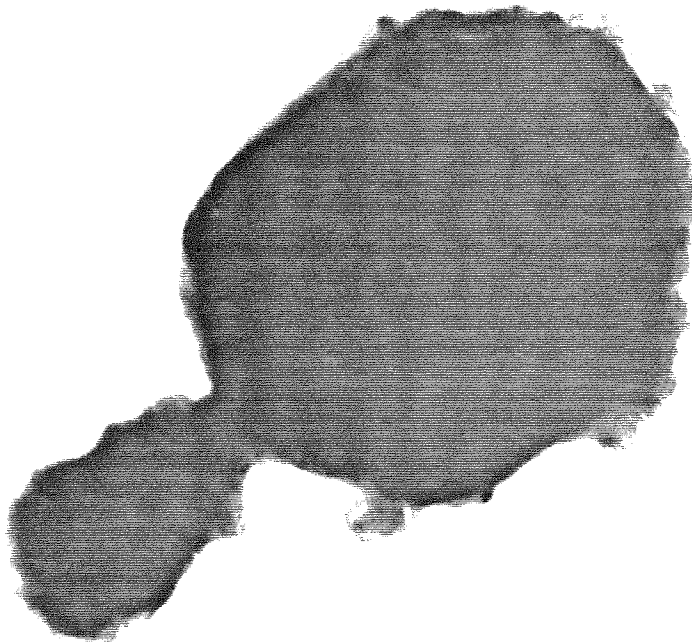


Figure 2-11

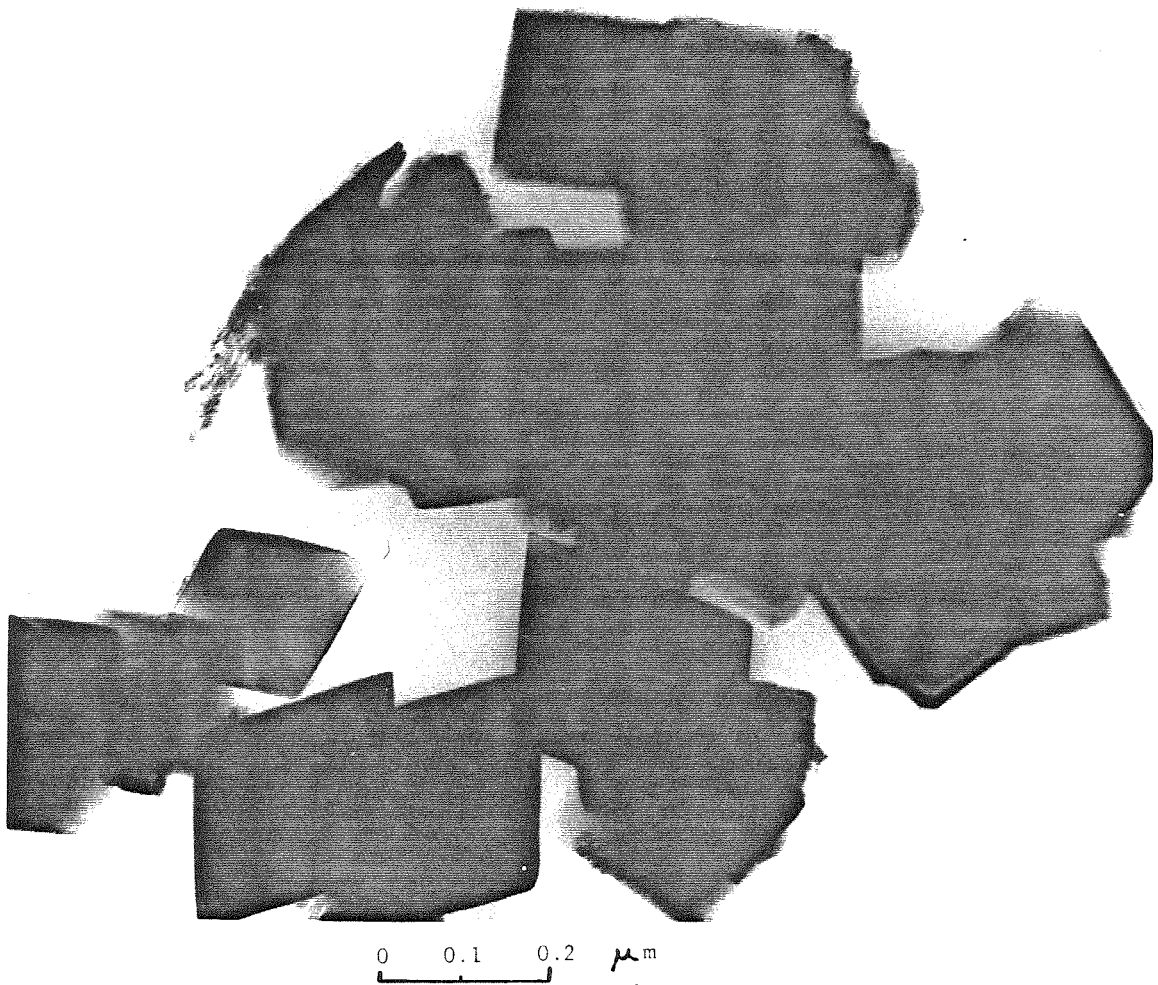


Figure 2-12



Figure 2-13

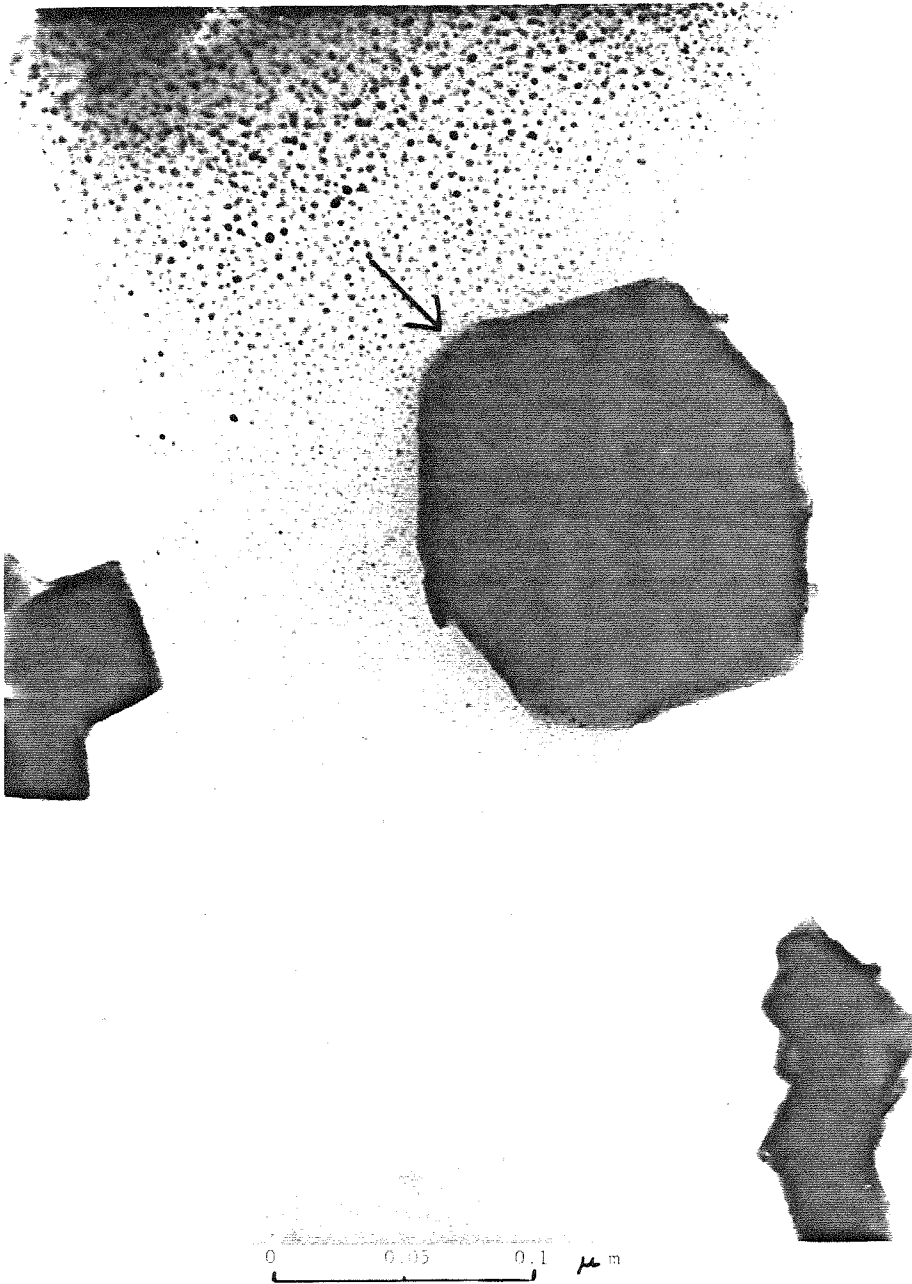
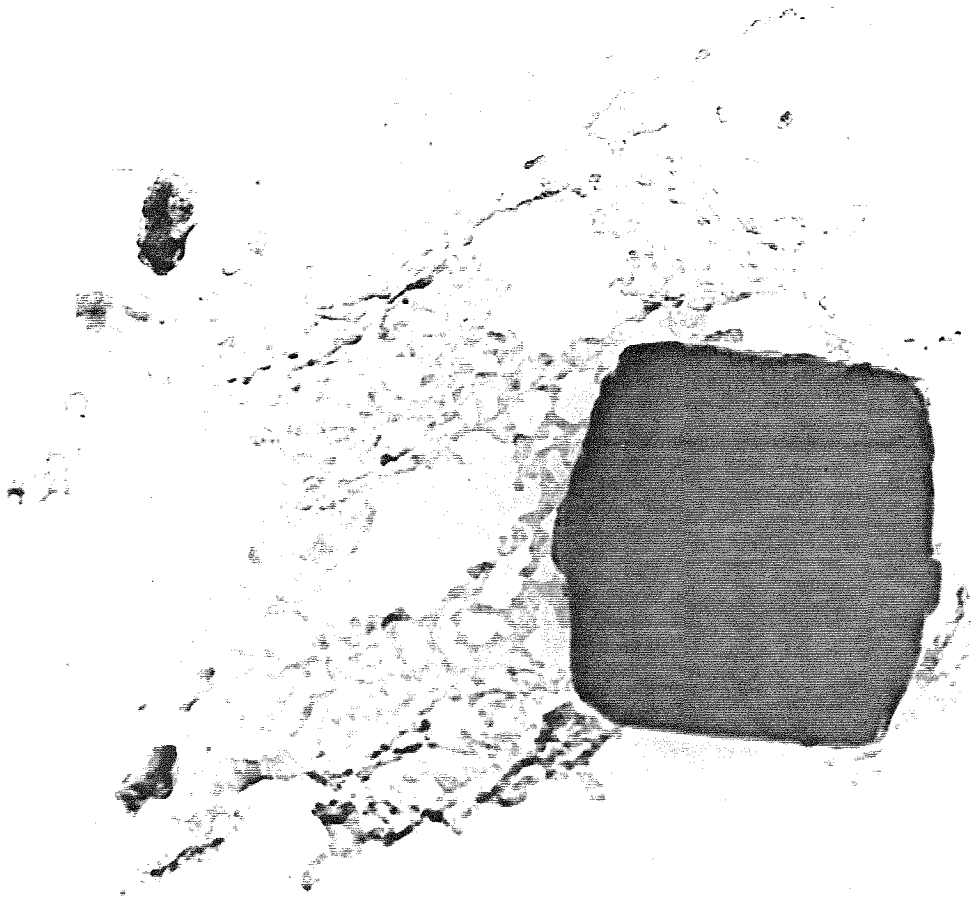
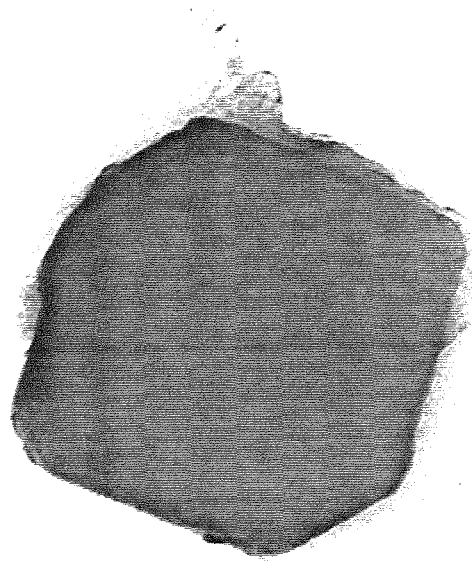


Figure 2-14



0.05 0.1  $\mu$  m

Figure 2-15



0 0.05 0.1  $\mu\text{m}$



Figure 2-16

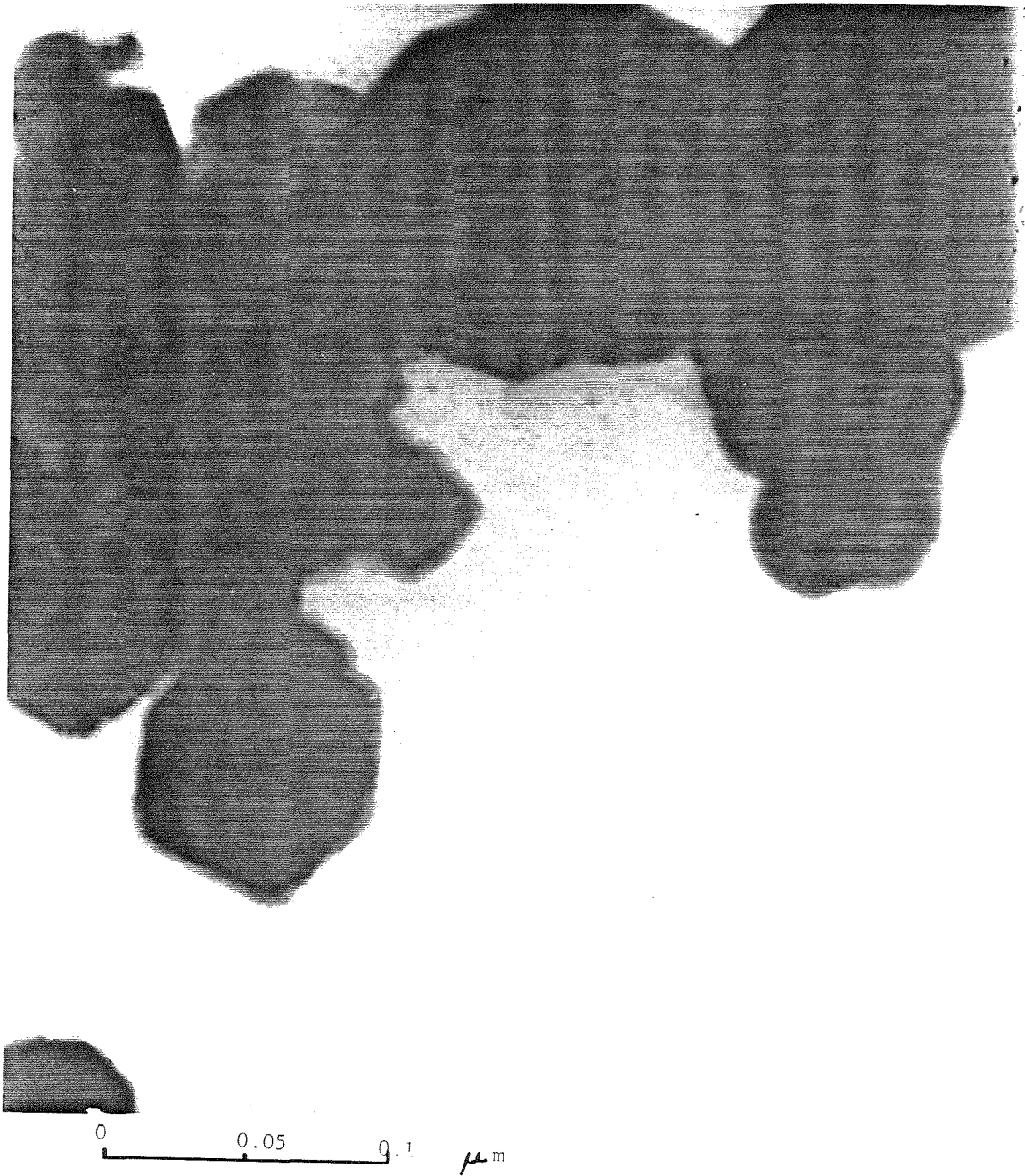
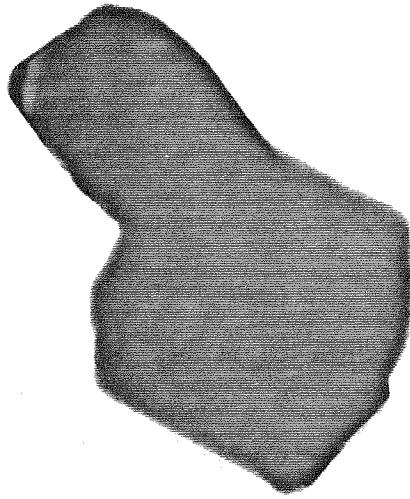


Figure 2-17



0 0.1 0.2  $\mu$  m

forms (D: Fig. 9, 10), are compatible with anomalous shapes of magnetite found in bacteria (cuboidal and tear-drop; Blakemore et al., 1981) and turtles (sphere; Perry et al., 1985). For the convenience of later discussion, we classified these four modes of occurrence as modes A, B, C, and D as listed above.

#### F. ORIGIN OF MAGNETITE

Grain-size distribution histograms have long been used by sedimentologists as a provenance indicator. Applying this to delineate the source of ultrafine magnetite in sediments is very important from the paleomagnetic point of view. Due to its high susceptibility and resistance to demagnetization, the presence of single-domain (SD) magnetite makes a significant contribution to the remanent magnetism of the rocks. In addition, the small size of SD magnetite particles ensures that it will have a slow settling velocity in aquatic environments. Depositional effects should not affect its alignment along the magnetic field.

Single-domain magnetite particles have been observed directly with TEM in a variety of igneous rocks. Evans et al. (1968) and Evans & Wayman (1970) found such particles as inclusions in pyroxene and plagioclase grains in gabbroic intrusions. Similarly, Smith (1979) found them as an auxiliary phase in glass of a mid-ocean ridge basalt and Geissman et al. (1983) report it from an ash-flow tuff. But the high Ti contents of these grains distinguish them from SD magnetite grains observed in this study. Various authors have used the revised Lowrie-Fuller test (Johnson et al., 1975) as a tool to determine the existence of SD magnetite particles in various types of sediments (e.g. limestone, Lowrie & Heller, 1982; lake sediments, Stober & Thompson,

1977), but no TEM observations have been made in these studies and the size and shape distribution of the grains inferred to be present can not be determined precisely. Of all the common magnetic mineral phases in soils tabulated by Schwertmann & Taylor (1977), magnetite was not listed. However, Ozdemir & Banerjee (1982) found ultrafine-grained magnetite particles with a size distribution in the SD to PSD stability field as a major magnetic component in the soil samples from west-central Minnesota. The other two occurrences of SD magnetite are biogenic and synthetic. Because the magnetic extraction techniques for sediments are still under development, reports on other occurrences of SD magnetite in nature are to be expected in the future. For the purpose of this study, one obvious question to be raised is, "What are the sources of SD magnetite in marine sediments?"

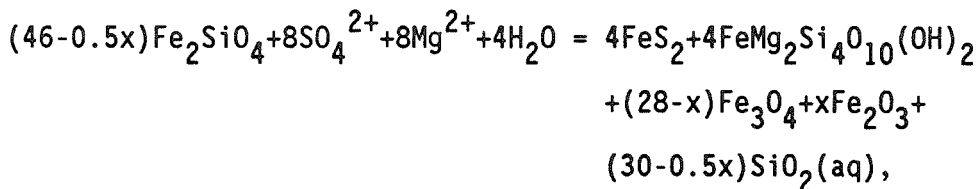
Magnetite in marine sedimentary environments might have one or more of the following origins: (1) cosmic, (2) volcanic, (3) terrigenous, (4) submarine weathering, (5) hydrothermal, (6) diagenetic, (7) hydrogenous (authigenic), and (8) biogenic. Industrial fallout (Doyle et al., 1976) should not have made any contributions to the magnetic mineralogy in ancient sedimentary rocks.

Magnetic spherules (10-200  $\mu$ m in diameter) consisting of metallic iron nuclei surrounded by a shell usually of magnetite, have been observed in recent sediments (Chester & Aston, 1976). Although the origin of these magnetic spherules is not clear, cosmic production has been proposed (Castaing & Frederickson, 1958). The scarcity of these cosmic magnetic spherules implies that they are not an important source of magnetite in sediments.

Terrigenous magnetic phases play a major role as the remanence carrier in some marine sediments (Verosub, 1977). Rounded and eroded

shapes would presumably be a result of water transport while sharp and angular forms would suggest aeolian transport of volcanic dust, for example. Magnetic studies have confirmed the presence of multi-domain magnetite in a variety of marine sedimentary rocks (Lowrie & Heller, 1982; Ensley & Verosub, 1982) and deep-sea cores (Lovlie et al., 1971). Rounded grains with pitted surfaces observed under SEM imply these magnetite particles are of detrital origin. Again, their size (0.2-30  $\mu$ m) is larger than the size of magnetite grains extracted from the Potamida clays. Nevertheless, the low resolution of SEM prevents the delineation of detailed grain size distribution histograms for grains < 1  $\mu$ m.

Magnetite might be formed in hydrothermal systems by the reaction (Shanks et al., 1981):



or it might be formed by submarine weathering of oceanic basalt (Fyfe & Lonsdale, 1981). The occurrences of magnetite in Red Sea hydrothermal system sediments (Hackett & Bischoff, 1973) and manganese nodules (Carpenter et al., 1972) have been confirmed by magnetic measurements, but no discrete magnetite grains have been observed. Geological evidence also does not support the presence of a hydrothermal system around Crete during the late Miocene.

Diagenetic magnetite is thermodynamically permissible in anoxic marine sediments (Berner, 1964). Recently, botryoidal and spheroidal magnetite crystal aggregates (3-20  $\mu$ m in diameter) found in the Upper Silurian and Lower Devonian Helderberg limestones and the Cambrian Bonnetterre dolomite have been inferred to be of diagenetic origin (McCabe

et al., 1983). However, geochemical models of diagenetic magnetite formation are not yet well developed. In addition, the size (0.5-2  $\mu\text{m}$ ) of their individual crystallites does not fall in the single-domain field.

As we mentioned before, a systematic survey of the size and shape distribution of ultrafine-grained magnetite with different provenance has not yet been made. Therefore the above comparison does not exclude any of the six occurrence modes (cosmic, volcanic, terrigenous, hydrothermal, submarine weathering, and diagenetic) as a possible source of magnetite in the Potamida clays. However, the comparisons do suggest that the majority of these magnetite grains are probably of hydrogenous or biogenic origin.

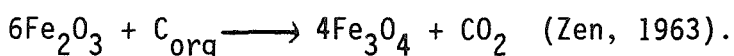
Henshaw & Merrill (1980) recently developed a new Eh-pH stability diagram for iron phases in marine depositional environments, using the actual average concentrations of S and Fe in the ocean and revised energy data for iron phase reactions. Their work indicates that magnetite may be an authigenic phase under suitably reducing conditions. Earlier, Harrison & Peterson (1965) suggested that the major remanence carrier in one of the Indian Ocean cores might be of authigenic origin, based on an unusual vertical elongation of the susceptibility anisotropy ellipsoid. However, no mechanism has been suggested to relate this abnormal susceptibility anisotropy with authigenesis. In any case, these analyses contradict the traditional view that magnetite is not a stable phase in most aqueous environments (Garrels & Christ, 1965).

On the other hand, SD magnetite has been successfully precipitated in the laboratory (Sugimoto & Matijevic, 1980) under conditions of slow reaction rate and relatively high temperature. These conditions rarely occur in natural depositional environments, but the similarity in shape

of the type B grains to the magnetite standard (Fig. 11) strongly argues for its inorganic origin. Two possible biologically-mediated mechanisms might promote this reaction directly or indirectly.

Iron bacteria, a type of chemoautotrophic microorganism with a typical body size from 1-10  $\mu$ m, will oxidize ferrous ion in the water and obtain energy from this reaction. The oxidized product of this biological mechanism is generally believed to be an iron hydroxide (Ehrlich, 1982). Because a conclusive phase identification has not been made, other possibilities can not be excluded.

The other possible way to precipitate iron oxide from sea water is through iron coagulation with organic material to form colloids of amorphous iron hydroxide or hematite. In estuarine environments, apparently large amounts of iron are removed through an iron coagulation mechanism of this sort (Hunter, 1983). Due to the small size (0.45  $\mu$ m) of colloids, no phase identification has been successfully made (J. Edmond, pers. comm.). The application of this mechanism to the marine environment has not been carefully studied. Biological removal apparently affects the Al and Ca concentration of surface sea water (Deuser et al., 1983). The short resident time of iron in sea water suggests that the biological removal mechanism of iron might work more efficiently. After these colloids settle down to the water-sediment interface, the Eh change in their surroundings might reduce them to magnetite as follows:



Mackereth (1971) and Thompson et al. (1980) both report positive correlations between the magnetite and organic material contents in lake sediments. Either biologically-mediated or organically-catalyzed production of magnetite could be responsible for these observations.

Type C grains are the most probable candidates for biogenic magnetite. The size of these grains overlaps with the typical bacterial magnetite size. We noticed that at certain viewing angles the octahedral grains will have a hexagonal image under TEM (Fig. 12). But if the grains were pseudohexagonal, the surface might not be straight or the interior of the grains might show asymmetric light intensity contrast. Portions of the grains show features which suggest an inorganic origin (Fig. 14). Other hexagonal grains, observed under very high magnification (200,000-650,000 X), have perfect crystal faces and symmetric interior light intensity contrasts (Fig. 8, 15, 16, 17, 18). These grains do not appear to be pseudohexagonal.

Although the biologic origin of these grains can not be ascertained just from morphologic observation, there appears to be hexagonal single-domain magnetite particles in these late Miocene sediments from northwest Crete. If these grains are really biogenic, they should be regarded as fossils as are other remains of organisms. However, the term "microfossil" is inappropriate for these particles as they are much smaller than any other microfossil reported to date, their size being less than the wavelength of visible light. The term "nanofossil" already has been applied to other groups, so we propose using the term "picofossil" for any biogenic objects in this size range.

Some of the type C grains are not distinguishable from cubes (Fig. 14), another rare crystal form of magnetite which is also present (apparently) in some bacteria (Balkwell et al., 1980). This occurrence of type D grains could be either biogenic or authigenic. Type A grains probably represent microscale oxidation or dissolution products of original biogenic or authigenic magnetite. After being put in dithionite-citrate solution for two days, the surficial oxidation



products (maghemite?) of these grains would be leached away to produce frothy surfaces.

Even though we can not determine which provenance (biogenic or authigenic) contributes the larger portion of magnetite in the Potamida clays, the significant point is that both authigenesis and biogenesis depend on the activity of organisms. The observed decrease of fine-grained magnetite in this section during a reversal might be caused by the decrease of biological activity due to environmental changes (small increase of Sun's radiation reaching the Earth's surface; variations of atmospheric circulation, etc.) during a transition (Black, 1967; Tarling, 1971) or caused by the decrease in magnetite precipitation by bacteria as Kirschvink (1982) suggested.

As the results show, the grain size of sample 60 in the Potamida section, which recorded normal polarity, is larger than that of sample 45 in the same section, which was deposited during a transition. This contradicts the predictions of the biogenic hypothesis, but since sample 45 is near a ferruginous layer (Fe II), it might not record the exact variation of grain size distribution during a reversal. The samples from the Skouloudhina section do not show magnetic intensity variations during the transition (Fig. 1). The grain size of extracted magnetite from samples in the Skouloudhina section also fall in the MD field. Such differences in magnetite grain size distribution between the lower Potamida section and the Skouloudhina section might correspond to changes in the depositional environments.

The Skouloudhina section is located in the same basin as Potamida (Laj et al., 1982), but is laterally closer to the neritic Fotokadhon Formation (Meulenkamp et al., 1979; Langereis, pers. comm.). Another source of magnetite, such as terrigenous detritus might be more

significant for contributing magnetite in this relatively shallower environment. In addition, the depositional age of both sections is close to the Mediterranean salinity crisis in the Messinian. The increase in magnetite grain size in the upper Potamida section probably also reflects a transition from open-marine environments to an early Messinian overall sea level submergence, resulting in semi-closed shallow embayments (Meulenkamp et al., 1979; Valet et al., 1983; Langereis & Zachariasse, in press) and terrigenous detritus might become the dominant phase. The fact that no euhedral magnetite grains have been found in samples 60 and 02A supports this deduction. The real relation between environmental changes and such magnetite grain size variations needs to be determined by detailed local depositional phase analysis.

#### G. CONCLUSION AND APPLICATIONS

The results shown above do not exclude the possibility of a non-biogenic origin for the magnetite in these sediments. But the evidence suggests a biologic origin for certain grains. Whether the bacterial magnetite is the dominant magnetite phase as predicted by Kirschvink (1982) can not as yet be determined from this study. We plan to investigate magnetite extracts from a variety of sediments and sedimentary rocks to see the size and shape distributions of detrital magnetite in different environments and different geological periods. In particular, comparison of the magnetite extracts from sediments with abundant fossils and organic material (like marl) and sediments which are apparently of inorganic origin (like loess) might provide a solution to this problem.

We can also use this method to evaluate the existence of SD magnetite as a primary component in varieties of rocks. This is extremely important for paleomagnetic studies on shale and other sedimentary rocks. Because the major mineral phases in shales are usually diagenetic clays, the remanent magnetism of shale might be secondary in origin. Apparently, this is not the case for the Potamida clays. It is highly possible that other shales also have primary remanent magnetism obtained by biological precipitation of iron oxide. More than half of all sedimentary rocks are shale, and an understanding of the processes through which they become magnetized is important to the science of paleomagnetism.

#### H. ACKNOWLEDGEMENTS

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CHAPTER THREE

THE MAGNETIZATION OF MARINE SEDIMENTS: A SEARCH  
FOR FOSSIL BIOGENIC MAGNETITE

MAGNETOTACTIC BACTERIA AS SOURCE OF ULTRAFINE-GRAINED MAGNETITE  
IN SURFACE SEDIMENTS FROM THE SANTA BARBARA BASIN

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Remanent magnetism in marine sediments has been used extensively over the past twenty years to calibrate the geological time scale, study geomagnetic reversals and secular variation, and measure the rates of seafloor spreading. Although these sediments may contain different magnetic minerals, magnetite is the most commonly observed and magnetically stable phase. The size, shape, and post-depositional fate of this magnetite affect the magnetic remanence. Biogenic magnetites are single-domain with a high natural magnetic remanence (NRM) and have been suggested as a significant source of magnetic remanence in marine sediments. We have studied surface sediments from the Santa Barbara Basin and report the occurrence of living magnetotactic bacteria and the deposition of biogenic ultrafine-grained, single-domain magnetite. Using a novel extraction technique, transmission electron microscopy and SQUID magnetometry, we show that these bacteria and the magnetite they produce are the major source of stable remanent magnetism in these sediments.

Studies on haemipelagic sediments from several localities from the eastern Pacific show a maximum intensity of magnetic remanence occurring in surface sediments (Karlin and Levi, 1983; Lund et al., 1983). Rock magnetic studies indicate a dramatic decrease of intensity with depth and correlate this with a loss of the fine-grained component (Karlin and

Levi, 1985; Leslie et al., 1984). The morphology of this magnetite and how it is formed had eluded researchers in previous studies because of the limited resolution of the techniques used (Chang and Kirschvink, 1985). The high intensity of natural magnetic remanence and bacterial activity in the surface sediments suggested biogenic magnetite as a probable source of the submicron-sized magnetite.

Our samples were collected from three different sites in the Santa Barbara Basin (34°14'N, 120°1'W) at a depth of 598 meters and a temperature of 8°C. The top three centimeters of sediment were removed from box cores and either fixed with 2.5% glutaraldehyde immediately after collection or left untreated. All the samples were kept at 8°C.

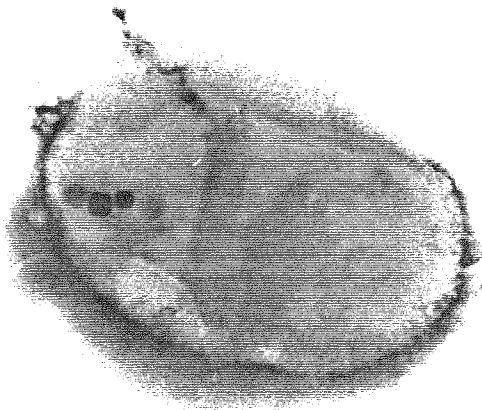
We examined the unfixed sediment under low power light microscopy (160X) by placing a drop of sediment on a glass slide. When the south end of a stirring bar magnet was placed next to the drop, magnetotactic bacteria present in the sediment accumulated at the edge of the drop. To study these bacteria and the ultrafine-grained magnetite they produce by transmission electron microscopy, we devised a novel extraction technique. Carbon-coated copper grids were placed face down on drops of sediment suspension and subjected to the south pole of a cobalt rare earth magnet suspended 1 cm above the drops, for 20 to 30 minutes. Some grids were treated with 1% uranyl acetate for 1 minute to stain the bacteria. The grids were observed with a Phillips 201 transmission electron microscope at 80kV. Identification of the crystals as magnetite was made by electron diffraction (Chang and Kirschvink, 1985; Towe, 1985).

We observed several morphological types of magnetotactic bacteria in preparations of unfixed sediment samples (Fig. 1). *Vibrio* and rod-shaped bacteria were seen (Fig. 1a,c), but the most common morphology

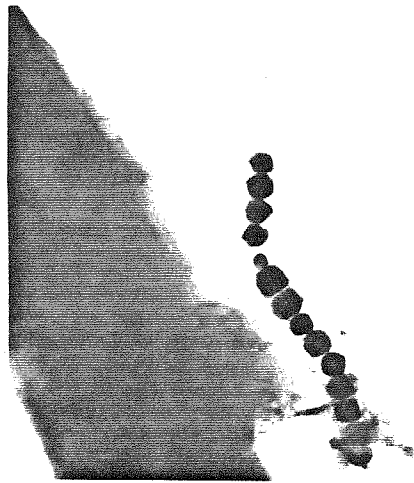
Figure 3-1 - Transmission electron micrographs of magnetotactic bacteria from the Santa Barbara Basin; all scale bars 200 nm. A, Vibrio with chain of 11 crystals of magnetite and one polar flagellum. Note the irregular shape of the crystals. B, Coccoid with chain of four crystals. C, Rod with chain of 13 crystals.



A



B



C

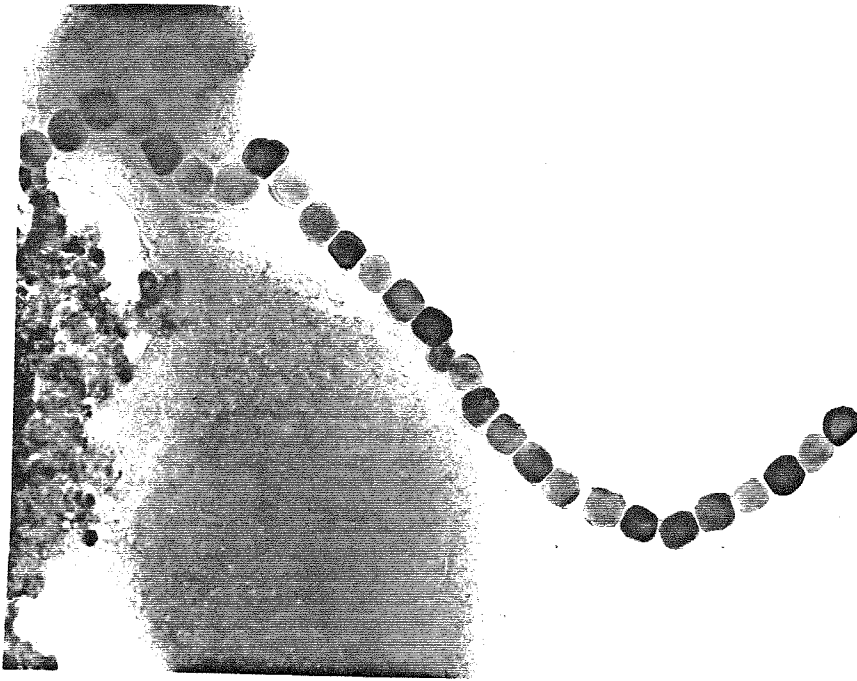


was coccoid (Fig. 1b). In each case, the crystals of magnetite were arranged in a chain 10 to 20 crystals in length. The individual crystals were between 40 and 60 nm in size and cuboidal, rectangular, or irregular in shape. The sizes of all the well-formed crystals fall within the calculated stability field for single-domain magnetite (Butler and Banerjee, 1975). In fact, to date, all reported sizes of bacterial magnetites fall within the single-domain range (Blakemore, 1982; Towe and Moench, 1981; Frankel, 1984). The irregular shaped crystals may be due to the dissolution of well-formed crystals (H.W. Lowenstam, pers. communication).

Aggregates and chains of ultrafine-grained magnetite free of bacteria were seen in both unfixed (Fig. 2a) and fixed material (Fig. 2b,c). Like the magnetite seen in the bacteria, most of the crystals were 40 to 60 nm in size and cuboidal, rectangular or irregular in shape. In one instance an intact magnetosome was observed (Fig. 2c). The gradual increase in size of the crystals in the chain with a few much smaller crystals at one end is characteristic of magnetosomes in many magnetotactic bacteria. Crystals which were roughly teardrop in shape and larger in size (100 to 120 nm) were also seen (Fig. 2d).

The magnetic properties of the sediment were analyzed using saturation isothermal remanent magnetization (sIRM) and alternating field demagnetization (AF) with a SQUID magnetometer (Fuller et al., 1985). Both fixed and unfixed sediments were examined. Quartz glass holders were filled with 0.1 g aliquots of sediment. The coercivity spectrum generated indicates the primary remanence carrier is single-domain magnetite (Fig. 3). In a previous study, the coercivity spectrum of a marine magnetotactic bacterium was determined (Fig. 3; Chang et al., 1987, see Chapter 4). Collected from a saltwater marsh, these

Figure 3-2 - Transmission electron micrographs of ultra-fine grained magnetite from the Santa Barbara Basin. All but A were from fixed material; scale bars 100 nm. A, Chain of 30 cuboidal crystals extracted from unfixed material. B, Cluster of prismatic and irregular magnetite crystals. C, Chain of crystals which appears to be an intact magnetosome. Note the smaller crystals at the right-hand terminus. D, Chain of irregular and teardrop-shaped crystals.



A



B



C

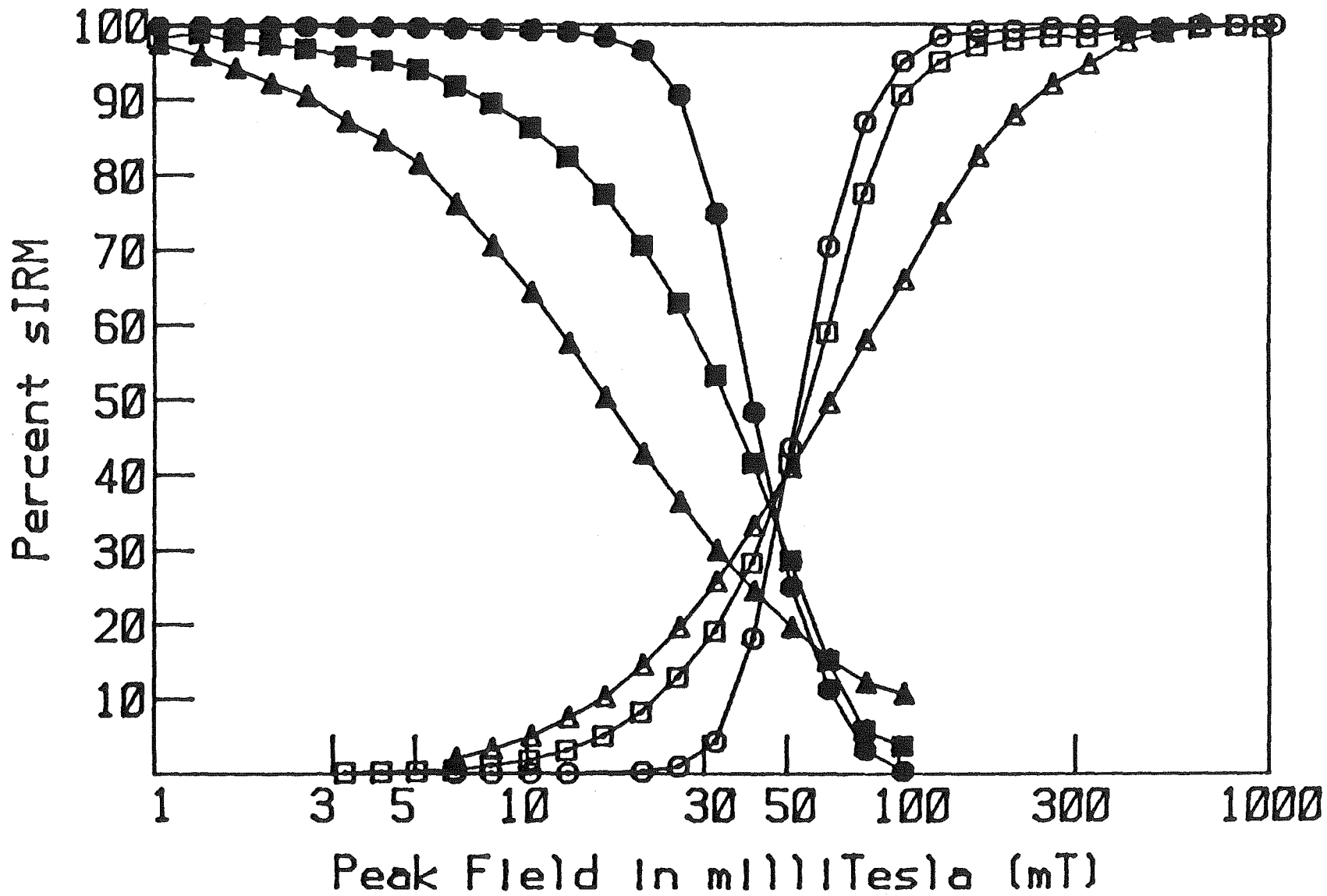


D





Figure 3-3 - Coercivity spectra of Santa Barbara Basin surface sediment (squares), pellet of marine magnetotactic bacteria from Laguna Figueroa, Baja California, Mexico (Circles) and beach sand with 10% w/w content of coarse-grained magnetite from Laguna Figueroa (triangles). Open symbols, IRM; solid symbols, AF demagnetization.



bacteria have prismatic crystals 90 by 120 nm aligned in a chain of ten crystals on average. The bacterial crystals saturate at about 100 milliTesla (1000 Oe) with an intersection at about 50 milliTesla (500 Oe). The coercivity spectrum of the Santa Barbara Basin material also saturates at about 100 milliTesla and intersects at about 50 milliTesla. Grain-grain interaction and the presence of other magnetic minerals (i.e., coarse-grained magnetite and haematite) in the sediment may account for the differences observed in the two spectra (Cisowski, 1981). A few particles of multi-domain magnetite ( $>1 \mu\text{m}$ ) were seen in sediment extracts. We compared the coercivity spectrum of the Santa Barbara sediment with that of a marine sediment which contained mostly coarse-grained magnetite and no bacterial magnetite (Fig. 3). Both the saturation values and the intersection point are markedly different. This suggests that the coarse-grain component does not contribute significantly to the magnetic properties of the surface sediments.

The maximum values of sIRM obtained for both fixed and unfixed samples ranged between  $2.5 \times 10^{-4}$  and  $1.25 \times 10^{-3}$  emu/g and agree with previously published measurements for haemipelagic sediments (Karlin and Levi, 1983; Lund et al., 1983). A magnetotactic bacterium, with a chain of cuboidal 50 nm crystals in a chain twenty crystals long, like those seen in the Santa Barbara bacteria, has a calculated saturation moment of  $10^{-12}$  emu/g (Blakemore, 1982; Frankel, 1984). If all the remanent magnetization is attributed to the bacteria, a population density of between  $10^7$  and  $10^8$  magnetotactic bacteria/gram of sediment is predicted. Such a population was never seen in the material we examined, although direct field counts at the time of collection could not be made. Populations of magnetotactic bacteria from other environments we have studied decline dramatically within hours or days

after collecting (Chang et al., 1986, see Chapter 4). The discrepancy in the magnetic remanence and the actual number of live bacteria observed in the Santa Barbara sediments may be explained by episodic increases in population, the persistence of ultrafine-grained magnetite in the surface sediments, the presence of other magnetic minerals (including some coarse-grained magnetite), and the death of much of the population during sample collection and storage. The bacteria contribute significantly to the natural magnetic remanence because each of the crystals is single-domain and is usually deposited in a chain. The discovery of an intact magnetosome and chains of magnetite in the sediment extracts suggests that these crystals remain aligned even outside the bacteria. Unlike bacterial magnetites, coarse-grained magnetites have very little effect on the natural magnetic remanence.

This study has concentrated on the surface sediments of the Santa Barbara Basin where the conditions of growth for the magnetotactic organisms may be optimal. A microbial mat community, dominated by species of Beggiatoa, a sulfur-oxidizing chemolithotroph, thrives on the surface (M. Kastner, pers. communication). Both the Beggiatoa and most magnetotactic bacteria are microaerophils, needing trace quantities of oxygen for their metabolism (Nelson and Jannasch, 1983). The abrupt disappearance within the top meter of the ultrafine-grained component in sediments from the California continental borderland (Lund et al., 1983; Karlin and Levi, 1985; Leslie et al., 1984) and the Gulf of California (Karlin and Levi, 1983, 1985) can be explained by the disappearance of the magnetotactic bacteria and the dissolution of the bacterial magnetites. In these sediments iron oxide reduction is coupled with the diagenesis of organic material (Karlin and Levi, 1983, 1985). The profiles for sulfur, sulfate, and oxygen concentrations corroborate this

explanation (Karlin and Levi, 1983, 1985; Savrda, 1984).

The results of this study and those we have conducted on two other marine environments (a lagoonal environment in Baja California, Mexico, and a carbonate environment in the Florida Keys, U.S.A., Chang et al., 1987, see Chapter 4) suggest that magnetotactic bacteria are the source of the primary remanence carrier (ultrafine-grained, single-domain magnetite) in many marine sediments. The eventual fate of this biogenic magnetite depends on a number of post-depositional factors. In environments where there is a strongly reducing zone with abundant sulfide, only greigite pseudomorphs of magnetite have been found (Demitrack, 1985). Maghemite pseudomorphs of bacterial magnetite have also been seen in deep-sea sediments (von Dobeneck et al., 1985). The loss of the ultrafine-grained bacterial magnetite component with depth in open ocean basins may limit the extent of the biogenic magnetite contribution to rock magnetism to marine sediments with low organic content like calcareous oozes and limestones.

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ULTRAFINE-GRAINED MAGNETITE IN DEEP-SEA SEDIMENTS:  
POSSIBLE BACTERIAL MAGNETOFOSSILS

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Abstract

A new extraction technique now permits ultrafine magnetite crystals to be separated from a variety of deep-sea sediments. Morphologic characterization of these particles with Transmission Electron Microscopy (TEM) reveals the presence of several distinct crystal types, some of which closely resemble those formed by the magnetotactic bacteria. The apparently biogenic magnetite particles are of single-domain size and dominate the population in calcareous deep-sea sediments. Bacterially precipitated magnetite may therefore be a major source of the stable magnetic remanence in some marine sediments. These objects possibly constitute the smallest mineral fossils yet recovered from the sedimentary record.

Introduction

Deep-sea sediments have been known to be stable carriers of natural remanent magnetization ever since the pioneering work of Opdyke et al. (1966) on piston core samples from the south Pacific Ocean. Subsequent paleomagnetic investigations on cores obtained by the Deep-Sea Drilling Project and from marine sequences now exposed on land provide the basis for the direct correlation between the magnetic polarity time scale deduced from marine magnetic lineations and the biostratigraphic time scale determined from the study of planktonic micro- and nano-fossils (e.g. Alvarez et al., 1977; Tauxe et al., 1983; Lowrie and Channel, 1983). As a result of these investigations, geomagnetic reversal

boundaries now provide the most reliable chronostratigraphic markers for post-Jurassic time (Harland et al., 1982) and form the basis for all estimates of sea-floor spreading rates.

Despite the importance of these studies, the mechanisms with which deep-sea sediments acquire their stable magnetization are poorly understood. Although a majority of rock-magnetic investigations implicate ultrafine-grained magnetite particles ( $<0.5\ \mu\text{m}$  across) as the carriers of the stable magnetization in marine sediments (Lowrie and Heller, 1982), most attempts to extract these particles from sediments have been plagued with low extraction efficiencies in this small size range and incomplete separation of magnetic minerals from other components of the sample. In some cases, small proportions of the total magnetic material have been isolated, and the particles which are removed fall at the large end of the grain size distribution (Kobayashi and Nomura, 1974). Compounding these extraction problems, several workers have used Scanning Electron Microscopy (SEM) rather than Transmission Electron Microscopy (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 multi-domain range for magnetite), and all such studies reveal objects of either terrigenous, volcanic or authigenic origin (Lovlie et al, 1971; McCabe et al., 1983). However, none of these studies shed light on the origin of particles in the extremely important sub- $0.1\ \mu\text{m}$  fraction.

Magnetite crystals biochemically precipitated by the magnetotactic bacteria 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). They exist

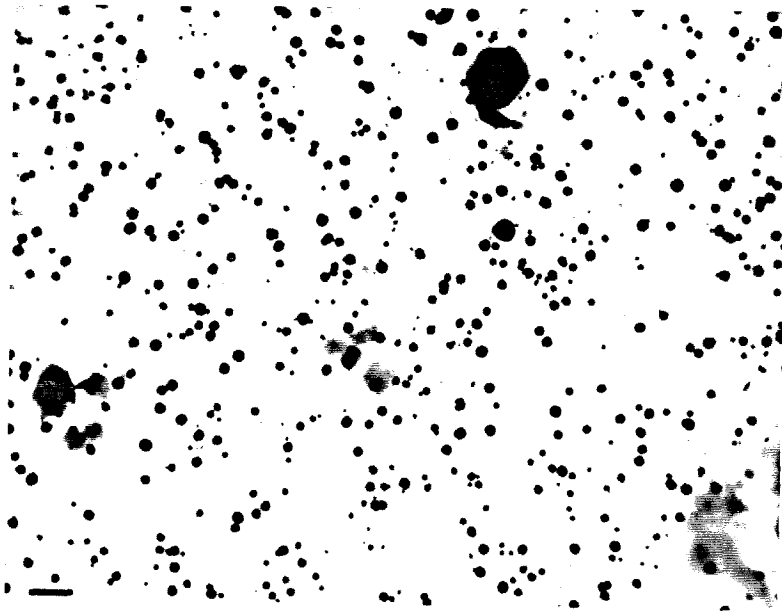
in both the northern and southern hemispheres and at the geomagnetic equator (Kirschvink, 1980; Blakemore et al., 1980; Frankel et al., 1981), and have been found in open marine environments (Blakemore and Frankel, 1982). The dimensions of all bacterial magnetite crystals measured with the TEM and published to date plot within the boundaries of the single-domain stability field as determined by Butler and Banerjee (1975) and shown here in Fig. 4. This property apparently results from natural selection for magnetotaxis on the size, shape and number of the crystals in each bacterium (Kirschvink, 1982; 1983). Three distinctive particle morphologies have been reported to date, including sub-rounded cubes and rectangles (Balkwill et al., 1979), hexagonal prisms with flat ends (Towe and Moench, 1981; Matsuda et al., 1983) and a rare "teardrop" shape in some bacteria from New Zealand (Blakemore et al., 1980). All of these forms are clearly distinct from the octahedral, spherical, and framboidal magnetite particles which commonly form through igneous, cosmic, and authigenic processes in nature.

We report here the development of new extraction, purification, and TEM sample preparation techniques specifically for magnetite which result in a higher yield of the fine-grained fraction and permit classification based on crystal morphology. Single-domain magnetite crystals for both biogenic and inorganic affinities appear to be present in varying amounts, but the biogenic fractions seem to dominate the calcareous oozes. These objects appear to be the smallest mineral fossils yet found in the sedimentary record and are bioinorganic particles of presumed prokaryotic origin.

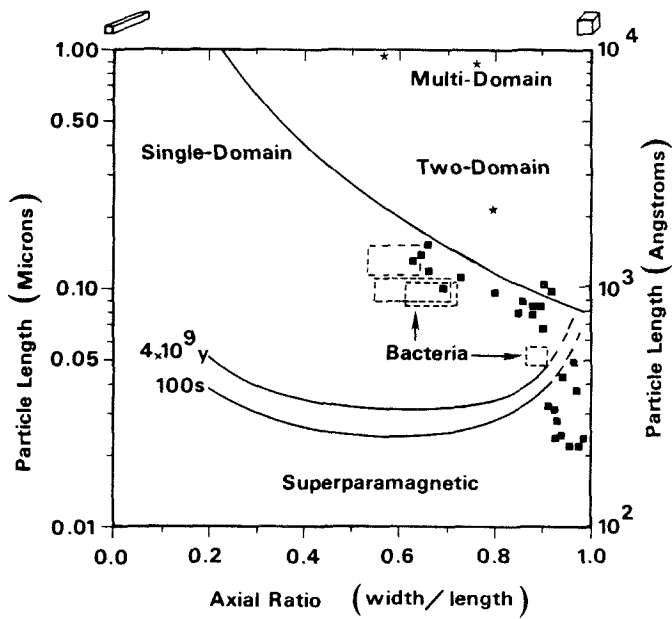


Figure 3-4 - (A) Low magnification (22,400 X) electron micrograph of magnetite extract from sample Core 31, Sec. 3, 9-11 cm of DSDP Leg 73 (approximately early Oligocene in age; Tauxe et al., 1983). Scale bar = 0.5 micron. (B) Plotted into the domain stability field diagram for magnetite (Butler & Banerjee, 1975), the size and shape distribution of grains shown in (A) spans from superparamagnetic to multi-domain (MD) field. Three distinctive assemblages of particles are classified and described in the text. These features are also common in other deep-sea foraminifera ooze samples examined by us.

(A)



(B)



## Materials and Methods

Deep-sea piston core samples of various sedimentary types were obtained from the Scripps Institute of Oceanography and the Lamont-Doherty Geologic Observatory. The sample sites range from the equator to mid-latitudes of the Pacific, Atlantic, and Indian Oceans, and vary in age from early Oligocene to recent. Various properties of samples examined to date are shown in Table 1. Cores which have been examined for paleomagnetism are marked by an asterisk and references for these studies are given.

The extraction and sample preparation procedures are the same as those described by Chang and Kirschvink (1985, see Chapter 2). The simplified scheme of the magnetite extraction procedure, which includes several steps for concentrating the magnetic minerals followed by a procedure to separate magnetite from other mineral phases, is shown in Figure 2 of Chapter 4. The isothermal remanent magnetization (IRM) acquisition experiment was performed on the bulk samples following a technique modified from Cisowski (1981) and described by Kirschvink (1983). X-ray analysis was made with the Debye-Scherrer method on magnetic separates.

## Results and Discussions

We tested the extraction efficiency of our purification procedure on flow-in material from two south Atlantic cores, RC 16-138 and RC 16-150. Three fractions of each sample were processed by steps shown in Table 2. After each step the saturated isothermal remanent magnetization (sIRM) of residues was measured and ratios of these values and the sIRM of bulk samples are included in Table 2. The sIRM of the non-magnetic residues after magnetic separation with a Franz isodynamic

TABLE 1. MAGNETIC GRANULOMETRY AND OTHER PROPERTIES OF DEEP SEA SAMPLES EXAMINED BY US.

Sample Property	RC 16-138	RC 16-150	14 PV	35 PV	35 PV	103 P	* DSDP Leg 73 Site 522 Core 2	* DSDP Leg 73 Site 522 Core 15	* DSDP Leg 73 Site 522 Core 31
Locality	Southwestern Atlantic (27°03'S, 40°10'W.)	Southwestern Atlantic (15°46.5'S, 38°38.7'W.)	Eastern Equatorial Pacific	Equatorial Pacific	Equatorial Pacific	Middle Equatorial Pacific	South Atlantic (26°07'S, 5°08'W.)	South Atlantic (26°07'S, 5°08'W.)	South Atlantic (26°07'S, 5°08'W.)
Depth (m)	3.1	3.5	4.1	0.2	5.5	3.6	5	57	124
Lithology	Foraminiferal Marl	Sandy Foraminiferal Marl	Siliceous Clay	Foraminiferal Radiolaria Marl	Marl	Foraminiferal Ooze	Calcareous Ooze	Marl	Calcareous Ooze
Carbonate Content	Moderate	Moderate	Low	Moderate	Low	High	High	Moderate	High
Color	Grayish Orange	Grayish Olive	Gray	Yellowish Brown	Dark Brown	Grayish Orange	Pale Grayish Orange	Grayish Brown	Yellowish Orange
Age (My)							0.8 (Pleistocene)	23 (Early Miocene)	35 (Early Oligocene)
NRM (E-7 Am <sup>2</sup> /kg)	8.31	1.59	0.32	2.90	3.32	6.91	7.21 (Sec. 2, 70cm) 6.35 (Sec. 3, 82cm)	33.40 (Sec. 3, 40cm) 22.10 (Sec. 2, 120cm)	7.52 (Sec. 3, 9cm) 6.10 (Sec. 2, 129cm)
IRM At a .720 Tesla Impulse (E-4 Am <sup>2</sup> /kg)	32.90	1.97	2.06	4.05	3.15	28.10	12.60 (Sec. 2, 90cm) 7.80 (Sec. 3, 82cm)	34.20 (Sec. 3, 40cm) 29.30 (Sec. 2, 120cm)	12.10 (Sec. 3, 9cm) 9.95 (Sec. 2, 129cm)
Sedimentation Rate (m/My)							9.3	1.6	9.2
Magnetic Granulometry	A: Rare B: Abundant C: None	A: Rare B: Rare C: None	A: Rare B: Rare C: None	A: Moderate B: Abundant C: None	A: Abundant B: Rare C: None	A: Rare B: Abundant C: Abundant	A: Rare B: Abundant C: Rare	A: Rare B: Rare C: None	A: Rare B: Abundant C: Abundant

Table 2. Ratios of the saturated isothermal remanent magnetization of residue ( $sIRM_{\text{residue}}$ ) and the saturated isothermal remanent magnetization of bulk sample ( $sIRM_{\text{bulk sample}}$ ) and major phase identified by the X-ray diffraction method in separates after three independent treatments.

treatment	Franz isodynamic separator	static magnet	DCB dissolution
$\frac{sIRM_{\text{residue}}}{sIRM_{\text{bulk sample}}}$	9 $\pm$ 5 %	37 $\pm$ 12 %	61 $\pm$ 9 %
major phases in separate (X-ray)	illite glauconite	magnetite maghemite	

separator drops to about 10% of the bulk sample, indicating that 90% of the magnetic particles in the samples have been removed. This efficiency is higher than 50% level reported by Lovlie et al. (1971), and may be due to our using prolonged ultrasonic dispersion and slower flow rates. The next magnetic separation with a permanent magnet removes 60% of the sIRM and concentrates it in a small volume. X-ray diffraction analysis on this extract shows that either magnetite or maghemite is the dominant phase, and the smoothness of the lines implies that fine-grained particles are abundant. Examination of the extract with optical microscopy also reveals that most particles are below visible resolution ( $<1 \mu\text{m}$ ) in size. These features are common for extracts of all sedimentary types that we have examined to date.

For determining the fraction of remanence carried by minerals other than magnetite, chemical dissolution experiments using solutions of dithionite-citrate buffered with bicarbonate (DCB) were performed on the bulk samples. DCB was first used by Mehra and Jackson (1960) to dissolve magnetic minerals in soils, and it is now routinely used in soil studies to determine non-magnetite iron fractions (e.g. Walker, 1983). We have shown that this solution can dissolve a variety of magnetic minerals including hematite, maghemite, goethite, and pyrrhotite in a few days without altering fine-grained magnetite (Kirschvink, 1981; Chang and Kirschvink, 1985). Therefore the sIRM decrease after this treatment measures the moment carried by minerals other than magnetite. Approximately 40% of the sIRM of our sample is removed with this treatment, indicating that about 60% of the sIRM is carried by magnetite.

Among these other magnetic minerals, maghemite has a saturation magnetization just slightly less than that of magnetite, and their X-ray

patterns are quite similar. It may therefore contribute a portion of the NRM in some marine sediments as suggested by Roggentine (1979), and probably exists as a minor phase in our magnetic extracts.

Although we have studied samples from only two deep-sea cores in this much detail, other work on the magnetic minerals in pelagic and hemipelagic sediments reveals that fine-grained magnetite is also the main magnetic phase (e.g. Lovlie et al., 1971; Karlin and Levi, 1983). In summary, the abundance of fine-grained magnetite implies that it plays an important, if not major, role in carrying remanence of some marine sediments.

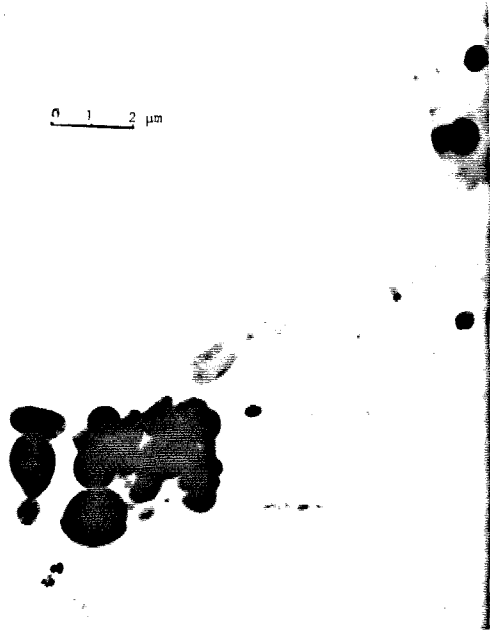
Results discussed in the preceding section say nothing about the biogenic vs. inorganic origin of the ultrafine-grained magnetite in marine sediments. As mentioned earlier, minerals which are precipitated biochemically under matrix-mediated control often have crystal shapes which are distinctly different from their inorganic counterparts (Lowenstam, 1981). It should therefore be possible to recognize some of the biogenic magnetites, particularly those from the magnetotactic bacteria, on the basis of particle size and morphology alone. In our samples, TEM examination reveals three general classes of fine-grained magnetite particles which we designate as A, B, and C as follows: Type A grains are 0.02 to 0.05  $\mu\text{m}$  in length with aspect ratios varying from 0.9-1.0 (e.g., superparamagnetic). Type B grains are 0.06 to 0.15  $\mu\text{m}$  in length with aspect ratios varying from 0.6-0.9 (single-domain), and type C grains are pseudo-single-domain and multi-domain particles larger than about 0.2  $\mu\text{m}$  in length.

As can be seen in Fig. 4, the sizes and shapes of particles measured from the final magnetite extract of one sample from the South Atlantic (Fig. 4) fall mainly in group B, which overlaps with those of

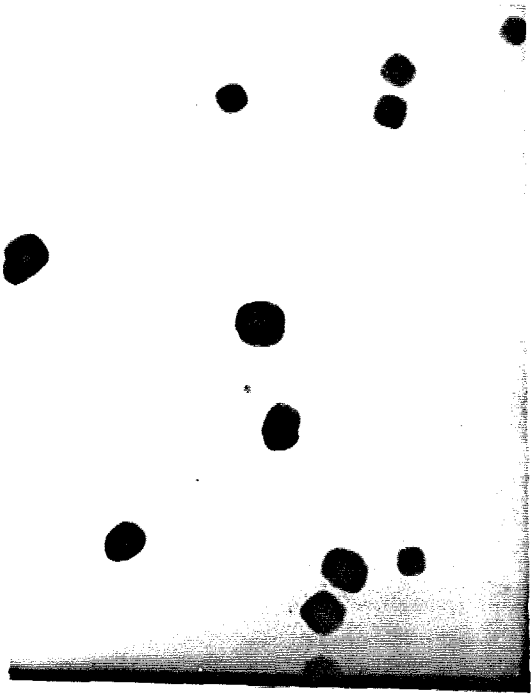
Figure 3-5 - (A) Electron micrograph of magnetite extract for sample 35PV, 55 cm. Subhedral MD particles with possible detrital origin are shown. Scale bar = 2 micron. (B) Electron micrograph of magnetite extract from sample Core 31, Sec. 2, 129 cm, showing typical single-domain particles. Scale bar = 0.1 micron. (C) Electron micrograph of magnetite extract from sample Core 2, Sec. 2, 70 cm. Scale bar = 0.5 micron. High magnification image of one superparamagnetic (SPM) grain (indicated by arrowhead) is shown in right upper corner (scale bar = 0.05 micron). Fuzzy outlines of SPM grains imply that they are remaining cores of surficially oxidized grains after the dissolution treatment.



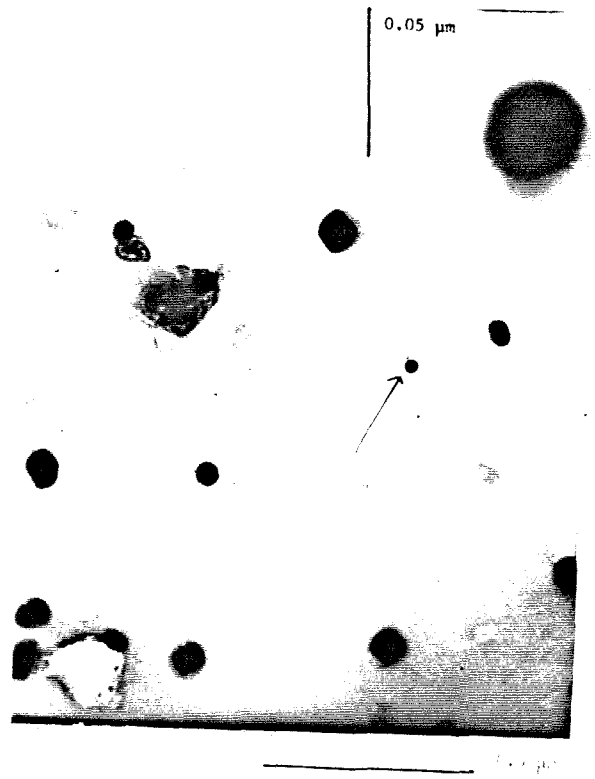
(A)



(B)



(C)



typical single-domain grains from magnetotactic bacteria. They also share some of the same cuboidal and hexagonal forms as those of bacterial magnetite.

The presence of numerous type A grains (superparamagnetic size) is probably an artifact of our magnetite extraction procedure, particularly the DCB treatment which removes all iron minerals except magnetite. We have not observed many of these particles in extracts prior to the DCB dissolution step, all which we have observed after treatments show fuzzy outlines (Fig. 5C). It seems probable that these are the remaining cores from larger type B grains which had been partially oxidized to maghemite on the surface. This would account for the significant maghemite component noted earlier as well as the SIRM drop during DCB treatment.

It is clear from these results that single-domain magnetite crystals which resemble those of biogenic origin are present in deep-sea sediments. Although there is as yet no direct evidence that these forms are produced by the magnetotactic bacteria, the similarity is striking. Based on observed population densities and growth rates, Kirschvink and Lowenstam (1979) and Towe and Moench (1981) both found that the potential bacterial contribution in the deep-sea was large enough to produce a significant fraction of the observed natural remanent magnetization. With the possible exception of the green algae and chitons (class Polyplacophora), none of the other organisms which are known to produce magnetite crystals (tuna, salmon, cetaceans, etc.) are found in large enough numbers to contribute a significant amount to the sediments. A typical yellowfin tuna, for example, makes only about 20 nanograms of magnetite in a small tissue within the dermethmoid bone (Walker et al., 1981), but the crystal morphology strongly resembles

those of the bacteria (Walker et al., 1983). Chiton-teeth have not yet been found in the fossil record, nor is the fate of the individual crystal clumps released by tooth-wear known (Kirschvink and Lowenstam, 1979). Similarly, reports of magnetotactic algae remain undocumented to date and no other magnetotactic microorganisms have been reported from marine plankton.

We have found abundant particles of single-domain magnetite in all sediments with medium to high  $\text{CaCO}_3$  contents and with relatively high sedimentation rates ( $>8$  m/My) examined so far. They are extremely rare or non-existent in silty clay, siliceous marl, and sediments with low deposition rates ( $<5$  m/My). High deposition rates may help to prevent oxidation of these particles as well as to minimize the exposure time to bacterial iron scavenging.

The presence of magnetite crystals of probable biogenic origin in deep-sea sediment raises many questions concerning the nature of the magnetization process. In particular, the laboratory redeposition experiments of magnetite-bearing sediments performed by Verosub (1977) and Barton and McElhinny (1979) probably do not accurately reflect the remanence acquisition process in nature because they were done too rapidly for significant bacterial growth to occur. The organic matrix material which holds the magnetite particles in place along the magnetosome of the bacteria (Balkwill et al., 1979) may also serve to bind them to other particles within the sediment after death. A "glue" of this sort could be responsible for the difficulties encountered by others who have tried to extract and purify the fine magnetic particles. Although the action of sediment burrowers may dislodge some of this "glue", the mucoproteins left behind with their fecal pellets may well serve a similar function by stimulating bacterial growth. Processes of

this sort would tend to reduce the acquisition of post-depositional remanence magnetization (pDRM) from Brownian motion, an effect commonly seen in the laboratory redeposition experiments from disaggregated sediments. This could explain why some deep-sea cores preserve high-resolution records of geomagnetic transitions (Opdyke et al., 1974; Clemens and Kent, 1983; Theyer et al., 1982). As yet, there is no evidence in the above studies to suggest a drop in the production of bacterial magnetite during a geomagnetic transition as has been suggested for two reversals in Crete (Valet and Laj, 1981; Kirschvink, 1982; Chang and Kirschvink, 1985).

### Conclusion

The presence of single-domain magnetite crystals of apparent biogenic origin may be responsible for much of the stable natural remanent magnetization found in marine sediments. If these particles are indeed of biogenic origin, they would be by far the smallest fossils yet discovered, and could justifiably be called either "picofossils" or "magnetofossils". We note that a wide variety of other prokaryotes are also known to precipitate similarly-sized mineral hard-parts (Lowenstam, 1981), but they have not yet been found in the fossil record.

### Acknowledgements

We are particularly grateful to Dr. Lisa Tauxe of the Scripps Institute of Oceanography, the Deep-Sea Drilling Project, and the Lamont-Doherty Geophysical Observatory for providing samples of deep-sea sediments. We thank Dr. Jean-Paul Revel for the use of the electron microscope.

THE EFFECT OF MAGNETOTACTIC BACTERIA  
ON THE MAGNETIC PROPERTIES OF MARINE SEDIMENTS

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ABSTRACT

Magnetotactic bacteria have been studied in three distinct sedimentary marine environments: a hypersaline lagoon, an intertidal carbonate marsh, and an open ocean basin. The bacteria and the ultrafine-grained, single-domain magnetite they produce were extracted from the sediments and studied with transmission electron microscopy. Magnetic properties of the sediments were measured by rock magnetic techniques using a SQUID magnetometer. Our results show that magnetotactic bacteria contribute a significant fraction of the natural remanent magnetization to their sedimentary environment and in some cases may be the sole source of the stable remanence-carrying mineral. The occurrence and abundance of these bacteria in a diversity of marine environments (e.g. from supratidal to deep ocean) implies that they may also play a role in the microbial iron cycle.

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## INTRODUCTION

Since their discovery by Blakemore over a decade ago, magnetotactic bacteria have been found in many marine and fresh water environments (Blakemore, 1975, 1982; Blakemore et al., 1980; Moench and Konetzka, 1978; Lins de Barros and Esquivel, 1985). These organisms not only synthesize and deposit crystals of magnetite intracellularly, but use it to orient themselves in the earth's magnetic field (Frankel, 1984). In the northern hemisphere they orient to the north, in the southern hemisphere to the south, and at the geomagnetic equator there are equal populations of both (Kirschvink, 1980; Blakemore et al., 1980). These organisms are able to orient in a magnetic field because of the composition, size and shape of the mineral deposit (Frankel, 1984; Kirschvink, 1983). Analyses of the magnetite from different magnetotactic bacteria including *A. magnetotacticum* by several different methods (electron diffraction, Mossbauer spectroscopy and lattice imaging ) has shown it to be composed of almost pure  $\text{Fe}_3\text{O}_4$  (Frankel et al., 1979; Matsuda et al., 1983; Mann et al., 1984a, b). To date, all reported sizes and shapes of bacterial magnetites fall within the single-domain stability field as calculated by Butler and Banerjee (1975) (Chang and Kirschvink, 1985; Chang et al., 1987). That is to say, each crystal behaves as a single magnet with a dipole moment. In most natural cases, the bacteria align the crystals in a chain so that the chain behaves like a single dipole magnet as well.

In 1979, Kirschvink and Lowenstam proposed that biogenic magnetites (produced by chitons and bacteria) could contribute significantly to the magnetic properties of marine sediments. Their conclusions, based on calculations made from the amount of chiton magnetite deposited annually, suggested biologically produced single-domain magnetite could

provide as much as  $10^{-6}$  emu/g of detrital remanent magnetization (DRM). They also made crude calculations as to the possible contribution of bacterial magnetites, but little was known then about the magnetic properties and occurrence of magnetotactic bacteria in marine environments. Towe and Moench (1981) subsequently increased these initial estimates by a factor of 10, based on more accurate population densities of magnetic bacteria from a few fresh water environments. In this study, we wanted to determine whether or not magnetic bacteria were equally abundant and diverse in geologically important marine environments and whether or not the single-domained magnetite they produce has an effect on the magnetic properties of the sediment. We studied three distinct marine sedimentary environments: a hypersaline lagoon, an intertidal carbonate marsh, and an open ocean basin.

## ENVIRONMENTS

### The hypersaline lagoon

Laguna Figueroa is a lagoonal complex situated 250 km south of the Mexico-United States border on the Pacific Ocean side of the Baja California peninsula. The hypersaline lagoon is separated from the Pacific Ocean by a barrier beach and dune. A salt marsh lies on the landward side of the dune and grades into an evaporite flat. At the salt marsh/evaporite flat interface, laminated sediments are being deposited by a stratified microbial mat community dominated by the cyanobacterium Mircocoleus chthonoplastes (Horodyski et al., 1977). These mats and the laminated sediments have been studied extensively because of their analogy with fossilized microbial communities and stromatolites (Horodyski et al., 1977; Margulis et al., 1980, 1983; Stolz and Margulis, 1984; Stolz, 1983, 1984a, b, 1985). The sediment is

composed of dune derived siliciclastics and evaporitic minerals (halite, gypsum, anhydrite, and aragonite) and is rich in organic material.

#### The intertidal carbonate marsh

Sugarloaf Key is the third to last in the string of Florida Keys. Mangroves are the predominant vegetation in the intertidal marsh. The sediment is a fine carbonate ooze with small shell fragments and is a modern analog of ancient limestone deposits (Ginsberg, 1964). The surface 2 mm is aerobic and underlain by anoxic, sulfide-rich carbonate ooze. Thumb-sized stromatolitic nodules, formed by a microbial community dominated by the cyanobacterium Schizothrix gracilis, dot the surface (Stolz, unpublished; Golubic and Focke, 1978).

#### The open ocean basin

The Santa Barbara Basin is an open ocean basin in the southern California borderland. It has a maximum depth of about 600 m and the sediments are anoxic laminated hemipelagic muds (Savrda et al., 1984; Karlin and Levi, 1985). The surface sediment is populated by a microbial community dominated by species of Beggiotoa, flexibacteria and heterotrophic bacteria and is typical of oxygen-poor environments.

## MATERIALS AND METHODS

At both Laguna Figueroa and Sugarloaf Key, we collected sediment samples from several sites at the sediment-water interface. Samples from the Santa Barbara Basin were collected and supplied to us by M. Kastner (Scripps Oceanographic Institution), from three different cores (34°14'N, 120°1'W) at a depth of 598 m and a temperature of 8°C. The top 3 cm of sediment were removed from the box cores and either fixed with 2.5% glutaraldehyde in seawater buffer immediately after collection, or left untreated. All these samples were kept at 8°C.



The presence of live magnetotactic bacteria was detected by placing a drop of sediment on a glass slide adjacent to the south end of a stirring bar magnet. Under low-power light microscopy (160 X), magnetic bacteria could be seen collecting at the edge of the drop next to the magnet (e.g., swimming towards magnetic north). For transmission electron microscopy (TEM), carbon-coated grids were placed on top of sediment drops and a cobalt rare-earth magnet was suspended 1 cm above the drops for 20-30 minutes (Stolz et al., 1986). To determine the morphology of the bacteria, some grids were negatively stained with 1% uranyl acetate for 1 minute. Pellets of the bacteria for thin section preparation were obtained using the method described in Moench and Konetzka (1978). The pellets were fixed with 2.5% glutaraldehyde in seawater buffer, post-fixed in osmium tetroxide, en bloc stained with uranyl acetate followed by dehydration in an ethanol series and propylene oxide, and embedded in Spurr's embedding medium (Stolz, 1983). Thin sections were stained with uranyl acetate and lead citrate. All samples were examined on a Phillips 201 transmission electron microscope at 80 kV. Identification of the crystals as magnetite was made by electron diffraction (Towe and Moench, 1981; Chang and Kirschvink, 1985; Towe, 1985).

Rock magnetic studies of the sediment and bacteria were done using a SQUID magnetometer (Fuller et al., 1985). Saturation isothermal remanent magnetization (sIRM) and alternating field (AF) demagnetization were used to determine the coercivity spectra (Kirschvink, 1983) which were then compared with known standards (Chang et al., 1987).

## RESULTS

Large populations of magnetotactic bacteria were discovered in salt marsh pools along the dune at Laguna Figueroa. The greatest

concentrations of bacteria are found in places where the top few millimeters of sediment are oxidized and a film of manganese and iron oxide is visible on the water surface. Many different morphologies are present including coccoids, rods, and a colonial coccoid. One particular coccoid was obtained in large numbers in enrichment cultures in the lab and a study of its ultrastructural morphology and magnetic properties was done. The cells are 2-4  $\mu$ m in diameter and have a gram negative wall (Figure 6A,B). They are motile by means of two flagellar bundles which insert at invaginations of the cell wall which are bounded by polar membrane (Figure 6 A,B). The cytoplasm contains several globular inclusions and one to two chains of magnetite. The crystals are cuboidal to slightly rectangular in shape with an average size of 90 x 110 nm (Figure 6B). The chains contain an average of 10 crystals. The rod (1x3  $\mu$ m) and colonial coccoid (8-10  $\mu$ m) were seen with light microscopy and documented on video tape, but analysis of the magnetite was not possible.

Coercivity spectra analysis of the coccoid indicates the magnetite to be single-domain (Figure 7A). The coercivity of the salt marsh laminated sediment suggests a large percentage of the magnetic component is multi-domain magnetite (Figure 7B). Examination of the sediments revealed coarse-grained magnetite as well as bacterial ultrafine-grained magnetite. The source of the coarse-grained magnetite is detrital magnetites in the dune-derived siliciclastic sediment (Figure 7C). The maximum values for sIRM ranged between  $1.5 \times 10^{-5}$  and  $1.9 \times 10^{-3}$  with an average value for the laminated sediment of  $5 \times 10^{-4}$  emu/g.

Several different morphologies of magnetotactic bacteria were seen in sediments from Sugarloaf Key including rods, coccoids and a colonial coccoid. The magnetite crystals are cuboidal to truncated rectangles

Figure 3-6 - Magnetotactic bacteria from marine sediments, transmission electron micrographs, all bars 100 nm. A. Magnetococcus from Laguna Figueroa, Baja California, Mexico. Negative stain preparation. (fb), flagellar bundle, (m), magnetosome. B. Magnetococcus from Laguna Figueroa. Thin section preparation. Note the invagination of the cell wall at the flagellar insertion (fi). C. Magnetococcus from Sugarloaf Key, Florida. Negative stain preparation. D. Extracted magnetosome from Sugarloaf Key sediments (unstained). E. Magnetovibrio from Santa Barbara Basin, California. Note one polar flagella (f). Negative stain preparation. F and G. Extracted bacterial magnetite from Santa Barbara Basin sediments. Glutaraldehyde fixed and unstained.

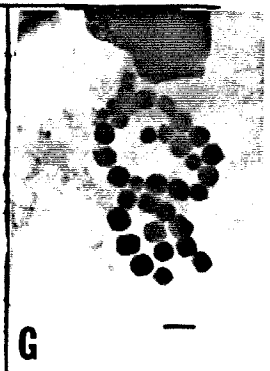
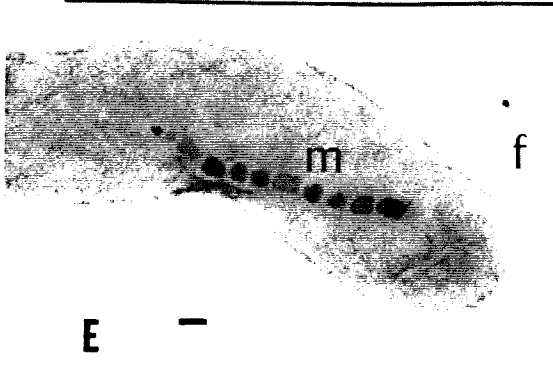
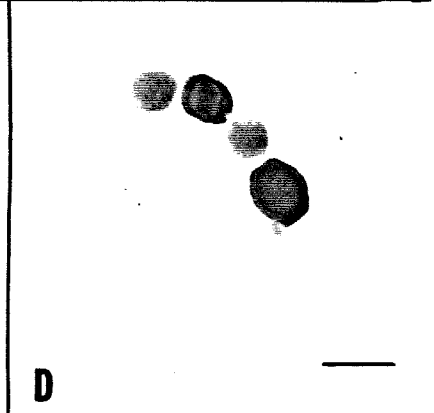
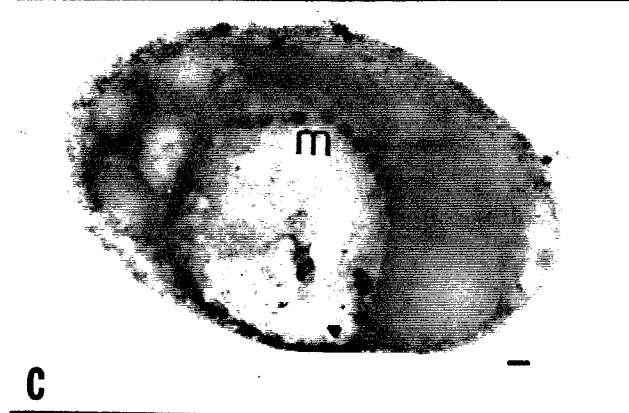
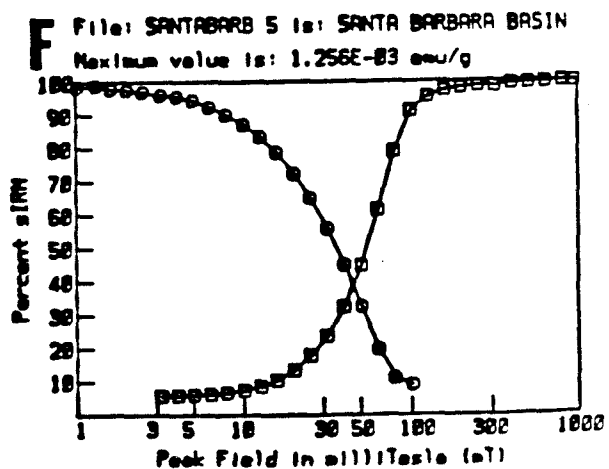
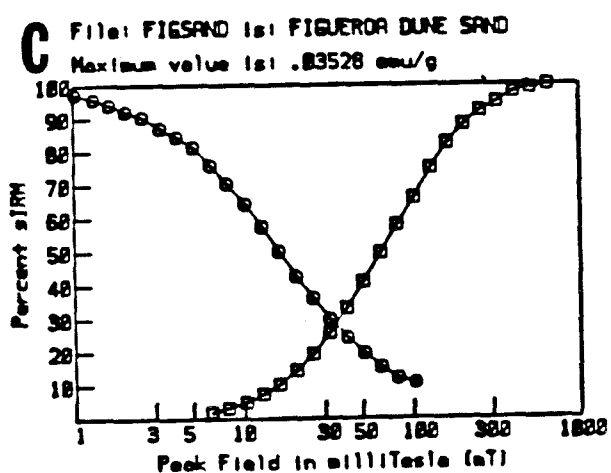
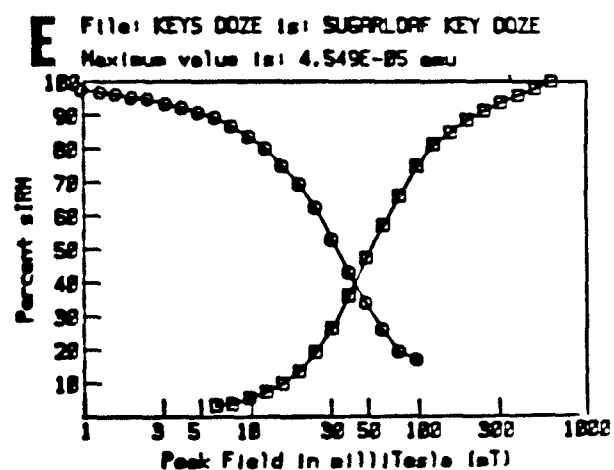
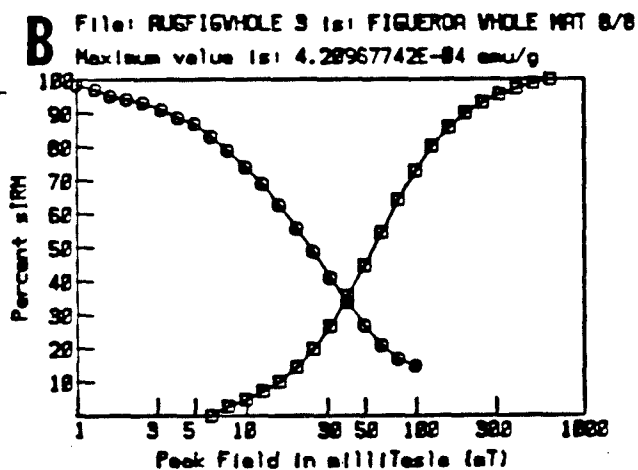
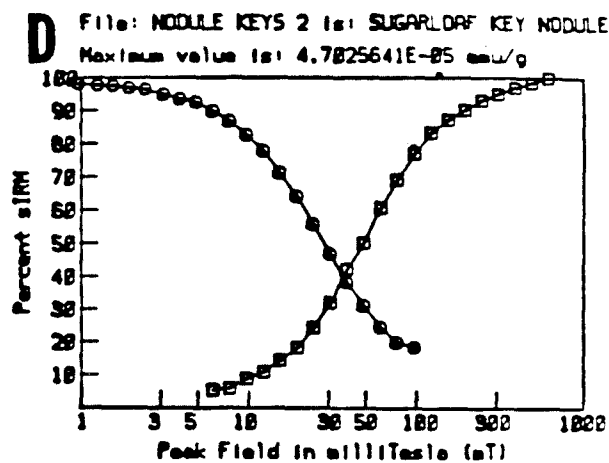
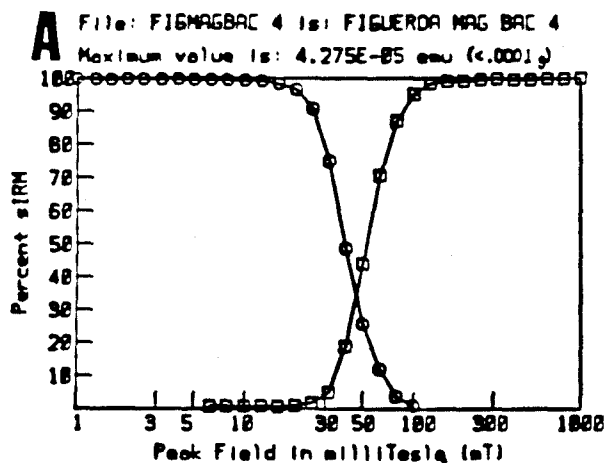


Figure 3-7 - Coercivity spectra measured by a SQUID magnetometer using saturation Isothermal Remanent Magnetization (sIRM) (squares) and Alternating Field (AF) demagnetization (circles). A. Pellet of magnetococcus from Laguna Figueroa. B. Microbial mat from Laguna Figueroa. C. Dune sand from Laguna Figueroa. D. Stromatolitic nodule from Sugarloaf Key. F. Surface sediments from Santa Barbara Basin.



and ranged in size from 40 to 100 nm (Figure 6C,D). Coercivity spectra of the stromatolitic nodules and carbonate ooze indicate the major magnetic component to be single-domain magnetite (Figure 7D,E). Examination of the sediment revealed only bacterial magnetite. Typical values for sIRM of both carbonate ooze and nodules average about  $4.5 \times 10^{-5}$  emu/g. It appears that in this environment bacterial magnetites provide the only source of magnetic remanence carrier (Chang et al., 1987).

One of the most exciting discoveries of this study was finding magnetotactic bacteria living in the surface sediments for the Santa Barbara Basin (Stolz et al., 1986). *Vibrio* and rod-shaped bacteria were seen in unfixed samples (Figure 6E). The crystals are cuboidal to rectangular and range in size from 40 to 60 nm. Chains of magnetite with an average number of 10 crystals were seen in several bacteria. Coercivity spectral analysis of both fixed and unfixed samples indicate the most abundant primary remanence carrier to be single-domain magnetite (Figure 7F). Examination of the sediment confirmed this (Figure 6F,G). Values for sIRM range between  $2.5 \times 10^{-4}$  and  $1.25 \times 10^{-3}$  emu/g.

## DISCUSSION

Laguna Figueroa presented the greatest difficulty in assessing the bacterial contribution to the magnetic properties of the sediment because of the large amount of coarse-grained detrital magnetite. The dune sands contained over 5% abiogenic magnetite. Comparing the coercivity spectra of coarse-grained magnetite standard, dune sand, and bacterial magnetite to those of the salt marsh pools and laminated sediment, however, reveals that the presence of single-domain, biogenic

magnetite does have an effect on the magnetic properties of the sediment (Chang et al., 1987). Bacterial magnetites are more difficult to demagnetize, but do so rapidly in an alternating field (AF) between 30 and 100 mT (Figure 7A). Coarse-grained, multi-domain magnetites begin to demagnetize in even low strength alternating fields (AF less than 3 mT, Figure 7C). In a mixture of ultrafine- and coarse-grained magnetite, an increase in single-domain magnetite makes the samples harder to demagnetize. This effect became more apparent in the Sugarloaf Key and Santa Barbara samples.

In a recent paper, Lins de Barros and Esquivel (1985) estimated the magnetic moments for several different types of magnetic microorganisms. Depending on the size of the organism and subsequently the amount of magnetite per cell, the values for smallest to largest ranged from  $0.3 \times 10^{-12}$  to  $5.4 \times 10^{-11}$  emu/cell. For the 2  $\mu$ m coccoid from Laguna Figueroa (a chain of 10 crystals, each 100 nm in size), we have calculated a moment of about  $1 \times 10^{-12}$  emu/cell (Chang et al., 1987). We could not, however, estimate the bacterial contribution to the magnetic remanence in the Laguna Figueroa sediments because of the abundance of coarse-grained magnetite.

Limestones, despite their typically low magnetization, have been frequently used in paleomagnetic studies because their fossil assemblages provide an independent stratigraphic correlation (Lowrie and Heller, 1982). How the sediments are magnetized, and what the primary remanence carrier is, are two questions which are poorly understood. The discovery of magnetotactic bacteria in carbonate oozes and bacterial magnetites in limestone deposits suggests that biogenic magnetites could be the primary remanence carriers (Chang et al., 1987). The average shape of the bacterial magnetite seen in both bacteria and sediment



extracts was rectangular, and about 80 x 100 nm in size (Figure 6C,D). Like the 2  $\mu\text{m}$  coccoid from Laguna Figueroa, the average moment for the Sugarloaf Key bacteria was  $10^{-12}$  emu. It would take a population of only  $10^7$  bacteria per gram of sediment to account for the observed magnetic remanence of  $10^{-5}$  emu/g. This estimate makes the assumption that all the magnetic remanence is due to bacterial magnetite whether the bacteria are alive or dead. Still it is conceivable that populations of this size do occur in nature (Moench and Konetzka, 1978; Blakemore, 1982) and that even episodic increases in population (i.e., blooms) could contribute to the amount of biogenic magnetite observed.

The Santa Barbara Basin sediments provide another dramatic example of the effect of bacterial magnetite on the sedimentary environment. The hemipelagic sediments of the California borderland have been studied extensively by paleomagnetists in order to understand the mechanisms of magnetization of rapidly deposited marine sediments (Karlin and Levi, 1983, 1985; Lund et al., 1983; Leslie et al., 1984). These studies show a maximum intensity of magnetic remanence occurring in the surface sediments (within the top meter). The significant decrease in intensity with depth has been correlated with a loss of fine-grained component. The discovery of magnetotactic bacteria living in the Santa Barbara Basin and the identification of the fine-grained component as biogenic magnetite provides an explanation for the above observations. The high natural remanence of the bacteria contributes to the remanence of the surface sediments where conditions for growth are optimum for the bacteria. At depth, both the lack of oxygen (needed for magnetite synthesis, Blakemore et al., 1984) and the increase in sulfide result in the absence of live bacteria and the dissolution of bacterial magnetites (Stolz et al., 1986).

The loss of bacterial magnetite with depth in some open ocean basins places doubt as to whether it can contribute to the magnetization of ocean sediments. Well-preserved fossil bacterial magnetites have, however, recently been discovered in deep-sea sediment cores ranging in age from recent to Oligocene (Chang and Kirschvink, 1985; Petersen and von Dobeneck, 1986).

The occurrence and abundance of magnetotactic bacteria in a variety of marine sedimentary environments suggest that they may play a role in the microbial iron cycle. Nealson (1983) acknowledged their possible contribution, but little was known of their distribution and numbers in marine sediments. Magnetite is a very interesting iron oxide containing both ferrous ( $\text{Fe}^{+2}$ ) and ferric ( $\text{Fe}^{+3}$ ) iron. Blakemore et al. (1984) have shown that A. magnetotacticum precipitates magnetite optimally under microaerobic conditions (1% PAL). In nature, many biogeochemical activities occur at the aerobic/anaerobic interface (Nealson, 1983). Magnetite may be oxidized to maghemite and hematite (deep-sea sediments), dissolved (Santa Barbara Basin), or transformed to an iron sulfide-like greigite or pyrite (Eel Marsh, Massachusetts; Demitrack, 1985). It is conceivable then that it could be used as a substrate for some of the iron metabolizing bacteria.

## CONCLUSIONS

We have documented the presence of magnetotactic bacteria living and depositing single-domain, ultrafine-grained magnetite in three distinct marine environments. The results of rock magnetic studies suggest that the bacteria have a variable influence on the magnetic properties of the sediments in which they live. This effect may be subtle, as in the case of Laguna Figueroa, where coarse-grained

magnetite is a significant component, or dramatic, like Sugarloaf Key where bacterial magnetites are the only remanence carriers. The discovery of magnetotactic bacteria in an open-ocean basin (Santa Barbara Basin) and fossil bacterial magnetites in deep-sea sediments suggest bacterial magnetite is a common occurrence in marine deposits. Although the eventual fate of the biogenic magnetite depends on post-depositional factors (e.g., oxidation, dissolution), they can be a primary remanence carrier in certain marine sedimentary rocks (e.g., limestones). Magnetotactic bacteria may also play a significant part in the microbial iron cycle. The occurrence and abundance of magnetotactic bacteria in marine sediments suggest they may also play a significant part in the microbial iron cycle.

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CHAPTER FOUR

BIOGENIC MAGNETITE AS A PRIMARY REMANENCE  
CARRIER IN LIMESTONE DEPOSITS

by

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ABSTRACT

Studies on the microbial communities and magnetic phases of samples collected from carbonate oozes at Sugarloaf Key, Florida, USA and calcareous laminated sediments from Laguna Figueroa, Baja California, Mexico have revealed the existence of magnetotactic bacteria and ultrafine-grained single-domain magnetite in both environments. Magnetotactic bacteria were identified by light and electron microscope. The single-domain magnetite was detected by coercivity spectra analysis with a SQUID magnetometer and examined under the transmission electron microscopy. The similarity, in terms of size and shape, between the single-domain magnetite found in these sediments and the magnetite observed in the bacterial magnetosome from enriched cultures indicates the ultrafine-grained magnetite in these two marine environments was formed biologically. The results, combined with the common occurrences of ultrafine-grained magnetite in limestone deposits detected rock magnetically, suggest biogenic magnetite may be present and contribute the magnetic remanence in these rocks. Several Cambrian limestone samples collected separately from Siberia, China, and Kazakhstan were examined for the presence of bacterial magnetite. Samples from the Lower Cambrian Sinskian Formation at Siberia Platform were found to contain both a large amount of apparently bacterial magnetite particles and a very stable primary magnetic component. Post-Cambrian diagenesis does not seem to affect the microgranulometry of these apparently bacterial magnetite crystals or the magnetic remanence carried by them. Assessing the potential role of biogenic magnetite as a primary remanence carrier in other Phanerozoic limestone deposits ought to be further pursued.

## INTRODUCTION

Limestone is the most abundant type of carbonate rock, which constitutes approximately 10% of the sedimentary mass exposed on land (Blatt et al., 1980). Numerous paleomagnetic studies have been conducted on limestones since the initiation and development of the modern science of paleomagnetism in the late 1940's and the 1950's. In the 1960's, as plate tectonic models gradually acquired general acceptance, paleomagnetic and magnetic stratigraphic studies on limestones became extremely important because auxiliary and independent paleogeographic and stratigraphic control could be easily obtained from analyses on fauna associated with limestones. However, in spite of the emerging necessity, the typical low magnetization ( $10^{-5}$ - $10^{-3}$  A/m) carried by limestones limited reliable paleomagnetic measurements to strongly magnetized samples using the traditional low sensitivity astatic or spinner magnetometer. In the 1970's, the development of the advanced spinner and computer-controlled fluxgate magnetometers (Molyneux, 1972) and the cryogenic magnetometer (Goree and Fuller, 1976) made reliable measurements on weakly magnetized samples possible. As a result, numerous paleomagnetic studies on limestones were carried out with diverse objectives (see Lowrie and Heller, 1982 for a general review). Despite the achievements of these recent studies, the primary remanence carriers and the magnetization process of limestones are still not well understood. This is mainly due to the extreme difficulty in obtaining representative magnetic extracts for rock magnetic study and optical examination from these low magnetization rocks.

Varieties of magnetic mineral phases, including magnetite, goethite, hematite, maghemite, pyrrhotite, and greigite have all been rock magnetically detected in certain limestone deposits (Lowrie and Heller,

1982). Among them, magnetite is the most commonly observed and magnetically stable phase. Previous direct observations employing the scanning electron microscope (SEM) and the optical microscope on magnetite extracts from limestones (Lowrie and Heller, 1982; McCabe et al., 1983) have only successfully identified the shape and texture of multi-domain (MD) magnetite grains due to the limited resolution ( $> 0.5 \mu\text{m}$ ) of these microscopes. These observations also revealed the common occurrences of ultrafine-grained magnetite particles ( $< 0.5 \mu\text{m}$ ), however, the detailed granulometry could not be determined. In addition, many rock magnetic studies have detected the existence of SD magnetite as a primary remanence carrier in a wide range of limestone deposits (Lowrie and Heller, 1982).

Several possible sources for the SD magnetite particles in limestone deposits exist. These include: (a) the inclusion in continental igneous rocks (Morgan and Smith, 1981) released by weathering and transported by rivers and ocean currents; (b) disseminated crystals in the glassy matrix of mid-oceanic ridge basalts (MORBs) (Smith, 1979) released by submarine weathering; (c) in situ biogenic precipitates by the magnetotactic bacteria (Frankel et al., 1979; Towe and Moench, 1981), magnetotactic algae (Frankel, pers. comm., 1986), and/or chitons (Lowenstam, 1962; Kirschvink and Lowenstam, 1979); and (d) chemical precipitates (Henshaw and Merrill, 1980). Among them, the chemical precipitation origin of magnetite has only been theoretically tabulated and therefore, assigning it as a possible source of SD magnetite in limestone sediments is highly speculative. SD magnetite particles have been previously obtained in the laboratory by aging a ferrous hydroxide gel (Sugimoto and Matijevic, 1980), but it is not yet known whether the required conditions exist in nature for processes of this type ( $>90^\circ\text{C}$

temperatures with an excess of  $\text{OH}^-$ ). MORBs are potential sources for SD magnetite in certain pelagic limestone deposits. On the other hand, it seems quite unlikely that the magnetite particles released from MORBs contribute to the primary remanence of more widespread continental shelf or marginal basin limestone deposits. Deposition of detrital grains is obviously the most important origin of the MD magnetite particles found in marine limestone sediments. The fraction of SD magnetite particles composed of detrital grains in marine limestones, however, would probably not be so significant. The transportation and the deposition of such small size magnetite crystals could easily be diverted and retarded by various physical and chemical processes operating in the ocean system (Amerigian, 1974; Kirschvink and Chang, 1984).

As first proposed by Kirschvink and Lowenstam (1979), both magnetite particles formed by magnetotactic bacteria (Frankel et al., 1979) and by chitons (Lowenstam, 1962) could contribute to the primary remanence in limestones. The occurrence of high population densities of magnetotactic bacteria has been noted in a variety of depositional environments (Moench and Konetzka, 1978; Blakemore, 1982), and these bacteria represent the largest source of biogenic magnetite which could be preserved in sediments (Towe and Moench, 1981). The detailed microgranulometry of magnetite crystals formed by fresh water magnetotactic coccoid cells (Towe and Moench, 1981; Matsuda et al., 1983; Mann et al., 1984a) and by Aquaspirillum magnetotacticum cells collected from a marsh environment (Balkwill et al., 1979; Mann et al., 1984b) have been extensively studied by transmission electron microscopy (TEM) and revealed to be distinct from magnetite particles formed by inorganic processes. (Bacterial magnetite tends to form as subrounded cubes and rectangles or hexagonal prisms with flat ends, while inorganic

magnetite is normally octahedral, spherical, or angular; see Chang and Kirschvink, 1985, for a detailed discussion.) In addition, the dimensions of all the bacterial magnetite crystals measured with the TEM and published to date plot within the boundaries of the single-domain (SD) stability field as determined by Butler and Banerjee (1975). Towe and Moench (1981) found that the titanium content of bacterial magnetite is extremely low (less than 0.5%), which is also in contrast with the generally high titanium content of magnetite formed by igneous processes (it ranges approximately from 2% for occurrences in pegmatite to 25% for occurrences in basalts; see Table Hg-20 in Haggerty, 1976). These characteristic features of bacterial magnetite particles make feasible the search and identification of them in sediments, providing the ultrafine-grained magnetite particles can be extracted and examined under the TEM. We recently developed several techniques (Kirschvink and Chang, 1984; Chang and Kirschvink, 1985; Stolz et al., 1986) which extract magnetite grains from sediments and place them onto copper grids for TEM study. Applying these techniques to several deep-sea core samples, we found abundant SD magnetite particles in calcareous oozes up to Oligocene in age (Kirschvink and Chang, 1984). Even though no occurrence of magnetotactic bacteria in deep-sea depositional environments had been reported before, these particles compared favorably with the published shape and texture of magnetite grains formed by Aquaspirillum magnetotacticum. The presence of large amounts of these apparently bacterial magnetite grains in deep-sea calcareous oozes led us (Kirschvink and Chang, 1984) to propose that much of the SD magnetite particles and the stable natural remanent magnetization (NRM) found in marine carbonate sediments might be due to the activity of organisms, especially bacteria. This paper further investigates the

possible biogenic contribution to the remanent magnetizations in limestones by studying the relation between the occurrences of magnetotactic bacteria and the distribution of bacterial magnetite in sediments in two modern marine carbonate depositing environments. Magnetic extracts of several Cambrian limestone samples collected from Siberia, Kazakstan, and China were also examined to determine whether the bacterial magnetite particles are present in the beginning of the Phanerozoic rock records. The results of these studies will help delineate the distribution range of magnetotactic bacteria through time and the possible diagenetic effects on the potentially preserved bacterial magnetite particles.

#### STUDIED ENVIRONMENTS AND METHODS

The two modern marine carbonate depositing environments we studied are the intertidal zone at Sugarloaf Key, Florida, U.S.A., and the hypersaline Laguna Figueroa at San Quintin, Baja California, Mexico. Sediments from Sugarloaf Key are made of 100% carbonate with abundant shell fragments and have been generally known as the standard precursors of limestone deposits (Ginsburg, 1964). There is no obvious source of detrital magnetite. Laguna Figueroa is a lagoon with extreme ecological conditions, where microbial mats are involved in the deposition of laminated sediments. As such, it has been extensively studied in the past and widely considered as a present-day analogue of the Precambrian stromatolitic environment (Horodyski et al., 1977; Margulis et al., 1980, 1983; Stolz and Margulis, 1984). Submillimeter-sized authigenic aragonite granules commonly occur in the surface layer as well as in underlying zones of laminated sediment (Horodyski et al., 1977). Unlike the Sugarloaf Key environment, the nearby barrier sand dune of Laguna



Figueroa has a nearly 5% concentration of coarse-grained magnetite and provides a source for detrital magnetite.

Jar samples were collected from the water-sediment interface at several sites in Sugarloaf Key and Laguna Figueroa. Two bar magnets were used to separate magnetotactic bacteria following the method developed by Moench and Konetzka (1978). For thin section examination, pelleted bacteria were fixed with 2.5% glutaraldehyde in a modified seawater buffer (Stolz, 1983). After dehydration in an ethanol series, the samples were imbedded in Spurr's low viscosity embedding medium. Sections were cut with a 1/4 inch glass knife and observed on a Phillips 201 TEM at 80 kV. A novel technique, which has been previously proven to be able to successfully extract bacterial magnetite from Santa Barbara Basin surface sediments (Stolz et al., 1986), as shown in Figure 1, was employed to pull the ultrafine-grained magnetite particles from a small drop of sediment suspension directly onto a grid for viewing under the TEM. For negative stain preparations of the bacteria, grids were stained with 1% uranyl acetate for 1 minute.

The magnetite extraction and TEM sample preparation procedure for sediments and Cambrian limestone samples are the same as those described by Chang and Kirschvink (1985) and illustrated in Figure 2. In order to evaluate the possible effects of oxidation of surface layer of magnetite to maghemite, DCB dissolution procedure, which has been shown to be able to easily destroy the maghemite without touching the magnetite (Kirschvink, 1981), was not performed on certain samples. In addition, this dissolution comparison experiment was carried out on several previously studied, apparently bacterial magnetite-containing deep-sea core samples (Kirschvink and Chang, 1984).

Figure 4-1 - Diagram of the novel technique used for extracting ultrafine-grained magnetite from recent sediments. S, sediment suspension; P, parafilm; G, carbon coated TEM grids (face down); M, rare-earth cobalt magnet. The running time for extraction varies from 30 min. to 1 hr.

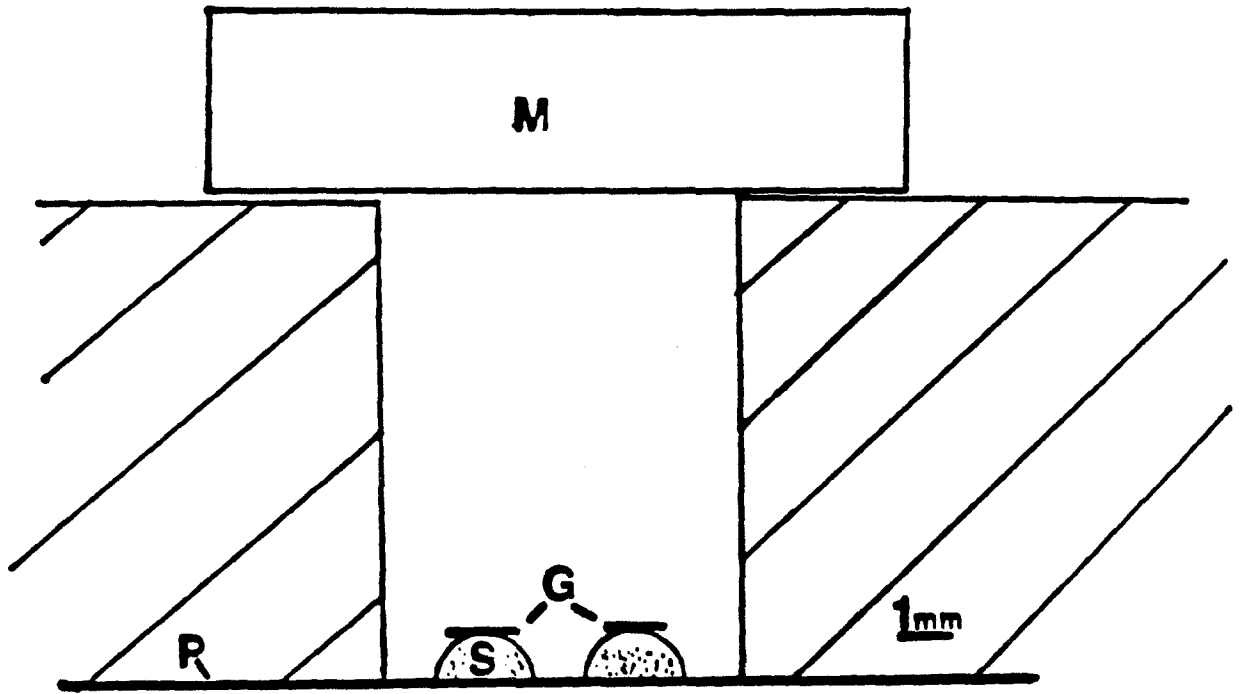
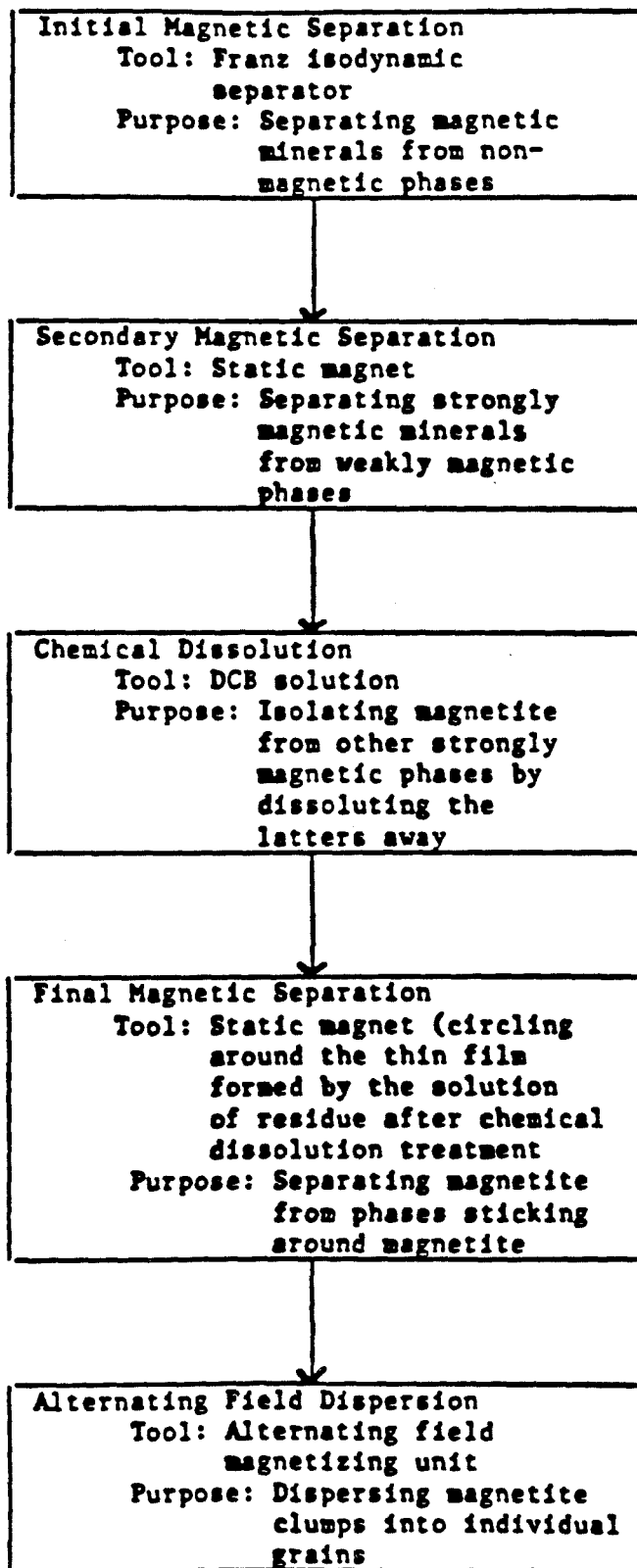


Figure 4-2 - Extraction scheme for separating magnetite from rock samples. Alternating Field Dispersion procedure is optional as it will destroy the possibly preserved chain structure of bacterial magnetite crystals. DCB: Dithionite-Citrate solution buffered by sodium Bicarbonate.



A revised coercivity spectra analysis combining parier isothermal remanent magnetization (IRM) acquisition and alternating field (AF) demagnetization experiments (Cisowski, 1981; Kirschvink, 1983) was used for roughly determining the main remanence carrier in the bulk sediment samples. The coercivity spectra of magnetite standard with varying grain size ranges, hematite standard and their mixtures were also analyzed to test the ability of this method to distinguish different magnetic carrier phases in sediments. Finally, the coercivity spectrum of magnetotactic bacteria, which contains only SD magnetite particles, was obtained for control. All the magnetic measurements were done with a SQUID magnetometer (2G Enterprises).

Electron diffraction was used to identify magnetite under the TEM. X-ray diffraction analysis with the standard Debye-Scherrer method was used to determine the crystal lattice structure of magnetite extract, from which the titanium content of magnetite can be inferred.

## RESULTS AND DISCUSSIONS

### Magnetotactic Bacteria and Bacterial Magnetite

Using Moench and Konetzka's (1978) method, we found a high population density of magnetotactic bacteria in both the Sugarloaf Key and the Laguna Figueroa sediments (Fig. 3). The TEM examination of magnetotactic bacteria collected from these two environments (Fig. 4) revealed the size and shape of magnetite particles formed in their magnetosome is about the same as that of other reported bacterial magnetite grains. Methods specific for determining the three-dimensional morphology of the crystals (e.g., shadowing; Towe and Moench, 1981) were not attempted, but most of the particles certainly are in prismatic form. Only some of the smaller and presumably immature

Figure 4-3 - Light micrograph of magnetotactic bacteria collected from  
Laguna Figueroa. Scale bar = 10 micron.

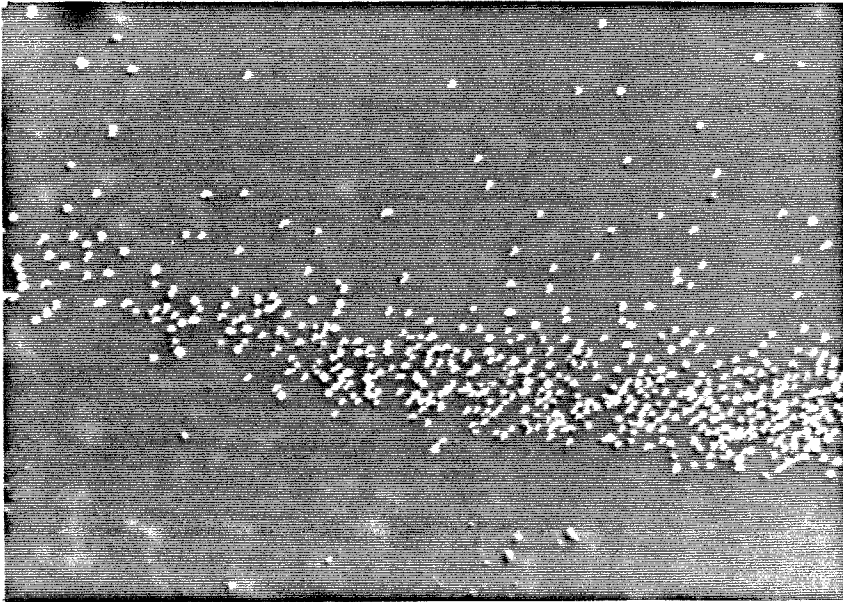


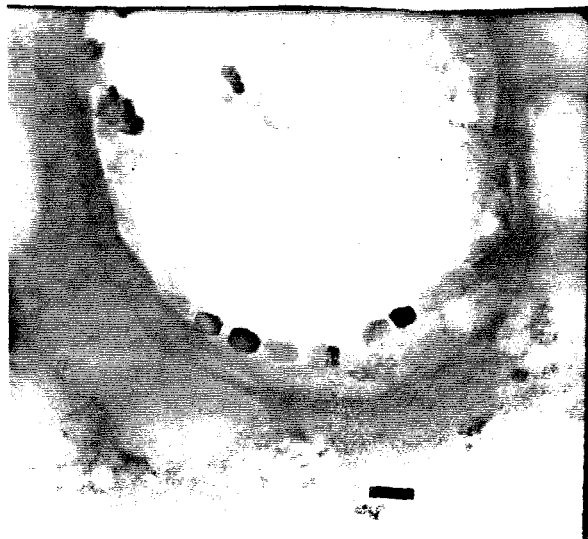


Figure 4-4 - Electron micrograph of magnetotactic bacteria collected from Laguna Figueroa (A) and from the intertidal zone of Sugarloaf Key (B). Scale bars = 0.1 micron.

(A)



(B)



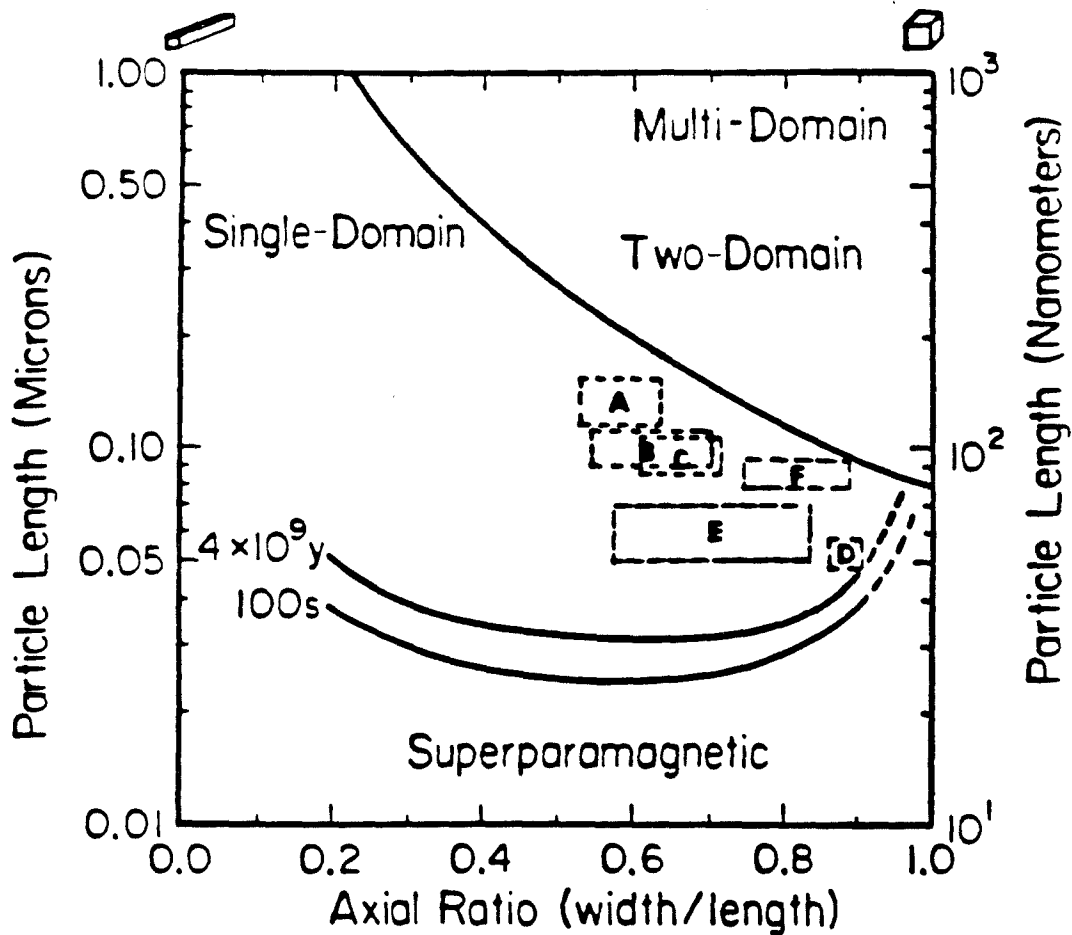
grains at the end of the magnetosomes are more cuboid in shape. Plotted into the magnetite stability field diagram developed by Butler and Banerjee (1975), these grains again fall in the single-domain field (Fig. 5). Detailed ultrastructural studies of magnetotactic bacteria found in the Laguna Figueroa environments and an assessment of the roles played by these organisms in both the modern and the Precambrian microbial communities will be presented elsewhere (Stolz et al., in preparation).

Due to their low concentration, magnetite particles from carbonate sediments at Sugarloaf Key are extremely difficult to extract. In the few successful cases, only ultrafine-grained magnetite particles were observed in the final extracts. The shape and size of these particles (Fig. 6) compares favorably with that of magnetite grains found in magnetotactic bacteria as reported in this study and previous investigations conducted by other groups (e.g. Towe and Moench, 1981; Blakemore, 1982). On the other hand, magnetite extracts of the Laguna Figueroa sediments are mainly composed of a coarse-grained detrital component, presumably transported from nearby sand dunes by wind or water. Ultrafine-grained and apparently bacterial magnetite grains, however, were also found in the sediments, and some of them, like those shown in Figure 7, were still bound with organic material to form a chain structure.

#### DCB Dissolution Experiment

To test the effects of the dithionite buffer, ultrafine-grained magnetite extracts from the Laguna Figueroa sediment and the DSDP sample Site 522, Core 30, Sec. 1, 80-82 cm were examined before and after the DCB dissolution treatment (Fig. 8). The non-DCB treated ultrafine-

Figure 4-5 - Size and shape distribution of magnetite particles found in magnetotactic bacteria from previously reported occurrences and the two new findings as plotted in the theoretical derived stability field diagram of magnetite (Butler and Banerjee, 1975).



- |   |   |
|---|---|
| A. Fresh water sediments of New Zealand (Blakemore et al., 1980). | D. Salt marshes of Cape Cod, Massachusetts (Blakemore, 1975).   |
| B. Complex simulated natural environment (Tove & Moench, 1981).   | E. Santa Barbara basin.   |
| C. Pyshwick sewage pond, Australia (Kirschvink, 1980).            | F. Laguna Figueroa, Baja California and Sugarloaf Key, Florida. |

Figure 4-6 - Bacterial magnetite crystals extracted from the surface  
sediments of Sugarloaf Key. Scale bar = 0.1 micron.

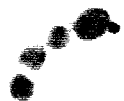
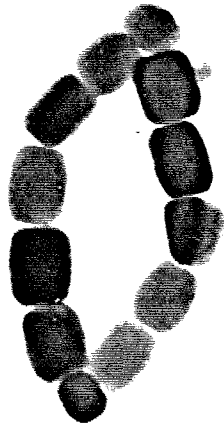


Figure 4-7 - Bacterial magnetite crystals extracted from the surface sediments of Laguna Figueroa. Scale bar = 0.1 micron.





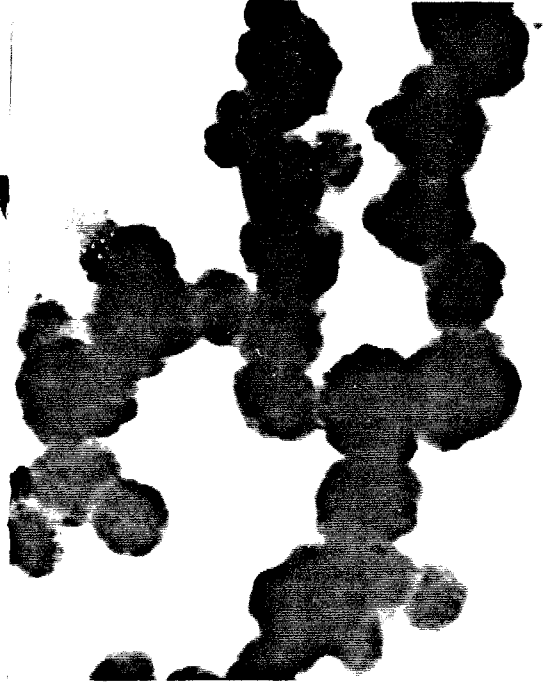
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Figure 4-8 - Ultrafine-grained magnetite particles extracted from (A and B) the Laguna Figueroa sediment and (C and D) from the DSDP sample site 522, Core, Sec. 1, 80-82 cm before (A and C) and after (B and D) dithionite treatment. Scale bars = 0.1 micron.

(A)



(B)



(C)



(D)



grained magnetite particles have much sharper boundaries and strongly resemble those magnetotactic bacteria formed crystals (Fig. 8A,C). On the other hand, the DCB-treated particles have fuzzy outlines which were presumably caused by the dissolution of the surface maghemite layer of these crystals (Fig. 8B,D). The contrast between the images of DCB-treated particles from the modern Laguna Figueroa sediment and the DSDP Site 522, Core 30 sample (Oligocene in age) is not obvious, which implies the surface maghemitization process occurred right after the deposition of these grains and this surface maghemite layer would protect these crystals from further oxidation. Recently, Banerjee et al. (1985) have shown that the surface maghemitization process does not affect the shape of original magnetite particles. Therefore, the unique bacterial magnetite granulometry should be still preserved in sediments regardless of all kinds of diagenetic process, except where dissolution and reprecipitation (which is probably the case for the bacterial magnetite in Santa Barbara Basin surface sediments; see Stolz et al., 1986), have taken place.

### Coercivity Spectra Analyses

Under ideal conditions, the intersection of the IRM acquisition vs. the AF demagnetization curves represents the coercivity of the sample being analyzed (Cisowski, 1981). This method serves as a quick way to distinguish the high coercivity phases (like hematite and goethite) from the low coercivity phases (like magnetite and maghemite). In addition, the coercivities of magnetite crystals vary from 20-25 mT for coarse-grained MD particles to 45-50 mT for ultrafine-grained SD particles and therefore, the coercivity spectrum of the bulk sample can also be used as a remanence carrier grain-size indicator (Cisowski, 1981).

Typical coercivity spectra for various magnetic phases standards, magnetotactic bacteria (representing characteristic curve for SD magnetite standard, which is difficult to be precipitated artificially or purchased commercially), and sediment samples from Sugarloaf Key and Laguna Figueroa are shown in Figures 9 and 10. The contrast between the spectra of pure hematite crystals (Fig. 9A) and pure MD or SD magnetite crystals (Fig. 10A,C) is obvious and mixtures (Fig. 9B,C) of hematite and magnetite (with both phases contributing half of the remanence in the mixture) have coercivity values larger than 50 mT, which are also quite distinguishable from the coercivity values ( $< 50$  mT) of various magnetite particles mixtures (Fig. 10B,E). Because hematite is generally recognized as either the end phase of iron oxides oxidation sequence or the product of continental weathering, the coexistence of bacterial magnetite and large amounts (enough for contributing half of the remanence carried by the sample as in our laboratory simulated case) of hematite crystals in sediments, especially marine limestones, seems quite unlikely. Therefore, in our further research on evaluating the role of bacterial magnetite as a primary remanence carrier in sediments, it is reasonable to exclude any hematite-rich samples as revealed by their high coercivity values. The ultrafine-grained magnetite standard (Fig. 10B) with size ranging from  $0.05 \mu\text{m}$  to  $0.5 \mu\text{m}$  (corresponding to the mixture of SD and two-domain magnetite particles) and the mixture of coarse- and ultrafine-grained magnetite standard (Fig. 10E) show intermediate coercivities (30-45 mT) between values of the MD ( $< 30$  mT; Fig. 10A) and the SD (close to 50 mT; Fig. 10C). Coercivity spectra of the Sugarloaf Key sediment (Fig. 10D) and the Laguna Figueroa sediment (Fig. 10F), which have been separately identified to contain a pure ultrafine-grained magnetite assemblage and a mixture of coarse- and

Figure 4-9 - Coercivity spectra of (A) hematite standard, (B) mixture of hematite standard and coarse-grained magnetite standard, (C) mixture of hematite standard and ultrafine-grained magnetite standard.

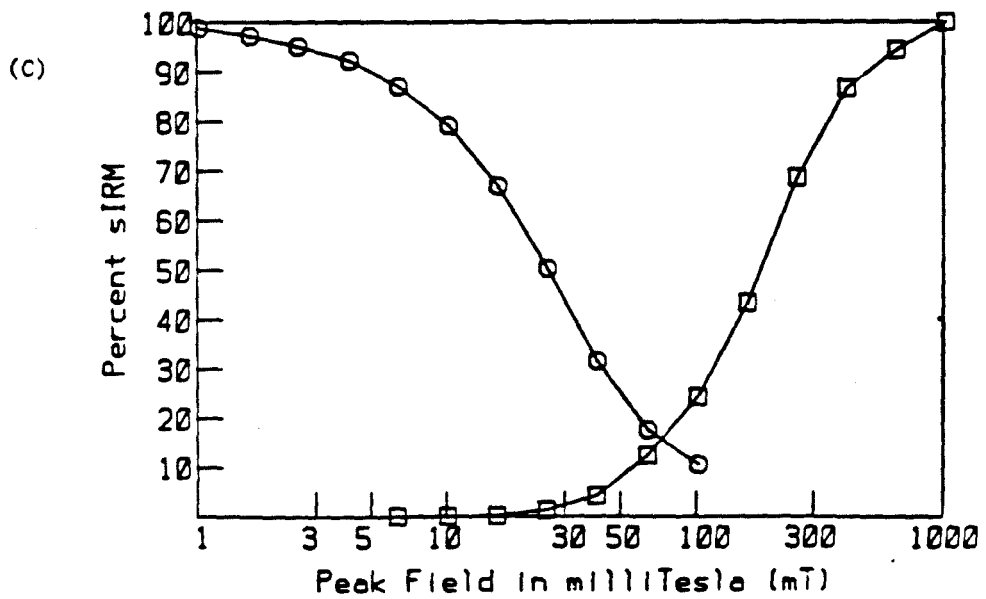
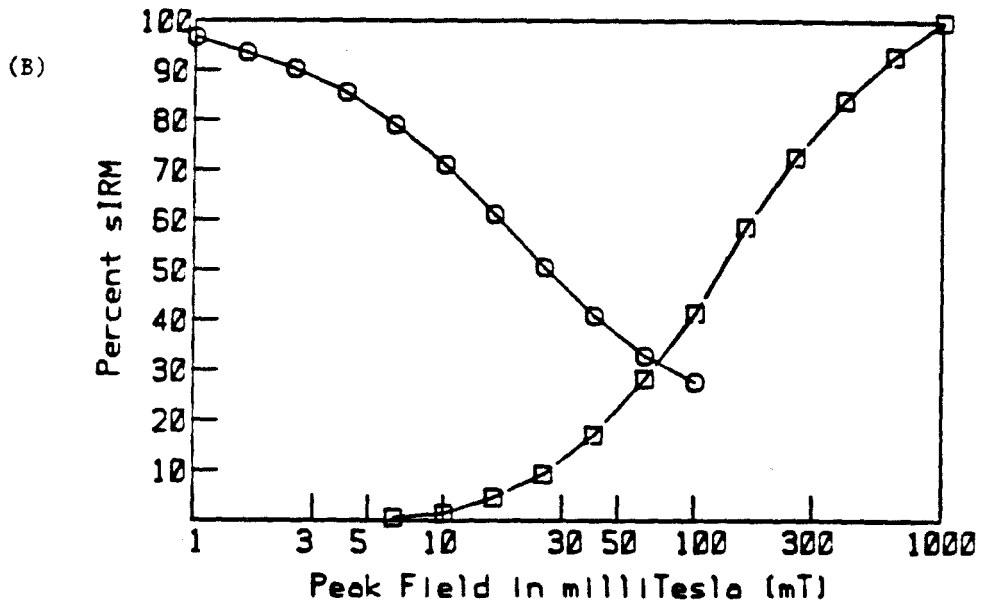
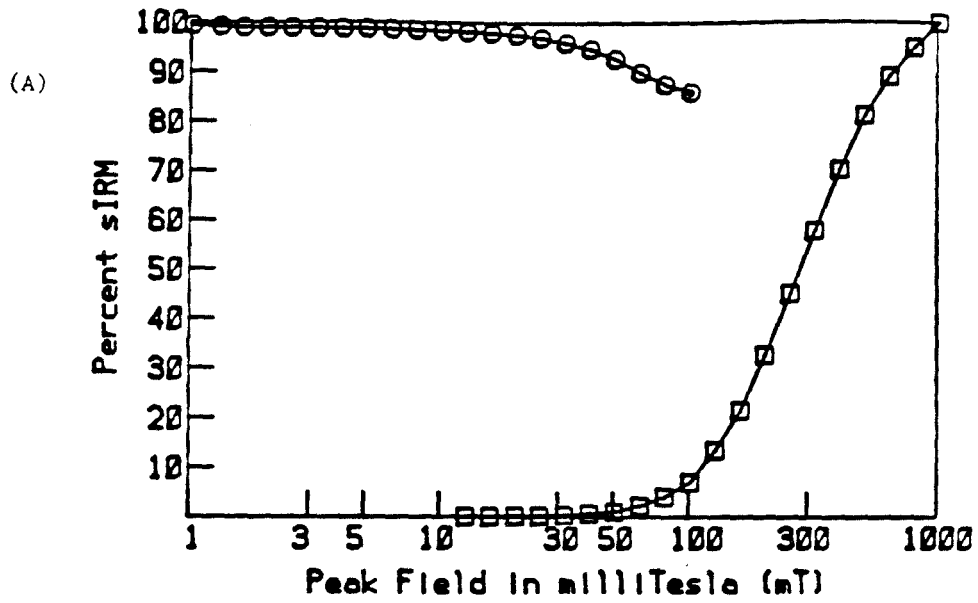
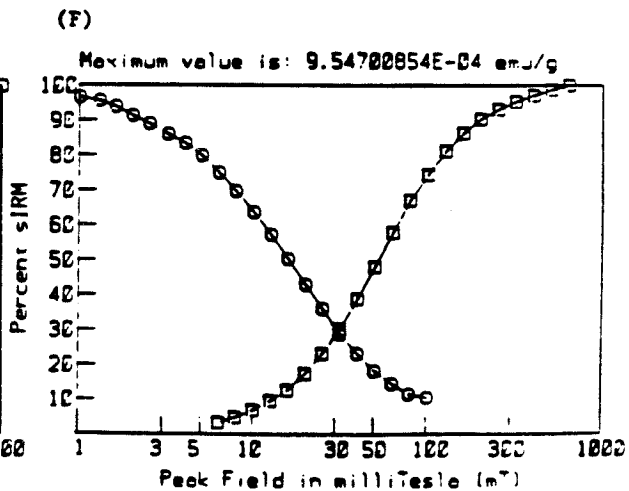
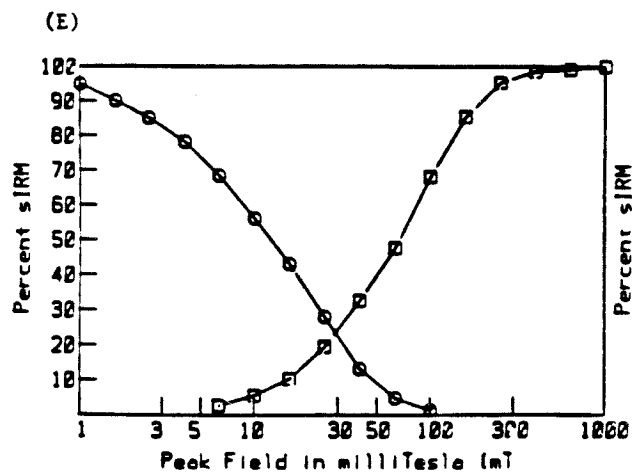
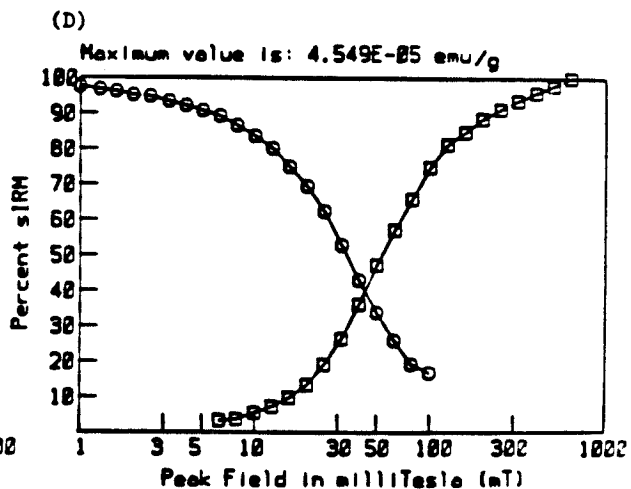
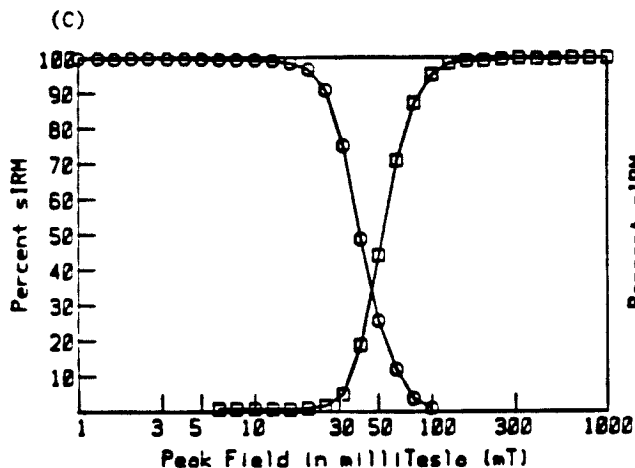
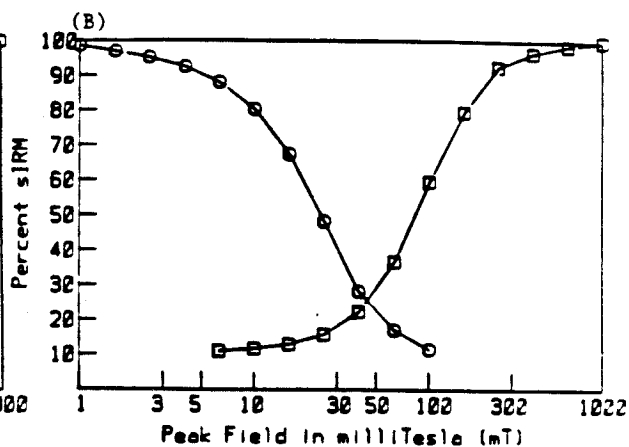
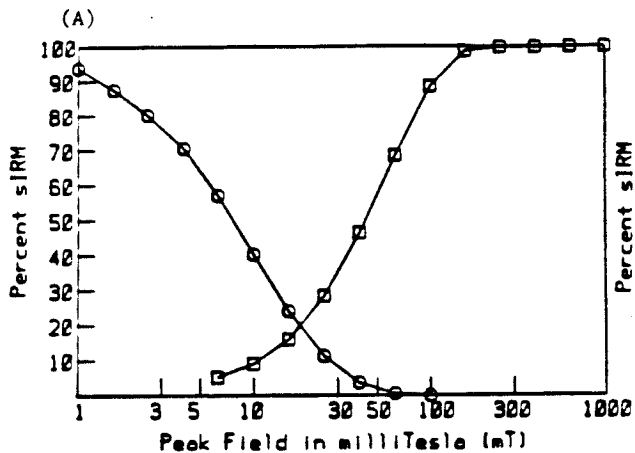


Figure 4-10 - Coercivity spectra of (A) coarse-grained magnetite standard, (B) ultrafine-grained magnetite standard (non-uniform in size as described in the text), (C) magnetotactic bacteria, (D) carbonate sediment from Sugarloaf Key, (E) mixture of coarse-grained and ultrafine-grained magnetite standard, and (F) sediment from Laguna Figueroa.





ultrafine-grained magnetite, compare favorably with the representative coercivity spectra of their laboratory simulated counterparts (Fig. 10C and E, respectively).

#### Bacterial Magnetite as a Primary Remanence Carrier and Implications

The typical saturated IRM (sIRM) of the carbonate sediments at Sugarloaf Key, in which apparently bacteria-formed SD magnetite is the only magnetic phase, has been identified, as shown in Figure 10D, and is about  $1 \times 10^{-1}$  A/m. Since the saturated remanence for magnetite is close to  $5 \times 10^5$  A/m,  $2 \times 10^{-7}$  cm<sup>3</sup>/cm<sup>3</sup> (or  $10^{-6}$  g/cm<sup>3</sup>) of magnetite in sediments would result in the sIRM shown above. Each magnetic domain inside the magnetotactic bacteria strain found in the Sugarloaf Key environment (Fig. 4B) contains about  $1 \times 10^{-14}$  g of magnetite. On the average, each bacterium has about 10 particles, and about  $1 \times 10^{-13}$  g per cell. With an optimum population density of  $10^7$  cells/ml (Blakemore et al., 1979), the magnetotactic bacteria would contribute about  $10^{-6}$  g/cm<sup>3</sup> of SD magnetite to the sediments which is consistent with the amount of magnetite required to contribute the typical sIRM of the Sugarloaf Key sediments. The discrepancy between the coercivity spectra of the Sugarloaf Key sediment and the pure magnetotactic bacteria culture is probably due to some paramagnetic carbonate phases present in the sediment. Both the coercivity spectrum and the sIRM value of the Sugarloaf Key carbonate sediment sample shown in Figure 8D are comparable with many limestone samples we examined. These preliminary data suggest that the bacterial magnetite might be an important remanence carrier in many limestone deposits.

Previous SEM studies (Lowrie and Heller, 1982; McCabe et al., 1983) on the coarse-grained magnetite extracts from limestones have revealed

three major types of crystals: (a) spherical or botryoidal, (2) eroded or rounded, and (3) angular or sharp. Spherical or botryoidal magnetite particles with size range 5-150  $\mu\text{m}$  were commonly observed in many Paleozoic Appalachian limestones (McCabe et al., 1983; Horton et al., 1984). The secondary and diagenetic nature of the chemical remanent magnetization (CRM) carried by these grains has been established through the corresponding apparent polar wandering path (APWP) comparison (Scotese et al., 1982; McCabe et al., 1984). Migrating fluids during the mountain building event have been proposed to be the agents responsible for chemical changes resulting in this secondary magnetization (McCabe et al., 1984). Even though the detailed mechanisms and reactions for forming these diagenetic magnetite particles are not clear at this stage, precisely evaluating the timing and the effects of this secondary remagnetization process will help us to clarify many tectonic complexities based on directions on non-primary magnetic components carried by them (Cisowski, 1984). Many criteria have been previously proposed to test the stability of the primary components in paleomagnetic samples (Van der Voo and Jackson, 1984). The presence of bacterial magnetite may serve as another independent guide for interpreting the nature of the natural remanent magnetization in samples used for paleomagnetic study. The bacterial magnetite particles should preserve their spatial orientations and magnetic remanence directions relative to the rock matrix, unless they are disrupted by major events of thermal, chemical, or physical alteration, which would also alter or destroy any other primary remanence carriers in the rock.

Eroded or rounded magnetite particles of presumably water-transported origin and angular or sharp magnetite grains of possible

volcanic origin have been observed both in deep-sea sediments (Lovlie et al., 1971) and in marine limestones (Lowrie and Heller, 1982). They are strong candidates for carrying post-depositional detrital magnetization (pDRM) in sediments and sedimentary rocks. In 1957, Irving first proposed that the pDRM acquired from the preferential alignment of detrital magnetite with the ambient geomagnetic field in water-filled interstitial voids was the cause of the magnetization in the Precambrian Torridonian sandstone series. Since then, many laboratory redeposition experiments had been conducted to study the detailed characteristics of this pDRM process (Irving and Major, 1964; Lovlie, 1974, 1976). The property of recording the ambient geomagnetic field without inclination error revealed by these studies led Verosub (1977) to conclude that the pDRM is the most important mechanism of primary magnetization in certain sedimentary environments. Lowrie and Heller (1982) have argued from the absence of inclination error in many limestones that this pDRM process is also the most important mechanism of primary magnetization of limestones. However, all the previous laboratory simulation studies on the pDRM were conducted on coarse-grained sediments or deep-sea core materials (King, 1955; Barton and McElhinny, 1979). The applicability of the theory derived from these experiments to low porosity and organic-rich limestone deposits has not been considered. On the other hand, if bacterial magnetite is the primary remanence carrier in sediments, the organic matrix material that holds the magnetite particles in place along the magnetosome (Balkwill et al., 1979) may also serve to bind them to other particles within the sediment after death. Therefore, the remanent magnetization carried by these bacterial magnetite grains should be depositional DRM rather than post-depositional DRM.

Other possible implications of this biogenic origin of magnetic remanence hypothesis include using the existence of large amounts of bacterial magnetite particles as a paleoxygen indicator (Chang and Kirschvink, 1984; Blakemore et al., 1985) and as a guide for excluding the possibility of drilling-induced remanence in carbonate rocks, which has been experimentally shown mainly residing in large MD magnetite grains (Jackson and Van der Voo, 1985).

#### Bacterial Magnetite in Cambrian Limestones

Several Cambrian limestone samples collected separately from Siberia and Kazakstan, Soviet Union and Hubei, China, which have been paleomagnetically shown to contain a stable magnetic phase (Kirschvink and Rozanov, 1984; Kirschvink and Kirschvink, in preparation), were examined to identify the presence of bacterial magnetite. The remanence carrier for the Kazakstan sample was revealed by its coercivity spectrum (Fig. 11A) to be some high coercivity phase, like hematite or goethite. No magnetite has been successfully extracted from this sample. The coercivity spectrum of the China sample (Fig. 11B) is characteristic for samples containing a mixture of magnetite and hematite. The shape of the magnetite particles in the extract as observed under the TEM (Fig. 12) is quite eroded and the size of them falls in MD field of magnetite. These features suggest a detrital origin for these particles. For the Siberia sample, the presence of SD magnetite was revealed by coercivity spectra analysis and detected directly by electron microscopy. The shape of the single dispersed non-dithionite-treated magnetite particle examined under the TEM (Fig. 13A) is prismatic or cuboidal, and not spherical or octahedral. Some of the dithionite-treated magnetite particles have fuzzy outlines and appear to form a chain structure (Fig.

Figure 4-11 - Coercivity spectra of (A) Upper Cambrian trilobite bearing limestone sample COB 5 from Batyrbay Ravine, Kazakhstan, (B) Lower Cambrian trilobite bearing limestone sample LCT 1 from Yantze River Gouge, Hubei, China, and (C) Lower Cambrian Sinskian Limestone sample LLR 200 from Labaia Lena River, Siberia, U.S.S.R.

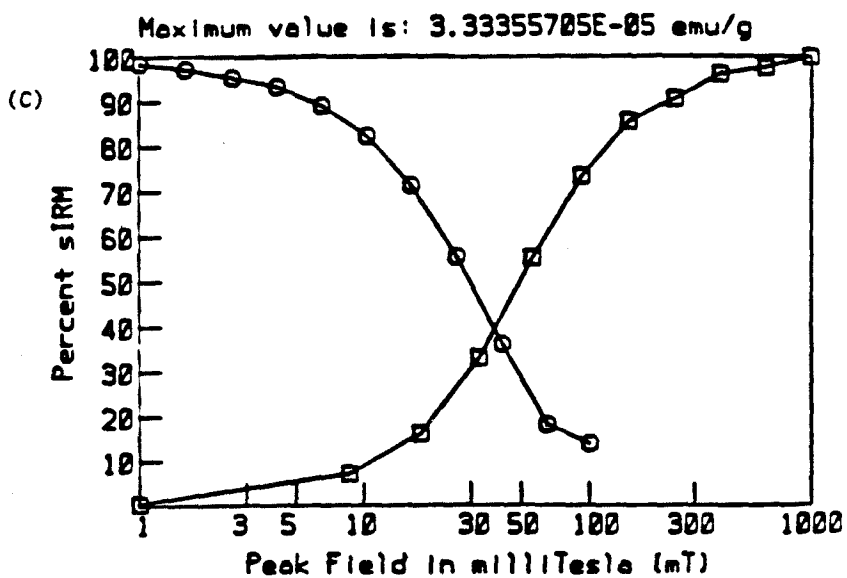
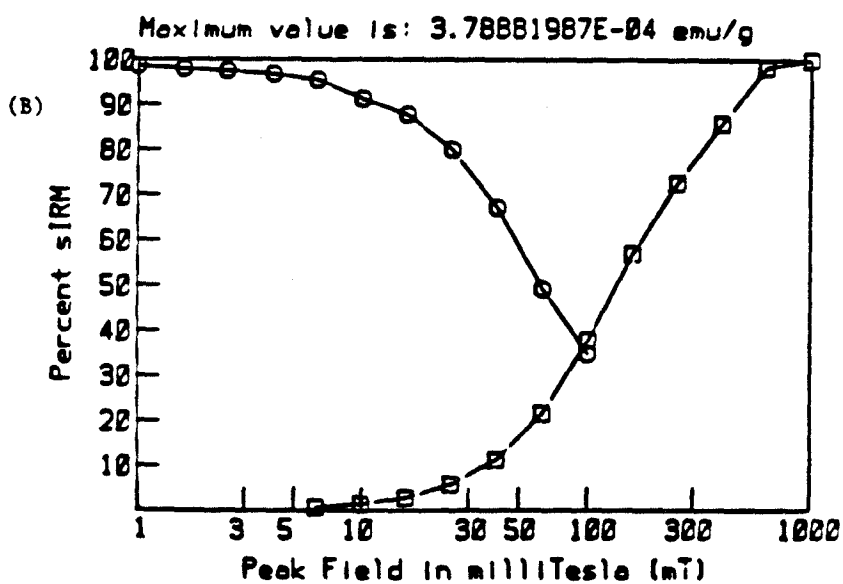
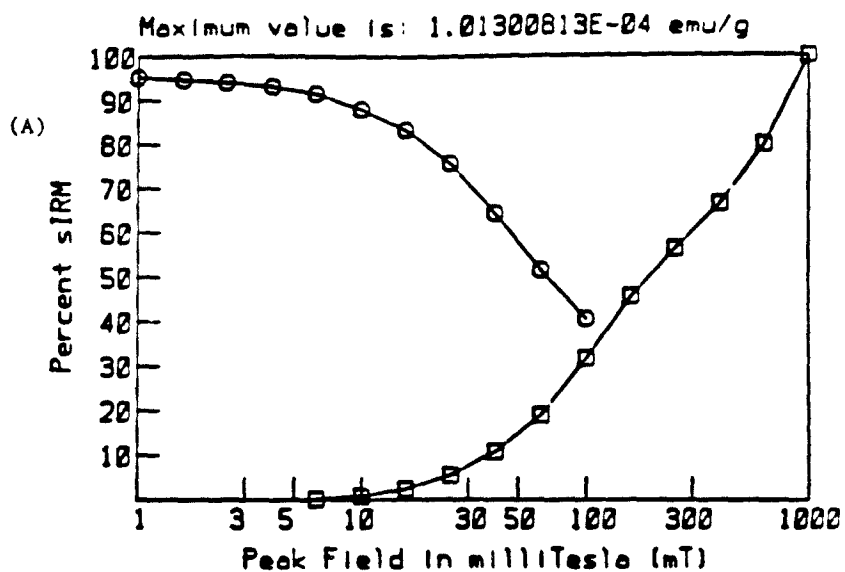
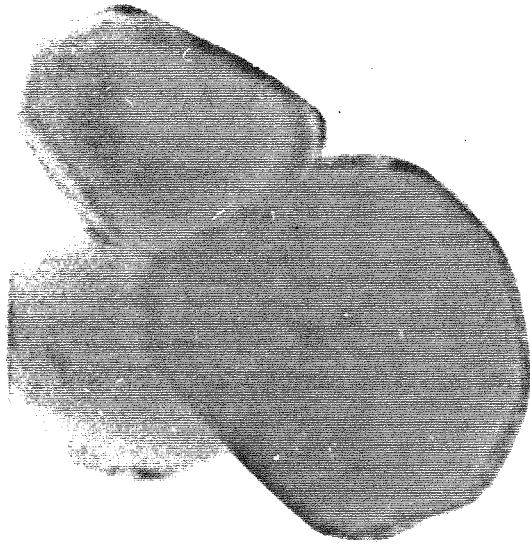


Figure 4-12 - Typical magnetite particles extracted from the sample LCT 1  
as revealed by the TEM. Scale bar = 0.1 micron.

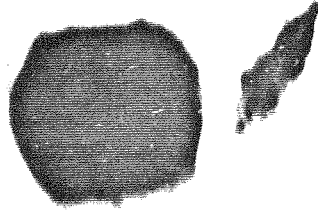




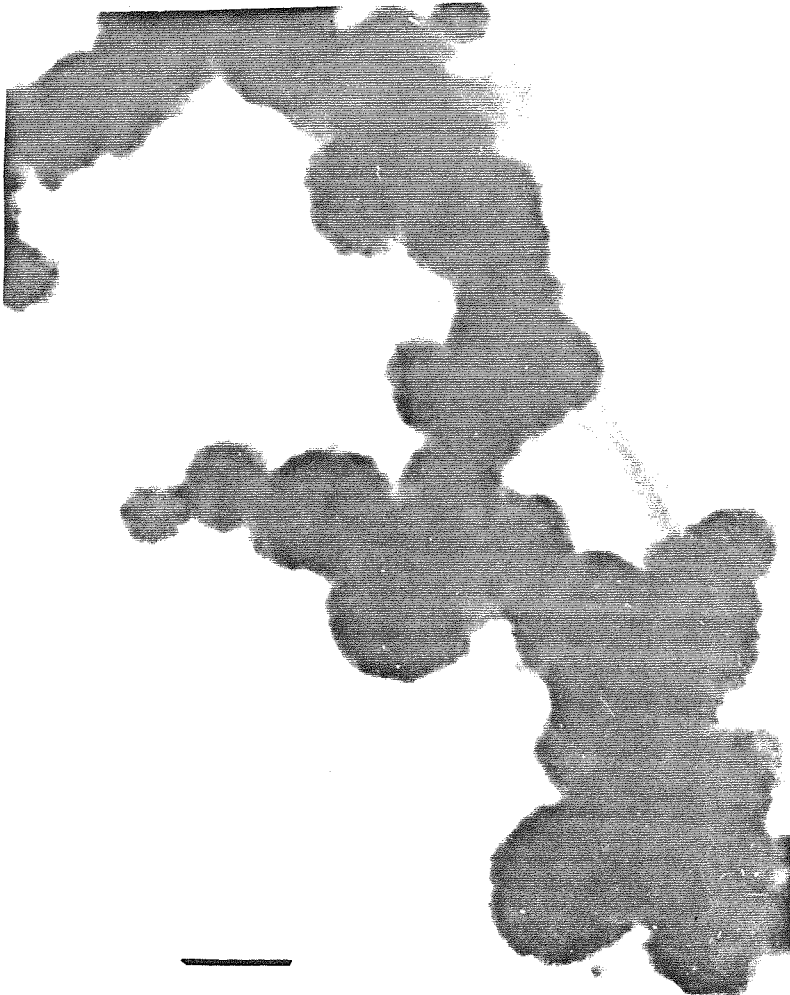
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Figure 4-13 - Electron micrographs of (A) a single dispersed SD magnetite (without dithionite treatment) and (B) an ultrafine-grained magnetite crystals assemblage (with dithionite treatment) extracted from the sample LLR 200. Scale bars = 0.1 micron.

(A)



(B)



13B) similar to that observed in the dithionite-treated magnetite extract of the Laguna Figueroa sediment (Fig. 8B). X-ray diffraction lines of the magnetite extract are pretty sharp and do not have too many coarse-grained particle-induced spots. The calculated d-spacing (8.39 Å) for the magnetite extract from the X-ray diffraction pattern is the same as that of pure magnetite (Tarling, 1983), which indicates that there is little or no titanium present in magnetite crystals. This further suggests the ultrafine-grained magnetite particles present in the Lower Cambrian Sinskian limestone are probably of bacterial origin. The long-term diagenesis does not seem to affect the morphology or the chemistry of these crystals. Bacterial magnetite particles could be present as a primary remanence carrier of other Phanerozoic limestone deposits as well.

### Conclusion

We extended the record of the apparently bacterial magnetite to the beginning of the Phanerozoic and demonstrated that the bacterial magnetite crystals may contribute to the natural remanent magnetization of limestones as well as the detrital and the diagenetic magnetite particles. The remanence they carry is primary in nature (probably depositional rather than post-depositional). Further evaluation of the role of bacterial magnetite as a primary remanence carrier in other Phanerozoic carbonate deposits will help to better understand the detailed mechanisms for the magnetization of limestones, which is one of the most frequently used tools for earth scientists to unravel the reversal patterns of the geomagnetic field and the movement and distribution of ancient plates.

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CHAPTER FIVE

**BIOGENIC MAGNETITE IN STROMATOLITES**

BIOGENIC MAGNETITE IN STROMATOLITES: I. OCCURRENCE IN MODERN  
SEDIMENTARY ENVIRONMENTS

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ABSTRACT

We report the occurrence of biogenic ultrafine-grained, single-domain magnetite in both marine and non-marine modern stromatolitic environments. Magnetotactic bacteria were found associated with the microbial communities involved in the deposition of laminated sediments at Laguna Figueroa, Baja California, Mexico and carbonate stromatolitic nodules at Sugarloaf Key, Florida, U.S.A. The presence of these bacteria and the single-domain magnetite they produce have a profound effect on the magnetic properties of the sediments and can be detected using rock magnetic methods and transmission electron microscopy (TEM). Examination by rock magnetic methods of microbial mats and laminated sediments from Solar Lake, Sinai, Guerrero Negro, Baja California, Mexico and Shark Bay, Australia as well as stromatolites from Shark Bay and Clifton Lake, Australia, Bacalar Lake and Laguna Garabital, Mexico, and Walker Lake, U.S.A. indicates these localities may also contain bacterial magnetites. Biogenic magnetites of bacterial origin have been extracted from Shark Bay mats and Walker Lake samples.

These findings suggest that bacterial magnetites can be recognized as the tiniest trace fossil and may be found preserved in fossil stromatolites and laminated sediments.

#### INTRODUCTION

The history of early life on the earth has been recorded in the rock record as stromatolites. These layered organo-sedimentary structures, formed as a result of the interaction of microbial communities with their sedimentary environment, have been found in rocks as old as 3.5 GA (Awramik et al., 1983; Barghoorn and Schopf, 1967; Knoll and Barghoorn, 1977). During the first 3 billion years of life, prokaryotes were the dominant, if not only type of life and stromatolites were widespread (Awramik, 1982; Barghoorn, 1971; Schopf, 1983). Reaching their zenith in diversity and abundance by the late Precambrian (Upper Riphean), stromatolites declined rapidly after the appearance of metazoans (Awramik, 1982). Today these structures and the microbial communities which construct them, are restricted to environments where the presence of organisms other than prokaryotes is inhibited (e.g. hypersaline lagoons, alkaline lake, thermal springs) (Cohen et.al., 1984).

Our understanding of what life was like in the Precambrian is based on the study of fossil stromatolites and their comparison with modern day microbial communities involved in the deposition of stromatolites and laminated sediments (Awramik, 1982; Schopf, 1983). These studies are

based primarily on the morphology and structural fabric of the fossil stromatolites because they contain very little preserved organic material. Occasionally, traces of microorganisms are found in fossil stromatolites and laminated sediments preserved as kerogenous microfossils silicified in chert. Over 100 microfossil assemblages have been described in the last thirty years (Awramik, 1982). Most of these fossil microorganisms have been interpreted to be cyanobacteria (Knoll and Golubic, 1979; Golubic, 1980; Awramik, 1982). The kerogenous microstructures, however, are only remnants of the original organisms and can be misinterpreted (Golubic and Barghoorn, 1977). It is only rarely that organisms are preserved well enough to be identified as members of extant genera (Golubic and Hoffman, 1976; Golubic and Campbell, 1979). The morphological entities preserved give little physiological information by themselves. Once preserved by artificial silicification it is very difficult to distinguish coccoid eukaryotic algae, chloroxybacteria, fungal spores or prebiotic microspheres from coccoid cyanobacteria of comparable size (Francis et al., 1978a,b).

Prokaryotes in general, do not produce recognizable hard parts, although many are involved in mineral transformations (iron and manganese oxides, calcium carbonates) (Krumbein, 1983). Magnetotactic bacteria are the only example known to date of a prokaryote that precipitates a mineral with distinctive morphology and composition. These bacteria deposit ultrafine-grained crystals of single-domain magnetite

(Fe<sub>3</sub>O<sub>4</sub>) intracellularly (Blakemore, 1982). They occur in both marine and lacustrine environments and are not limited to any particular cellular morphology (e.g. rod, coccus, vibrio, spirillum) (Blakemore, 1982). In most cases, the individual crystals of magnetite are aligned in a chain which acts as a dipole magnet (Frankel, 1984). The bacteria use this intracellular magnet to orient in the Earth's magnetic field; in the northern hemisphere to the north and in the southern hemisphere to the south (Frankel, 1984).

Shortly after their discovery by Blakemore (1975), Kirschvink and Lowenstam (1979) proposed that the unique crystals these bacteria produce might not only affect the magnetic properties of sediments, but could be used as a trace fossil. The first evidence for fossil bacterial magnetite was found in marine sediments. The ultrafine-grained, single-domain magnetite extracted from Oligocene deep-sea sediments (Kirschvink and Chang, 1984) and late Miocene marine clays from Crete (Chang and Kirschvink, 1985) had the morphology and composition of biogenic magnetite. More recently, further examination of deep-sea sediments as old as 50 my (Eocene) have yielded extremely well-preserved bacterial magnetites (Peterson et al., 1986). The purpose of this study was to establish whether magnetotactic bacteria occur in stromatolitic environments and if magnetofossils can be found in fossil stromatolites and microfossiliferous cherts. This paper presents the results of our study of modern stromatolitic environments while the following paper (Chang et al.) reports on fossil bacterial

magnetites.

#### MATERIALS AND METHODS

Samples of sediment were collected at the sediment-water interface from several sites at Laguna Figueroa, Baja California, Mexico and Sugarloaf Key, Florida, U.S.A..

500 ml jars were filled with 1/3 sediment, 1/3 water and left with a head space of atmosphere. Magnetotactic bacteria were detected with low power (160 X) light microscopy by placing the south end of a stirring bar magnet next to a drop of sediment on a glass slide. The bacteria congregated to the edge of the droplet closest to the magnet. Pellets of bacteria were collected with a stirring bar and cobalt-rare earth magnet by the method described in Moench and Konetzka (1978). For examination of the bacteria by TEM whole cells were negatively stained with 1% uranyl acetate (1 min.) on carbon coated grids according to the methods described in Stolz et al. (1986).

Hand samples of microbial mats and recent stromatolites were obtained from various sources (see Tables 1). The ultrafine-grained magnetite component in the sediments was extracted using the techniques described in Chang and Kirschvink (1985). The magnetite extracts were placed on carbon coated grids and examined by TEM. All TEM was done on a Philips 201 at 80 kV. Identification of the magnetite was made by electron diffraction (Chang and Kirschvink, 1985; Towe, 1985).

Rock magnetic studies were carried out on a SQUID



magnetometer. The development of the SQUIDs followed theoretical and experimental work on superconductivity which culminated in the late 1950s and early 1960s. In the superconducting state, metals are able to transport a dc current with zero resistance. When a metal is cooled below its transition temperature, a fraction of the electrons condense into the superconducting state. The colder the metal, the larger the fraction of condensed electrons becomes.

The SQUID sensor consists of a superconducting ring or loop of inductance  $L$  in series with a weak link. The designs of the weak link took many different forms ranging from a piece of wire with a blob of solder on it to a cylinder with saw cuts. The factors which govern the shape of the loops are their inductance, shielding, mechanical stability, and flux coupling efficiency.

The low temperatures at which presently available superconductors operate require that the SQUIDs, and associated flux transformers, be maintained at temperatures in the vicinity of 10 degrees Kelvin. Therefore, the operation of SQUID magnetometers necessitates the use of liquid helium.

Storage and transport of liquid helium is best accomplished in commercial superinsulated storage dewars such as those manufactured by Airco and Cryofab. These are available in light weight and highly efficient models constructed from aluminum and/or stainless steel.

Following measurements were conducted on a SQUID

magnetometer using the techniques described in Fuller et al. (1985). Saturation isothermal remanent magnetization (sIRM), anhysterhetic remanent magnetization (ARM) and alternating field (AF) demagnetization were determined for each sample. The presence of single-domain magnetite was determined rock magnetically using the Lowrey-Fuller test (Lowrey and Fuller, 1971). Cores of microbial mat and laminated sediment from Laguna Figueroa were taken with a 5 cm diameter plastic (PVC) corer and dissected with non-magnetic glass cover slips and wooden chop sticks.

## RESULTS AND DISCUSSION

### Laguna Figueroa

Laguna Figueroa, located 20 km north of San Quintin, Baja California, Mexico, is a lagoonal complex with a salt marsh and evaporite flat separated from the ocean by a barrier dune and beach (Horodyski and Vonder Haar, 1975; Gorsline and Vonder Haar, 1977). Laminated sediments are being deposited in the area between the salt marsh and evaporite flat by a microbial community dominated by Microcoleus chthonoplastes (Horodyski et al., 1977). The annual laminations are occasionally interrupted by episodic flooding. The last of these floods occurred over a period of two years (1978-1980) and resulted in the decimation of the microbial mat community and the deposition of 5-10 cm of non-laminated sediment (Stolz, 1983, 1984a,b, 1985). These mats and the laminated sediments they produce have been studied extensively as analogs to fossilized microbial communities and stromatolites (Horodyski et al.,

1977; Margulis et al., 1980, 1983; Stolz and Margulis, 1984; Stolz, 1983, 1984a,b, 1985).

Magnetotactic bacteria were found in salt marsh pools which border the evaporite flat. The greatest abundance was seen in surface sediments from pools which had a bacterially precipitated film of iron and manganese oxide on the water surface. Magnetococci were the most common although rods, vibrios and a colonial coccoid were also observed. The two different types of magnetococci were differentiated by both size and the location of the flagella. The larger, 5  $\mu\text{m}$  coccoid had a single chain of magnetite crystals which was aligned perpendicular to a veil of flagella which covered approximately one quarter of the cell surface (Figure 1a). Each crystal was rectangular averaging 90 x 110  $\mu\text{m}$  in size (Figure 1b). The second coccoid, 2  $\mu\text{m}$  in diameter, has a magnetosome aligned perpendicularly to two tufts of flagella (Figure 1c). The crystals are also rectangular in shape and average 90 x 110  $\mu\text{m}$  in size (Figure 1c).

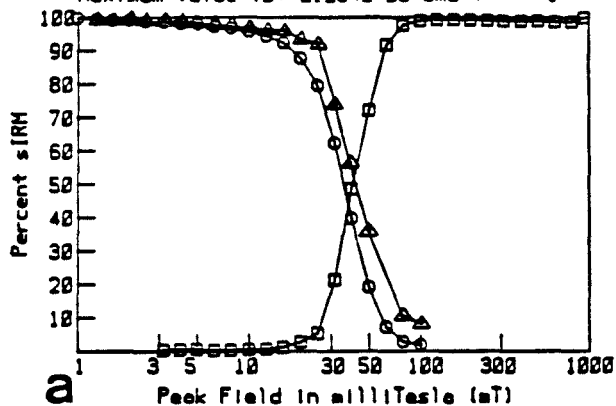
Single-domain, ultrafine-grained bacterial magnetite has a very distinctive coercivity spectra (Figure 2a). Each crystal behaves as a single dipole magnetic and imparts a strong natural remanent magnetization (NRM) to sediments (Stolz et al., 1986). A detailed analysis of the magnetic properties of the laminated sediments at Laguna Figueroa was carried out to determine whether bacterial magnetites were being deposited and preserved in them. These analyses were hampered by the presence of coarse-grained magnetite. Sand from the adjacent dunes was found to contain over 5% (wt/wt)

Figure 5-1 - Magnetotactic bacteria and bacterial magnetite from stromatolitic environments. Laguna Figueroa a-d, Sugarloaf Key e and f. a. magnetococcus with polar veil of flagella, b. magnetosomes from magnetococcus, c. magnetococcus with two tufts of flagella, d. magnetosomes extracted from sediments, e. magnetococcus with hexagonal shaped crystals, f. magnetosome with hexagonal shaped crystals extracted from carbonate sediments. F, flagella, M, magnetosome, all bars 200 nm.

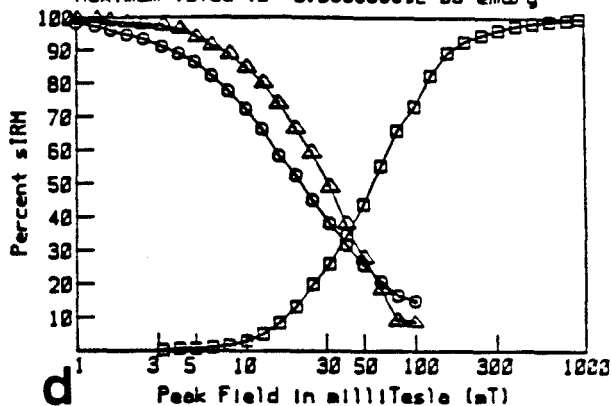


Figure 5-2 - Coercivity spectra with sIRM (squares), AF demagnetization of sIRM (circles) and AF demagnetization of ARM (triangles).  
a. bacterial pellet treated with 1% perchlorate, b. dune sand from Laguna Figueroa, c. surface laminated sediments, Laguna Figueroa, d. flood-derived sediments, Laguna Figueroa, e. old laminations, Laguna Figueroa, f. carbonate sediments, Sugarloaf Key.

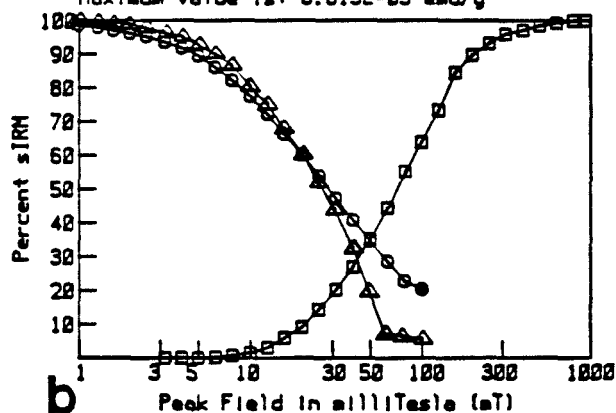
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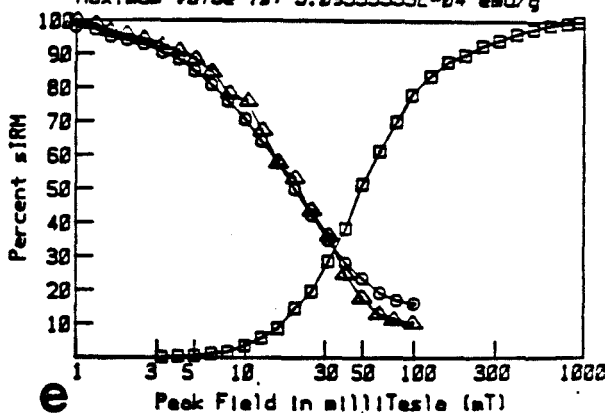
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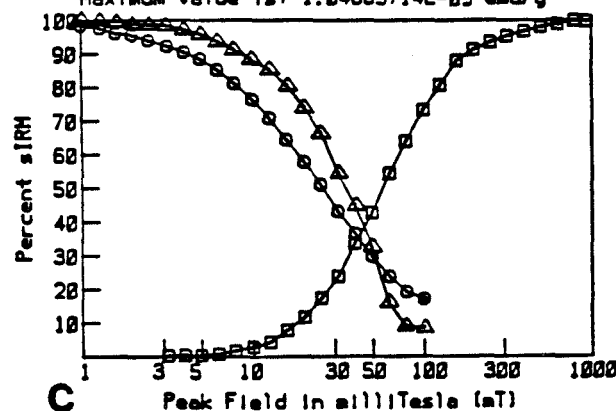
File: FIGDUNESAND 1 is: FIGUEROA DUNE SAND  
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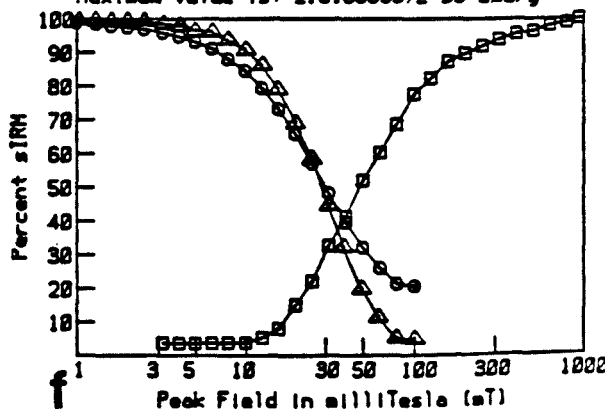
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File: SUGARLOAF 1 is: SUGARLOAF KEY NODULE  
Maximum value is: 2.51666667E-05 emu/g



coarse-grained magnetite. Rock magnetic studies were performed on the dune sand and used as a standard (Figure 2b).

Cores collected from site 5 (Stolz, 1984b) in the fall of 1985, had 1 cm of laminated sediment underlain by 4 cm of flood-derived sediment and 5 cm of old laminated sediment. The top 1 cm could be further differentiated into a 4 mm stratified microbial community and two sets of annual laminations. This stratified microbial community consisted of two surface layers dominated by oxygenic phototrophic bacteria (e.g. cyanobacteria) and two layers dominated by anoxygenic phototrophic bacteria (e.g. green and purple phototrophic bacteria).

Rock magnetic studies showed that the surface laminations contained a mixture of ultrafine-grained and coarse-grained magnetite with a slight enrichment (~2 times greater) of magnetic material in the two oxygenic layers (Figure 2C). The flood-derived sediments also contained a mixture, but contained at least ten times as much magnetite as the surface layers (Figure 2D). Surprisingly, the old laminations (pre-flood) apparently contained only coarse-grained magnetite (Figure 2E).

The incorporation of the bacterial magnetite into the laminated sediments appears to be dependent on the periodic submersion of the microbial mats as well as post-depositional factors. Magnetotactic bacteria have not been observed in the microbial mats of aerially exposed sediments. When the lagoon is flooded by either extreme high tides or the rare influx of meteoric water, magnetotactic bacteria inhabit the oxidized



surface sediments. Magnetotactic bacteria were observed in the surface sediments which covered the evaporite flat when Laguna Figueroa was flooded with 3 meters of water in the spring of 1980 (Kirschvink, unpublished). Although the flooding also brought an influx of coarse-grained component, the net result was the ten fold increase in magnetic material. It is also apparent that much of the bacterial magnetite may be removed in the older laminations by post-depositional factors. Similar to what occurs to the bacterial magnetites in the Santa Barbara Basin, the high concentrations of sulfide combined with anoxic and slightly acidic conditions favor their dissolution (Stolz et al., 1986).

#### Sugarloaf Key

The carbonate sediments of the Florida Keys (of which Sugarloaf Key is the third to last) have been recognized as a modern analog to ancient limestone deposits (Ginsberg, 1964) and stromatolitic domes were reported (Golubic and Focke, 1978). The intertidal marsh at Sugarloaf Key is a mangrove swamp with sediments composed of fine carbonate ooze and shelly fragments. On the surface, thumb-sized stromatolitic nodules are being deposited by a microbial community dominated by the cyanobacterium Schizothrix gracilis (Stolz unpublished, Golubic and Focke, 1978). Magnetotactic bacteria were seen in the carbonate sediments where the stromatolitic nodules were forming. Rods and a colonial coccoid were seen, but the most abundant morphology was an elongate coccoid with hexagonal shaped magnetite crystals (Figure 1e). The magnetite extracted

from these sediments is clearly bacterial in origin (Figure 1f).

Rock magnetic studies of both the stromatolitic nodules and the surrounding carbonate ooze indicated the presence of single-domain magnetite (Figure 2f). Unlike Laguna Figueroa, there is no apparent source of coarse-grained magnetite and most if not all of the magnetite in these sediments is biogenic (Chang et al., 1987). In addition, the environment of deposition is ideal for the preservation of bacterial magnetites.

#### Other Localities

We examined hand samples of laminated sediments and stromatolites from other localities for the presence of biogenic magnetites (Table 1). The results of the rock magnetic studies suggest that ultrafine-grained magnetite is present in all of them. Bacterial magnetites have successfully been extracted from carbonaceous sediments from the Bahamas, flat laminated mat from the North Point locality of Shark Bay, Australia and carbonate stromatolites from Walker Lake, Nevada (Figure 3).

#### CONCLUSIONS

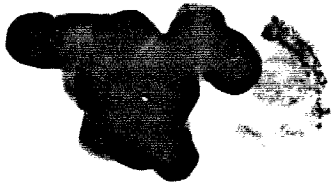
We have demonstrated that magnetotactic bacteria are found in environments where laminated sediments and stromatolites are being deposited. The ultrafine-grained magnetite they produce is being incorporated into these sediments and contributes to the magnetic properties. The preservation of this magnetite is dependent on post-

depositional factors.

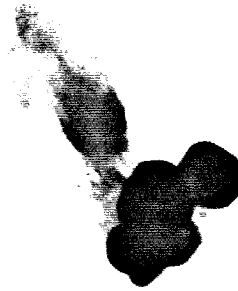
Figure 5-3 - Magnetite extracts from modern marine and stromatolitic environments. All have euhedral and prismatic crystals, characteristic of bacterially precipitated magnetite.

- a. carbonate sediments from Palma Solo Pond, Bahamas.,
- b. flat laminated mat from the North Point locality, Shark Bay, Australia,
- c. lacustrine Walker Lake, Nevada.

All bars 200 nm.



**a**



**b**



**c**



**d**



**e**

BIOGENIC MAGNETITE IN STROMATOLITES: II. OCCURRENCE IN  
ANCIENT SEDIMENTARY ENVIRONMENTS

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ABSTRACT

We report the discovery of fossil bacterial, single-domain magnetite particles in ancient stromatolites. The biogenicity of the crystals was determined by the following criteria: 1) distinctive morphology and habit, 2) composition, and 3) environment of deposition. Stromatolites ranging in age from Early Proterozoic to Pleistocene, composed of both carbonate and chert, were analyzed for the presence of single-domain magnetite using rock magnetic methods. The granulometry and composition of the ultrafine-grained magnetite crystals extracted were determined by transmission electron microscopy and electron diffraction. The oldest magnetofossils were extracted from stromatolitic chert of the approximately 2000 Ma old Gunflint Iron Formation. The implications of these finds and the potential uses of fossil

bacterial magnetite in studies of the evolution of biomineralization and prokaryotic metabolic processes, paleomagnetism, and as an indicator of ancient oxygen levels are discussed. Bacterial magnetite represents the oldest evidence of biomineralization yet discovered in the fossil record.

#### INTRODUCTION

Biomineralization producing hard parts was a major innovation in the history of life (Lowenstam and Margulis, 1980). The most profound biomineralization event took place at the base of the Cambrian System, some 540 to 570 Ma ago, when cyanobacteria, algae and numerous phylogenetically distant invertebrates developed the ability to secrete hard parts. Although the cause(s) of this event is unknown studies on extant organisms indicate that the mineral-forming mechanisms range from "matrix-mediated" to "biologically-induced" (Lowenstam, 1981). Biologically-induced minerals have crystal habits and chemical signatures that are governed by the same equilibrium principles that control the crystallization of their inorganic counterparts. In contrast to this, matrix-mediated minerals are usually grown in a pre-formed organic framework (the matrix). A high level of biochemical control makes their size, shape and chemical signature distinguishable from possible inorganic counterparts.

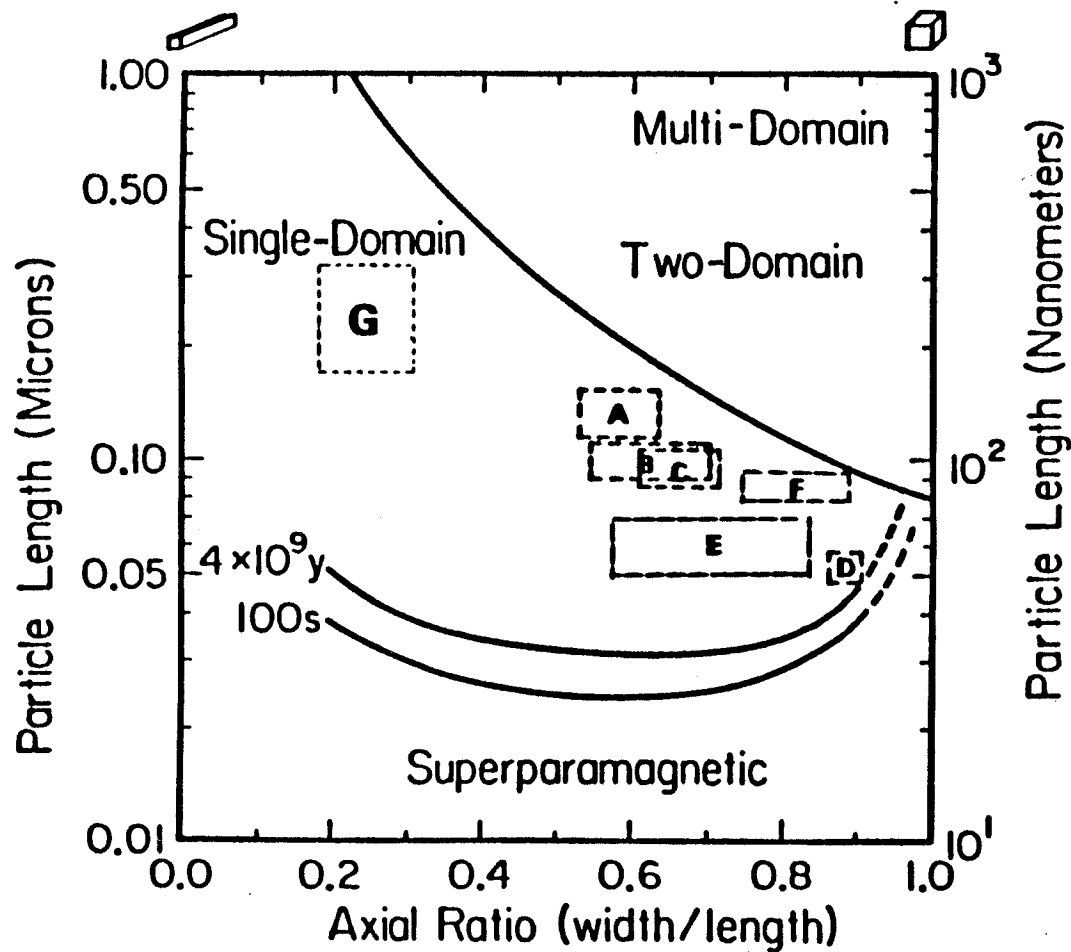
It was recognized by Blakemore (1975) that members of the bacteria have the ability to biomineralize magnetite

within their cells and it is a clear example of a matrix-mediated mineral (Lowenstam and Kirschvink, 1985). The morphology, structure and composition of bacterial magnetite have been well studied (Frankel et al., 1979; Towe and Moench, 1981; Blakemore, 1982; Matsuda et al., 1983; Mann et al., 1984a,b). The crystal morphologies generally fall into one of three categories: 1) hexagonal prisms (Towe and Moench, 1981; Matsuda et al., 1983; Mann et al., 1984a), 2) cuboid (Frankel et al., 1979; Mann et al., 1984b), and 3) tear-drop (Blakemore, 1982). These shapes are all quite different from the typical octahedral morphology of inorganically formed magnetite. In addition, biogenic magnetites tend to be chemically pure (Towe and Moench, 1981; Mann, 1985) in contrast to igneous and metamorphic magnetites which often have higher levels of some other transitional metals such as titanium (Haggerty, 1976).

Besides their distinctive shape and composition, bacterial magnetites have a unique size distribution. All of the bacterial magnetite crystals studied by high resolution TEM to date have sizes ranging from 0.05 to 0.3  $\mu\text{m}$  that fall within the size range of single-domain stability field of magnetite (Towe and Moench, 1981; Chang et al., 1987; see also Fig. 4). The restricted size range for these biogenic magnetites has been interpreted to be the result of natural selection operating on organisms that use their internally-formed magnetite for directional sensitivity (Blakemore, 1975; Kirschvink, 1983). These characteristic



Figure 5-4 - Size and shape distribution of magnetite particles found in magnetotactic bacteria and magnetotactic algae from previously reported occurrences as plotted in the theoretical derived stability field diagram of magnetite (Butler and Banerjee, 1975).



- A. Fresh water sediments of New Zealand (Blakemore et al., 1980).
- B. Complex simulated natural environment (Towe & Moench, 1981).
- C. Fyshwick sewage pond, Australia (Kirschvink, 1980)
- D. Salt marshes of Cape Cod, Massachusetts (Blakemore, 1975).
- E. Santa Barbara Basin (Stolz et al., 1986).
- F. Laguna Figueroa, Baja California and Sugarloaf Key, Florida (Stolz et al., 1987).
- G. Magnetotactic Algae (Torres de Araujo et al., 1986) and tear-drop shaped magnetite in magnetotactic bacteria from New Zealand (Blakemore et al., 1980)

properties, combined with the widespread distribution and abundance of magnetotactic bacteria (Moench and Konetzka, 1978; Chang et al., 1987), suggest that biogenic magnetite should be present and recognizable in the rock record.

The formation of magnetite in Aquaspirillum magnetotacticum is known to require some amount of free oxygen (Blakemore et al., 1985; maximum yield of magnetite is obtained with the initial oxygen concentration at about 5% of the present oxygen level and virtually no magnetite is formed when the oxygen concentration goes below 2.5% of present atmospheric level). To our knowledge, all natural environments in which living magnetotactic bacteria have been found are microaerobic (typical niche of magnetotactic bacteria is at the sediment-water interface where the abrupt decrease of oxygen concentration is observed). The study of bacterial magnetite crystals in the fossil record could therefore provide constraints on the chemistry of bottom waters through the Phanerozoic, and may ultimately shed light on the evolution of free oxygen during the Precambrian. Furthermore, because magnetotactic bacteria use the magnetite they produce as a compass orientation (Frankel, 1984), the presence of fossil bacterial magnetites in the pre-Phanerozoic would imply the existence of a geomagnetic field.

#### MATERIAL AND METHODS

Samples from sixteen localities spanning almost 3,500 Ma of geological time from the Middle Archaean to the

late Cenozoic were examined for biogenic magnetite (Table 2). Obsidian samples that are rock-magnetically shown to contain single-domain magnetite as their major remanence carrier were studied as a reference for examining the morphology of typically inorganically-formed ultrafine-grained magnetite particles.

The rock magnetic techniques used in this study have been described elsewhere (Stolz et al., 1987). Saturated isothermal remanent magnetization (sIRM) acquisition and alternating fields (AF) demagnetization (coercivity spectra) analyses were employed to determine the major magnetic phase in each sample. If magnetite was found as the main magnetic carrier, the revised Lowie-Fuller test (Johnson et al., 1975) was then performed to determine the size distribution of these particles. Only those samples that were shown by these methods to contain single-domain magnetite particles of the characteristic size underwent magnetic extraction.

The magnetic extraction procedure is basically the same as that used by Chang and Kirschvink (1985) for marine sediment. Two minor differences are that the chert samples were pulverized to a sub-micron sized powder to separate the magnetic particles from the chert matrix and the carbonate samples were treated with 5N acetic acid (Chang et al., 1987) to dissolve carbonate phases before the general extraction procedure. For testing the effects of grinding on the geometry of ultrafine-grained magnetite particles, magnetite standard particles (around 0.2  $\mu\text{m}$  in size) were

Table 2

## OCCURRENCES OF FOSSIL MAGNETITE PARTICLES

Formation and Location	Age	Description	Extract	SQUID
Furnace Creek California (1)	Pliocene	stromatolitic limestone	N.D.	H
Ocean sediment Bahamas (2)	Pliocene	calcite sediments	cuboidal, tear-drop	SD
Potamida Clay Crete (3)	Miocene	marine clays	prismatic, hexagonal	SD, MD
DSDP 522 core South Atlantic (4)	Oligocene	deep-ocean sediments	cuboidal, euhedral	SD, MD
DSDP 523 core South Atlantic (5)	Eocene	deep-ocean sediments	prismatic, tear-drop	SD, MD
Green River Wyoming (1)	Eocene	stromatolitic limestone	N.D.	MD
Sinskian, Siberia, USSR (6)	Cambrian	black marine limestone	cuboidal	SD
Nama, South Africa (9)	700 Ma	black limestone	cuboidal	SD
Beck Spring California	> 850 Ma	stromatolitic chert	octahedral	SD, MD
Bitter Springs Australia (1)	850 Ma	stromatolitic chert	cuboidal, octahedral	SD, MD
Bitter Springs Australia (1)	850 Ma	intercolumnar chert	N.D.	H
Skillogalee Australia (7)	1000 Ma	black chert	octahedral	SD, MD
Dismal Lake Canada (7)	1200 Ma	black chert	octahedral	SD, MD
Vempalle India (7)	1400 Ma	stromatolitic chert	prismatic, octahedral	SD, MD
Gunflint Canada (1)	2000 Ma	stromatolitic chert	cuboidal, octahedral	SD, MD
Foetescue Australia (8)	2700 Ma	gray limestone	octahedral	MD
Warrawoona (7)	3500 Ma	black	N.D.	H

1. S. Awramik, UC Santa Barbara, CA
2. McNeill et al., 1987
3. Chang and Kirschvink, 1985.
4. Kirschvink and Chang, 1984.
5. Petersen et al., 1986.
6. Chang et al., 1987
7. Schopf, J. W., UCLA
8. Buick, R., Harvard
9. Grant, S., Harvard

N.D. not determined; SD single-domain magnetite; MD multi-domain magnetite  
H high coercivity phase (hematite or goethite).

also ground and examined by TEM.

The final magnetite extracts were placed on carbon coated grids and observed with a Phillips 201 transmission electron microscope at 80 kV. Several magnetite extracts were also examined by a JOEL JSM-840 high resolution scanning electron microscope (SEM). Electron diffraction on the TEM (Towe, 1985) and energy dispersive X-ray analysis on the SEM were used to determine the phase and composition of the extracts.

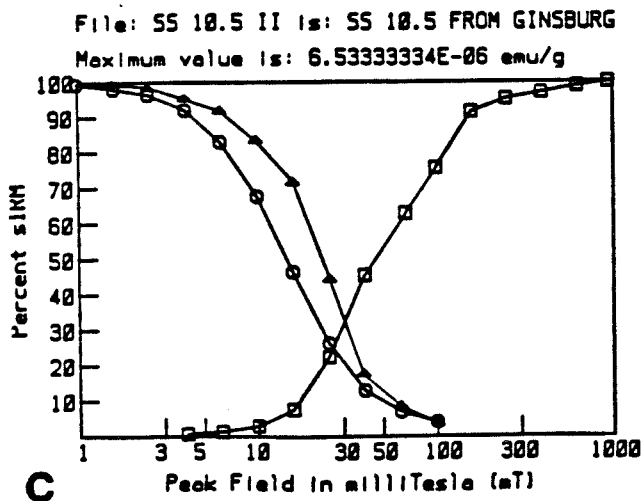
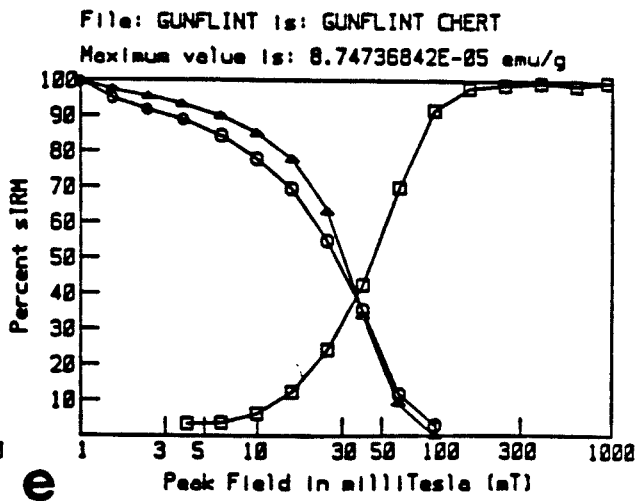
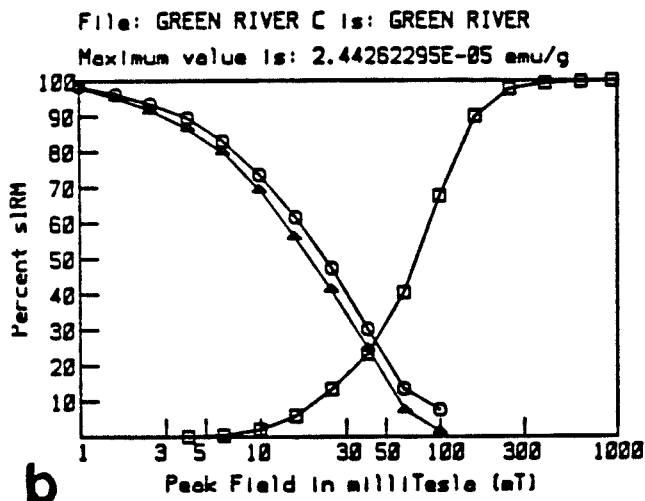
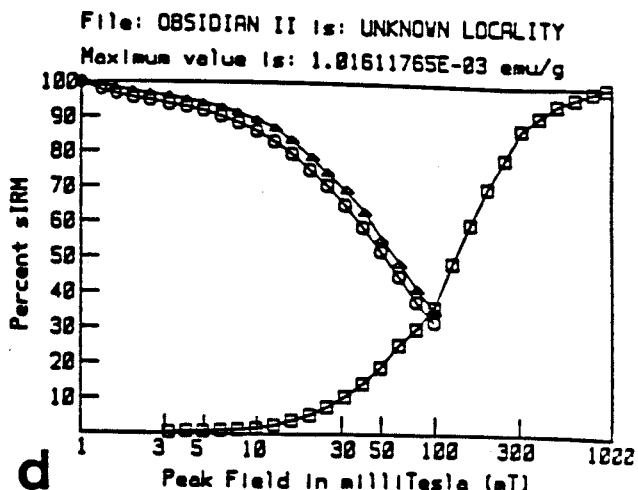
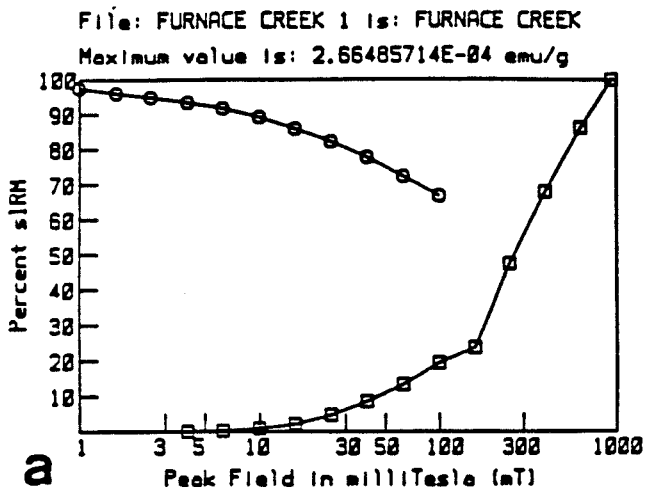
## RESULTS AND DISCUSSIONS

### Cenozoic Stromatolites

Two Cenozoic stromatolite samples were studied: one from the Pliocene Furnace Creek Formation, Death Valley, California (see Pitts, 1983) and the other from the Eocene Green River Formation, Colorado (see Surdam and Wray, 1976). Both stromatolites are columnar, well laminated, composed of limestone and formed in lacustrine environments. No organic walled microbial fossils have been detected in this material. Although single-domain biogenic magnetite has been detected in extant lacustrine stromatolites from several localities (Stolz, et al., in press), the rock magnetic studies of the fossil examples did not reveal the presence of any single-domain magnetite in either sample.

The Furnace Creek sample is heavily leached and superficially stained by reddish iron oxides, probably hematite. Coercivity spectral analysis (Fig. 5A) suggests

Figure 5-5 - Spectra with IRM (squares) acquisition, AF demagnetization of sIRM or IRM gained at 10000 Gauss (circles), and AF demagnetization of ARM (triangles). The intersection point of the IRM acquisition and the AF demagnetization of IRM curves generally represents the coercivity of the sample. Comparing the median destructive field (MDF) of the sIRM and the ARM (so called the Lowrie-Fuller test) will tell you whether the single-domain (if the MDF of the ARM is larger than that of the sIRM) or the multi-domain (if vice versa) magnetite is the major remanence carrier in the sample. a. stromatolite from Pliocene Furnace Creek Formation, Death Valley, California, b. stromatolite from Eocene Green River Formation, Wyoming, c. carbonate core sample from San Salvador Island, Bahama Islands, d. obsidian sample from unknown locality, e. The Gunflint chert sample, this spectrum is commonly observed for other Precambrian chert samples we analyzed. 1 mT = 10 Gauss.





its remanence resides in some high coercivity phases, like hematite or goethite. In contrast, both the coercivity spectral and the Lowrie-Fuller test (Fig. 5B) for the Green River sample show some very low coercivity phases, such as multi-domain magnetite or maghemite, as their major remanence carriers.

The mesoscopic and microscopic nature of the lamination of the Green River stromatolite is superficially similar to the microstructure found in many extant laminated stromatolites and microbial mats such as those forming in the hypersaline marine environment of Hamelin Pool, Shark Bay, Western Australia (Surdam and Wray, 1976) and in Laguna Figueroa, Baja California, Mexico (Margulis et al., 1980). We have detected both magnetotactic bacteria and bacterial magnetite within the fixed microbial mat samples from the surface of these two extant stromatolite localities (Chang et al., 1987; Stolz et al., in press). Our study of the magnetic grain-size variations in laminated microbial sediments from Laguna Figueroa revealed the disappearance of single-domain magnetite crystals with depth, which we interpret as the result of iron reduction coupled with decay of organic matter (Stolz et al., in press). The same type of biologically induced chemical dissolution processes could have occurred in the Eocene Green River environment and account for the absence of single-domain magnetite from the sample. Early cementation/lithification of degrading microbial mat material which may have not

occurred with the Green River samples and does not occur at Laguna Figueroa, may be conducive for the preservation of biogenic magnetite.

### Cenozoic Marine Sediments

In contrast to these Cenozoic lacustrine stromatolites, previous studies by some of us (Kirschvink and Chang, 1984; Chang and Kirschvink, 1985) and that of Patterson et al. (1986) have demonstrated a widespread distribution of fossil bacterial magnetite in marine sediments. No Cenozoic marine stromatolites were available for comparison in this study. The discrepancy concerning the preservation of bacterial magnetite in different depositional environments led us to reassess our selection of material for analysis.

If the proposed mechanism for the disappearance of single-domain magnetite (iron reduction coupled with decay of organic matter; Karlin and Levi, 1983, 1985; Stolz et al., in press) is correct, we should be able to see an inverse correlation between the abundance of bacterial magnetite preserved and the total organic carbon (TOC) content of the sediment. Johnson-Ibach (1982) has compiled analyses of TOC in numerous DSDP core samples and obtained a relationship between the TOC and sedimentation rate; generally speaking, TOC decreases with increasing sedimentation rate due to the clastic dilution of the organic input. In the same study, he also found that, at a given sedimentation rate, the TOC by weight percent increases incrementally from calcareous sediments to

calcareous-siliceous sediments to siliceous sediments to black shale. If one then assumes a constant supply of bacterial magnetite into the sediments, the bacterial magnetite particles should appear to be most abundant and best preserved in calcareous sediments with a high sedimentation rate. This is exactly what we observed in DSDP site 522 and other deep sea core samples (see Table 1 of Kirschvink and Chang, 1984). Similarly, bacterial magnetites are well preserved in the flood derived sediments at Laguna Figueroa, an observation that can also be explained by the clastic dilution of organic material during the flood period.

Another potential complication in our study of the Proterozoic stromatolites is the effect of the long term geological processes on the bacterial magnetite. Until now, reports of bacterial magnetite crystals have been restricted to clays and deep sea soft sediments, with no definitive reports from consolidated sedimentary deposits. To test for possible effects of lithification on biogenic magnetite, we studied a set of marine carbonate core samples of Pliocene to Recent age from the island of San Salvador in the Bahamas that had been subjected to a minimum of diagenetic alteration (McNeill et al., 1988). We have previously detected both magnetotactic bacteria and bacterial magnetite in the surface sediments of the Florida Keys (Chang et al., 1987; Stolz et al., in press), which has a similar depositional setting as the Bahama Banks (Ginsburg, 1964). A typical coercivity

spectrum and ARM Lowrie-Fuller test (Fig. 5C) for these samples indicate that single-domain magnetite is the primary magnetic mineral present. Two types of single-domain magnetite particles were identified from the magnetic extracts; one that has a tear-drop shape (Fig. 6A), and another that is cuboidal (Fig. 6B). Both of these types are commonly observed in magnetotactic organisms (e.g. Blakemore, 1982; Torres de Araujo et al., 1986), strongly suggesting a biogenic origin. The edges of the crystals are well defined and do not seem to have been affected by secondary diagenetic processes. On the other hand, single-domain magnetite crystals recovered from much older limestone samples of the Early Cambrian Sinskian Formation of the Siberian Platform (Chang et al., in press; Fig. 3C) show much fuzzier outlines. This degradation of morphology is probably due to partial oxidation and alteration of the crystal surface to maghemite and other iron oxides, which are then removed during the magnetic extraction process (Kirschvink and Chang, 1984). Nevertheless, the alignment of the crystals in a chain and their generally cuboidal shape still imply a bacterial origin.

#### Proterozoic Stromatolites and Microfossiliferous Cherts

Table 2 lists data for eight representative stromatolitic chert samples, some of which are microfossiliferous, spanning from Middle Archean to Late Proterozoic which we have studied. Samples were selected on the basis of known paleontological significance and availability to us. Details on the

Figure 5-6 - Ultrafine-grained magnetite from ancient stromatolitic and other depositional environments (a-c, f-j), obsidian (e), and ultrafine-grained magnetite standard after grinding (d). a-b. carbonate core sample from San Salvador Island, c. Cambrian Sinskian Formation, Labaia Lena River, Siberia, f,h,j, the Gunflint chert, the octahedral crystal assemblage shown in f has been identified from other Precambrian chert samples we examined. g. the Bitter Spring chert, i. the Vampalle chert. Scale bars 100nm except d-f 500nm.



biogeology and a general overview on the geology of each formation from which the samples were collected are also on Table 2. Each of the samples were reduced to sub-micrometer sized powders in a motor-driven ceramic grinder before subjecting to magnetic extraction. Fig. 6D shows some of the ultrafine-grained magnetite particles remained intact after grinding. As a control, we also applied some grinding and magnetic extraction procedure to a cryptocrystalline obsidian sample for which the Lowrie-Fuller test (Fig. 5D) suggested that single-domain magnetite as the primary phase. We found only euhedral single-domain magnetite with no evidence of abrasion due to the grinding. The shape of these inorganically formed magnetite particles is mostly octahedral (Fig. 6E), which is easily distinguished from that of bacterial magnetite.

Rock magnetic analyses of Archean Warrawoona Group and Fortescue Group samples show their remanences mainly reside in a high coercivity phase (the former) or multi-domain magnetite particles (the latter). In contrast, rock magnetic analyses of Proterozoic samples generally show a mixture of multi-domain and single-domain magnetite as their major remanence carrier. In three of them (Skillogalee, Dismal Lake and Beck Spring), multi-domain and single-domain octahedral crystals are the dominant type observed in the magnetic extracts (Fig. 6F). In magnetic extracts of the Bitter Springs, Vampalle and Gunflint samples, in addition to octahedral crystals, we have detected prismatic and

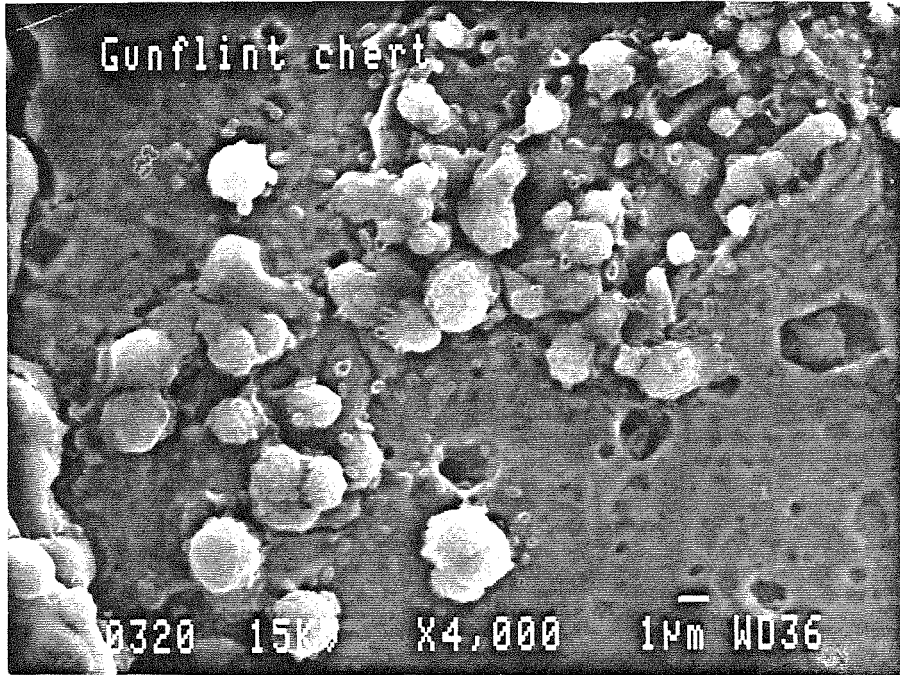
cuboidal single-domain magnetite crystals which resemble bacterial magnetite particles (Figs. 6G, H, I, J). Some multi-domain magnetite spheres (Fig. 7) with a presumably diagenetic or or authigenic origin were found associated with the ultrafine portion of magnetite extract. The paragenetic relationship between these spheres and the bacterial magnetite-like particles is difficult to determine. Although we can not definitively prove a biogenic origin for these prismatic and cuboidal single-domain magnetite crystals, they are certainly distinct from single-domain magnetite particles isolated from the obsidian sample and resemble forms of modern biogenic (bacterial) magnetite.

#### IMPLICATIONS

If the bacterial magnetite identified in the Gunflint stromatolites are indeed of biogenic origin, it would represent the oldest evidence for matrix-mediated biomineralization. As for other implications, only certain speculations can be made from these results. These findings agree with a previously published report that the present level of the Earth's magnetic field strength appeared by 2000 Ma ago (Merrill and McElhinny, 1983). The magnetotactic bacteria in the Gunflint provides independent evidence that agrees with other evidence and conclusions that free oxygen had begun to accumulate in the environment somewhat before 2000 Ma ago (Walker et al., 1983). However, using bacterial magnetite as a paleoxygen level indicator is somewhat tenuous because of the problem of localized



Figure 5-7 - Magnetite assemblage extracted from the Gunflint chert sample as examined under the high resolution SEM. EDAX analysis shows Fe is the only cation phase present. Notice the association of the magnetite spheres with the ultrafine-grained magnetite. The morphology of these ultrafine-grained magnetite particles is hard to be resolved.



oxygen production by cyanobacterial blooms or microbial mats need to be accounted for. Whether the Gunflint bacterial magnetite reflects global atmospheric oxygen content that had reached 5% PAL is doubtful. In the future, sediments from well mixed environments in which magnetotactic bacteria are not associated with oxygenic microbiota ought to be examined.

#### CONCLUSIONS

Fossil bacterial magnetite particles with distinctive morphology have been identified from ancient consolidated carbonates from the Bahamas. Single-domain magnetite particles strongly resembling bacterial magnetite or aligned as a chain with fuzzy outlines were identified in Proterozoic Bitter Springs, Vampalle, and Gunflint chert samples. The apparent occurrence of bacterial magnetite in the Gunflint sample suggests that matrix-mediated biomineralization appeared at least as early as 2,000 My ago. It also supports currently accepted hypotheses about the evolution of the Earth's magnetic field and the Precambrian atmospheric oxygen level.

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APPENDICES

## APPENDIX I

### A Candidate Magnetic Sense Organ in the Yellowfin Tuna, *Thunnus albacares*

**Abstract.** *Single-domain magnetite crystals have been isolated and characterized from tissue located in a sinus within the dermethmoid bone of the skull of the yellowfin tuna, Thunnus albacares. Their chemical composition, narrow size distribution, and distinctive crystal morphology indicate that these crystals are biochemical precipitates. Experiments on the interaction between particles reveal the organization of the particles in situ and suggest a possible form for candidate magnetoreceptor organelles. The consistent localization of such particles with similar arrangement within the dermethmoids of this and other pelagic fishes suggests that the ethmoid region is a possible location for a vertebrate magnetic sense organ.*

Magnetic material has been detected in the tissues of various metazoan species (1-5). Although the material is inferred to be magnetite, in many cases this has not yet been established, and external contaminants have not been excluded as possible sources of magnetic remanence. Even in the homing pigeon and the honey bee, detailed localization of the magnetite has proved difficult to ascertain, and the particles have not been isolated or characterized previously (3, 4). For many of the species studied, behavioral evidence for magnetic sensitivity is lacking or in dispute.

Earlier we reported reproducible conditioned responses to earth-strength magnetic fields in the yellowfin tuna, *Thunnus albacares* (6). We now report the detection, extraction, and characterization of magnetite crystals from tissue within a sinus formed by the dermethmoid bone of the skull of this species. The crystals have a narrow size distribution, are single magnetic domains, and have morphologies similar to other biochemically formed magnetites. Studies of the interactions between particles suggest that the crystals are arranged in groups or chains in the dermethmoid tissue. Magnetite-based magnetoreceptor organelles arranged in vivo in a form consistent with these observations could provide these fish with a sensitive magnetoreception system.

To distinguish magnetic material with a possible magnetoreceptive function from other deposits, we sought to identify a tissue with the following characteristics: (i) it should have a high remanent magnetic moment concentrated in a

small volume of sample compared with other tissues from the same fish; (ii) the anatomical position of the magnetic tissue must be consistent from fish to fish; (iii) the bulk magnetic properties, including particle coercivity, should be similar in different individuals and in different species of fish; and (iv) it should be innervated.

Tissue and organ samples, including bones of the body and the skull, skin, sense organs, viscera, and swimming muscles, were dissected from three 1-year-old yellowfin tuna (fork length, 40 to 50 cm) with glass microtome knives and handled with nonmetallic tools in a magnetically shielded, dust-free clean room. Although subsequent dissections focused on the most magnetic tissue, other samples were measured in all fish. Samples were washed in glass-distilled water, frozen in liquid nitrogen, exposed to strong fields from a cobalt-samarium magnet or an air-core impulse solenoid (7), and tested for isothermal remanent magnetization (IRM) in a superconducting magnetometer. We extracted the magnetic material for other tests by combining the magnetic tissue from several fish, grinding the tissues in a glass tissue grinder, extracting released fats with ether, digesting the remaining cellular material in Millipore filtered 5 percent sodium hypochlorite solution (commercial bleach), and briefly treating the residue with 0.5M EDTA (pH 7.1). After centrifuging and washing, aggregates of black particles could be separated magnetically from the residue; control samples of originally nonmagnetic tissues yielded no such product. The magnetic

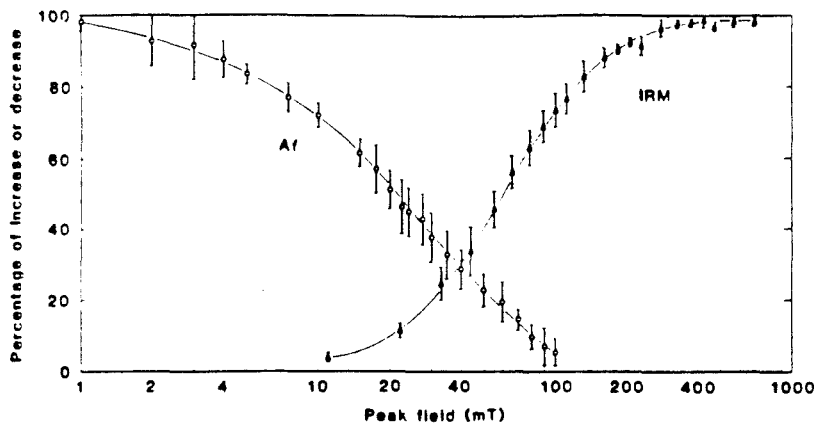


Fig. 1. The one-axis Af demagnetization and IRM acquisition curves for the dermethmoids of four yellowfin tuna. Saturation magnetization ( $1$  to  $3 \times 10^3$  pA·m<sup>2</sup>) is 100 percent and natural remanent magnetization is 0 percent in both plots. Error bars represent standard errors of the means.

powder extracted from the dermethmoid tissue was analyzed by x-ray diffraction, electron microprobe, and transmission electron microscopy (TEM).

Of 17 tissues and organ samples examined for magnetic remanence, 15 had mean moments less than 500 pA·m<sup>2</sup>, and two (eye tissue and dermethmoid bone) had moments greater than 1000 pA·m<sup>2</sup> (8). The intensities of magnetization of these samples identified the frontal and dermethmoid bones as the samples containing the greatest concentrations of magnetic material (8). Subdivision and remeasurement of the dermethmoids from a number of fish suggested that the magnetic material was contained in a sinus formed within the dermethmoid bone. Because the dermethmoid bones acquired greater moments (260 to 3000 pA·m<sup>2</sup>) than the frontal bones (59 to 300 pA·m<sup>2</sup>) and were always clearly magnetic, we focused our remaining studies on the dermethmoid bone and on the tissue it contained in particular.

The frozen dermethmoid tissues of seven yellowfin tuna had natural remanent magnetization moments at or below the instrument noise level ( $< 50$  pA·m<sup>2</sup>). We magnetized these samples (600 to 3000 pA·m<sup>2</sup>) and allowed them to warm to room temperature, measuring their moments at 5-minute intervals. The moments retained by the samples all decayed with time, although not all lost their moments completely within the period of the experiments (1 hour). This observation suggests that, as the tissues thawed, the orientation of the magnetic particles became randomized through thermal agitation.

We washed and refroze the dermethmoids of four fish, subjected them to magnetic fields of progressively increasing strength with the impulse solenoid,

and then demagnetized them with progressively increasing alternating fields (Af). The magnetic moment remaining after each step in these procedures was measured in the magnetometer. The dermethmoids acquired virtually all of their magnetization in fields between 10 and 200 mT and lost it again in alternating fields between 10 and 100 mT (Fig. 1). The absence of the multi-domain magnetite particles detected by Zoeger *et al.* (5) in the Pacific dolphin, *Delphinus delphis*, is indicated by the flatness of the Af demagnetization curve below peak fields of 10 mT. The almost complete saturation of the samples in fields above 200 mT rules out the presence of hematite and metallic iron alloys, which will continue to acquire remanence in fields above 1000 mT.

If the magnetic particles producing the moment were uniformly dispersed throughout the dermethmoid tissue, the IRM acquisition and Af demagnetization curves would be symmetrical about the

50 percent magnetization point. This follows because magnetic moments that are aligned by a given impulse field level should also be moved by an alternating field of the same strength. Interactions between the particles aid Af demagnetization and inhibit IRM acquisition, displacing the curves and causing their intersection to fall below the 50 percent magnetization point (9). However, the abscissa of the intersection point still provides a good estimate of the median coercivity of magnetic particles in the sample (9). The ordinate and the abscissa of the intersection of the Af demagnetization and IRM acquisition curves for the yellowfin tuna dermethmoids were at 30 percent magnetization and 40 mT, respectively (Fig. 1). These data are compatible with the presence of about  $8.5 \times 10^7$  single-domain magnetite particles in the dermethmoid tissue: these particles are approximately 50 nm in length, have axial ratios of about 0.8 (10), and are organized into interacting groups or chains (9, 11).

An x-ray diffraction pattern identified magnetic particles extracted from the dermethmoid tissue as crystalline magnetite (12). Electron microprobe (Cameca MBX) analysis showed that the crystals were pure, containing no measurable titanium, chromium, or manganese (11). In TEM, the isolated crystals were  $45 \pm 5$  nm in length and  $38 \pm 5$  nm in diameter (mean  $\pm$  standard error of the mean) (Fig. 2). These dimensions fall within the single-domain stability field of magnetite (13), and their sizes and axial ratios match the particle coercivities measured in whole tissues. The crystals do not conform to the octahedral crystal morphology or lognormal size-frequency distributions normally shown by geologic or synthetic magnetites (14). Nonoctahedral crystal habits and uniform size distributions are characteristic of chiton and bacterial magnetites (15), which suggests that crystal morphology is a useful means of distinguishing biologic from nonbiologic magnetites (15, 16).

The properties and organization of the magnetite particles in the dermethmoid tissue of the yellowfin tuna meet preconditions for use in magnetoreception and suggest a possible form for magnetite based magnetoreceptors. Their chemical composition, uniform size, and biologically distinctive morphology are evidence of closely controlled biomineralization processes and, consequently, magnetic properties. The crystals will have a coupling energy with the geomagnetic field of about 0.1 kT. They are therefore too small to contribute individually to magnetoreception since their net

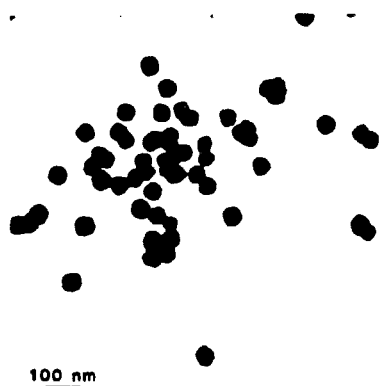


Fig. 2. Isolated magnetite crystals from the yellowfin tuna dermethmoid tissue. Scale bar is 100 nm.

alignment, as given by the Langevin function, will be poor (17). Organization of the particles into chains similar to those in the magnetosomes of magnetotactic bacteria (18) will yield greater coupling energies and is consistent with the interactions between the particles detected in the dermethmoid tissue. The decay with warming of the IRM acquired by the dermethmoid tissue indicates that the particle groups are at least partially free to rotate. Taken together, these results suggest an association of the particles with a mechanoreceptor that detects the position or movement of the groups. Theoretical analyses (19) show that chains of 20 to 60 particles would provide ideal coupling energies with the geomagnetic field for use in magnetoreception. Assuming that the  $8.5 \times 10^7$  particles detected in the dermethmoid tissue are arranged in such a fashion, a magnetite-based magnetoreception system in the yellowfin tuna could resolve magnetic field direction to within a few seconds of arc, or magnetic field intensity differences of 1 to 100 nT (19).

Gross dissection of the dermethmoid region of the yellowfin tuna revealed the supraophthalmic trunk nerve, which carries branches of the trigeminal, facial, and anterior lateral line nerves and which ramifies in the ethmoid region. Histological studies have suggested the presence of nerve axons in the dermethmoid tissue (20). A suitable physical and possible neural basis for previously demonstrated behavioral responses to magnetic fields has thus been demonstrated for the first time in one species. Our magnetometry results are consistent in phylogenetically distant fishes (12) and, along with similar results for other vertebrates (1, 4, 5), suggest that the ethmoid region of the skull is a likely site for a vertebrate magnetic sense organ.

*Note added in proof:* Magnetite crystals isolated from the dermethmoid tissue of chinook salmon, *Oncorhynchus tshawytscha*, are organized in chains when viewed in TEM (21).

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## Chains of single-domain magnetite particles in chinook salmon, *Oncorhynchus tshawytscha*

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**Summary.** Although the presence of magnetite in their tissues is correlated with the ability of different species to detect magnetic fields, proof that the magnetite is involved in magnetoreception has not yet been provided. Using the approach employed to localize and isolate magnetic particles in the yellowfin tuna, we found that single-domain magnetite occurs in chains of particles in tissue contained within the dermethmoid cartilage of adult chinook salmon, *Oncorhynchus tshawytscha*. The particles are present in sufficient numbers to provide the adult fish with a very sensitive magnetoreceptor system. Magnetite in the chinook can be correlated with responses to magnetic fields in a congeneric species, the sockeye salmon. Based on the presence of the chains of particles, we propose behavioral experiments that exploit the responses of sockeye salmon fry to magnetic fields to test explicit predictions of the ferromagnetic magnetoreception hypothesis.

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### Introduction

Discoveries of fine-grained magnetite in the bodies of honeybees and homing pigeons (Gould et al. 1978; Walcott et al. 1979) stimulated theoretical analyses of the suitability of the particles for use in magnetoreception (e.g. Yorke 1979, 1981; Kirschvink 1979; Kirschvink and Gould 1981) and attempts to demonstrate magnetite and magnetosensory abilities in other species. For example, recent studies found conditioned responses to magnetic field stimuli and approximately 100 million interacting particles of pure single-domain magnetite, possibly associated with nervous tissue, in tis-

sue contained within the dermethmoid bone of the skull of the yellowfin tuna, *Thunnus albacares* (Walker 1984; Walker et al. 1984). Magnetic material, at least some of which is fine-grained magnetite, has been found in tissue from the premaxilloethmovomerine block of bones in the skull of the European eel, *Anguilla anguilla* (Hanson et al. 1984a, b), which also responds to magnetic fields (Branover et al. 1971; Tesch 1974). These results from phylogenetically distant species imply that magnetite and magnetosensory abilities are widespread among teleost fishes.

Proof that magnetite mediates magnetoreception, however, will depend on behavioral tests of predictions of the magnetite-based magnetoreception hypothesis. Such tests require identification of species that make appropriate responses to magnetic fields in experimental situations and that also possess magnetite suitable for use in magnetoreception. One possibility is juvenile sockeye salmon, *Oncorhynchus nerka*, which exhibit spontaneous directional preferences in orientation arenas that generally correspond to the axis of the nursery lake to which newly emerged fry migrate (Brannon 1972). In a series of investigations into the behavior of sockeye salmon, Quinn and his colleagues (Quinn 1980; Quinn et al. 1981; Quinn and Brannon 1982) have shown that the directional preferences in orientation arenas of lake-migrating sockeye salmon fry and smolts can be controlled by magnetic fields. Quinn et al. (1981) were able to predict from their behavioral observations that the magnetoreceptor of the salmon must be capable of operating in the dark, in the absence of water flow in both fresh and sea water, and be adaptable to geomagnetic field changes occurring over geologic time. These predictions are compatible with

the hypothesis that the magnetoreceptor of the salmon is based on magnetite. Demonstration of magnetite in salmon, therefore, should open the way for adaptation of currently available procedures for behavioral tests of predictions of the ferromagnetic magnetoreception hypothesis.

Here we report that single-domain magnetite occurs in tissue from the same area of the skull of adult chinook salmon, *Oncorhynchus tshawytscha*, as it has been found in the yellowfin tuna and the European eel. We also have isolated chains of the particles from the tissue where previously we could not, although the particles had been inferred to lie in small clumps or chains from their magnetic properties (Walker et al. 1984). Sufficient numbers of the particles are present to form a very sensitive magnetoreceptor organ. We conclude by proposing behavioral tests of the magnetite-based magnetoreception hypothesis that exploit the responses of sockeye salmon fry to magnetic field polarity in the orientation arenas used by Quinn et al. (1981).

The magnetite-based magnetoreception hypothesis predicts, *inter alia*, that for magnetic particles to be used in magnetoreception they, or groups of them, must (1) be magnetized uniformly and be large enough to align with the geomagnetic field against the randomizing effects of thermal buffeting (Kirschvink 1983; Kirschvink and Walker, in press), and (2) be biochemical precipitates to provide the uniform magnetophysical properties necessary for magnetoreception. Magnetic material that could be used for detecting both magnetic field direction and intensity (see Discussion) therefore should have a high remanent magnetic moment concentrated in a small volume of sample, a consistent anatomical position, and similar bulk magnetic properties within and among species (Walker et al. 1984). Magnetic material has been located most consistently in the heads of vertebrates (Walcott et al. 1979; Mather and Baker 1981; Zoeger et al. 1981; Baker et al. 1983; Beason and Nicholls 1984; Perry et al., in press), and in the front of the skull in particular in fishes. From these results we predict that magnetite should be located in the front of the skull of the salmon.

## Materials and methods

Heads from four adult, net-caught chinook salmon were dissected using glass knives and non-metallic tools in a magnetically-shielded, dust and magnetic particle-free clean laboratory at the California Institute of Technology. The techniques for conducting non-magnetic dissections and avoiding contamination of samples have been described extensively, elsewhere (Kirschvink 1983; Walker et al. in press). Tissue samples were

removed from each head, washed in glass distilled water, and rapidly frozen in liquid nitrogen. Each sample was exposed to a 4 ms duration, unidirectional magnetic pulse with a peak magnetic field of 0.7 Tesla (7,000 Gauss) generated by an impulse magnetizer (Furth and Wanick 1956; Kirschvink 1983) and immediately assayed for Isothermal Remanent Magnetization (IRM, a measure of the total volume of ferromagnetic material present) in the zero field environment of a superconducting magnetometer of the type described by Goree and Fuller (1976). The procedure was repeated for each sample, after which the mass of each sample was measured to the nearest 0.1 g. Tissues sampled in all fish included muscle, eye, brain, cartilage from the skull, and fatty tissue from within the anterior portion of the skull (the dermethmoid region). Other samples not taken in all fish included the olfactory rosette, the olfactory nerve, and gills.

The background signal in the magnetometer fluctuated at or below  $5 \text{ pA}^2$  ( $5 \times 10^{-9}$  emu), while the empty sample holder was kept below the  $50 \text{ pA}^2$  level by regular washing and ultrasonic cleaning. A tissue sample was judged to be magnetic when the signal from the magnetometer, the magnetometer's signal to noise ratio at the time of measurement, and the calculated intensity of magnetization (moment/volume) were high compared with those obtained from other tissues taken from the same fish. Samples that were magnetic in all fish then were subjected to progressive alternating field (Af) demagnetization and IRM acquisition experiments similar to those done to geological samples by Cisowski (1981) and to yellowfin tuna by Walker et al. (1984). In these experiments, samples were frozen to and suspended from a thin, non-magnetic cotton thread as described by Kirschvink (1983). The advantage of this technique is that the measurement sensitivity is limited only by the noise of the vertical field sensor ( $\approx 5 \text{ pA}^2$ ) rather than the sample holder. While frozen, the samples were Af demagnetized completely by placing them in a strong, 400 Hz vertically oscillating magnetic field produced by an air core solenoid which was itself in a zero-field environment. As the alternating field decays linearly from an initial amplitude of 0.1 Tesla to zero over about 15 s, it leaves equal numbers of the still fully magnetized particles with their magnetic moments oriented in opposite directions, leaving the sample with no net magnetic moment. The frozen samples then were exposed to a series of progressively stronger magnetic impulses, and their moments remeasured after each step. After the samples reached saturation (that is, they gained no further remanence with increasing pulse strength), they were sequentially demagnetized and remeasured in a similar fashion using progressively stronger peak oscillating fields.

We extracted the magnetic material for other experiments by grinding the magnetic tissues from several fish in a glass tissue grinder, separating the released fats by dissolving them in ether, and digesting the remaining tissue in nitrocellulose (0.42  $\mu\text{m}$  pore size)-filtered 5% sodium hypochlorite solution (commercial bleach). Aggregates of magnetic particles released by this procedure were treated briefly with EGTA solution (rather than with EDTA as done previously; Walker et al. 1984). After washing, centrifugation, and magnetic separation, the fine powder obtained was identified by X-ray diffraction. Particles then were dispersed magnetically in an alternating magnetic field and mounted on carbon-coated copper mesh grids for transmission electron microscope (TEM) analysis.

## Results

We found inducible remanent magnetization in several of the tissue samples examined (Table 1).

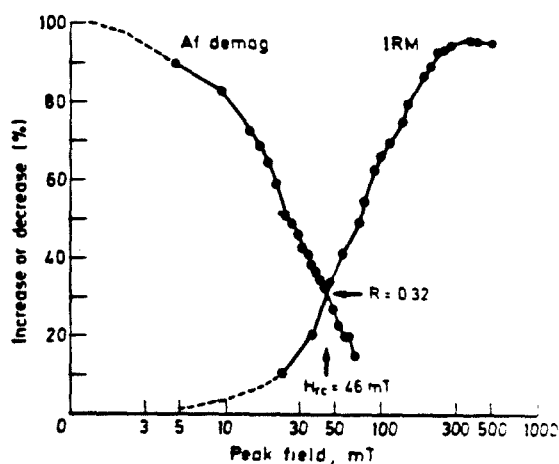


**Table 1.** Magnetic survey of selected tissues in four chinook salmon. For each tissue type examined, the mass is reported in g, the moment in units of  $10^{-12} \text{ A}^2$  ( $10^{-9} \text{ emu}$ ), the intensity in pT, and the S/N quantity gives the signal to noise ratio of the sample holder and instrument at the time of measurement. A 0.6 g sample of the olfactory rosette from fish no 1 also had low values (moment, intensity, and S/N) of 4.0, 6.6, and 0.8 respectively

	Muscle				Eye				Brain				Dermethmoid			
	Mass (g)	Moment $10^{-12} \text{ A}^2$	Int. pT	S/N	Mass (g)	Moment $10^{-12} \text{ A}^2$	Int. pT	S/N	Mass (g)	Moment $10^{-12} \text{ A}^2$	Int. pT	S/N	Mass (g)	Moment $10^{-12} \text{ A}^2$	Int. pT	S/N
Fish # 1	1.3	50	3.9	0.7	9.0	163	1.8	3.3	1.4	52	3.7	1.1	0.5	895	178.0	11.9
Fish # 2	1.8	140	7.8	2.8	6.3	3,300	52.4	97	1.3	51	3.9	0.8	1.0	517	51.7	14.6
Fish # 3	2.1	730	34.7	40.7	6.9	270	3.9	20.9	1.9	25	1.4	2.5	0.3	320	106.7	24.8
Fish # 4	2.0	140	7.0	10.9	5.0	551	11.0	42.7	1.3	776	59.7	60.2	1.2	300	25.0	10.1

Measures of magnetization were sufficiently low for most muscle and brain samples to permit the conclusion that these tissues were non-magnetic in these fish and could serve as control samples. Although the eye was sufficiently magnetic in at least two fish to invite more detailed study, two features of the data suggested it was unlikely to be the site of magnetoreception. First, the magnetic moment acquired by the eye was more variable from individual to individual than were the muscle and brain samples and, because the eye is in contact with the environment, the possibility that magnetic contaminants contributed to the moments acquired by the eyes examined can not be excluded. Second, the eye was the most massive sample measured in all fish. Eyes for three of the animals examined had intensities of magnetization, a measure of the concentration of magnetic particles in a sample, in the same range as the muscle and brain samples from the same fish. In contrast, moments acquired by the dermethmoid tissues were far less variable among fish and the intensities of magnetization were consistently higher for these samples than for muscle and brain samples from the same individuals. These results are consistent with the prediction that magnetic particles involved in magnetoreception should be concentrated in a small volume of tissue in a consistent anatomical position and led us to focus more detailed studies on the dermethmoid tissue.

Upon warming to room temperature, the dermethmoid tissues lost much of their remanent magnetization, indicating that the magnetic particles were at least partly free to rotate under the influence of thermal agitation in the low field environment of the magnetometer enclosure. When the dermethmoid tissue samples were subjected to the progressive IRM acquisition and Af demagnetization procedure described above, they acquired virtually all their remanence in fields less than 200 mTesla (mT), and lost it again in alternating



**Fig. 1.** Progressive acquisition and Af demagnetization of IRM for dermethmoid tissues from four chinook salmon. The intersection point of the two curves yields an estimate of the remanent coercive field ( $H_{rc}$ ) of 46 mT, as well as the R value of interaction described in the text. These data are consistent with an assemblage of moderately interacting single-domain magnetite crystals

fields of less than 100 mT (Fig. 1). Acquisition and loss of remanence over this range of fields is consistent with the presence in the dermethmoid tissue of large numbers of single-domain crystals of magnetite. The flattening of the IRM acquisition curve at fields above 200 mT rules out most of the common ferromagnetic contaminants such as hematite ( $\alpha \text{ Fe}_2\text{O}_3$ ) or metallic iron alloys, which continue to acquire remanence in much higher fields, and also multi-domain magnetite particles, which acquire and lose remanence at much lower fields than observed here (Zoeger et al. 1981; Kirschvink 1983; Walker et al. in press).

As shown by Cisowski (1981) and Walker et al. (1984) for the magnetite particles in chiton teeth and the dermethmoid tissue of the yellowfin tuna respectively, the intersection of the Af demagneti-

zation and IRM acquisition curves falls below the 50% magnetization point. For samples with completely non-interacting single-domain particles these curves should be symmetrical about the 50% magnetization point because particle moments will be aligned or randomized equally easily by unidirectional or alternating fields of equal intensities. The interactions between the fields produced by the particles themselves increase and decrease the fields necessary to align and randomize the particle moments respectively (Dunlop and West 1969), causing the IRM acquisition and Af demagnetization curves to shift apart and their intersection to fall below the 50% magnetization point. These data therefore imply that the magnetic particles in the dermethmoid tissue of the salmon are close enough to some of their neighbors to interact with each other (e.g. within one grain diameter).

Limited constraints on the average size and shape of the particles are provided by the abscissa of the intersection point of the IRM acquisition and Af demagnetization curves. This value approximates the remanent coercive field ( $H_{rc}$ ) for the particles (Cisowski 1981) and is about 46 mT for the salmon. From Fig. 2, which combines the single-domain stability field boundaries of Butler and Banerjee (1975) with the contours of equal coercivity given by McElhinny (1973), a tentative length range of 40–100 nm can be established for the particles. Depending on the distribution of particle sizes, somewhere between 1 and 100 million such crystals would be necessary to produce the magnetic remanence observed in the salmon dermethmoid tissue. These numbers compare favorably with those reported for honeybees (Gould et al. 1978), homing pigeons (Walcott et al. 1979) and yellowfin tuna (Walker et al. 1984) and, if organized into interacting groups of several particles, would be more than enough to provide the salmon with a magneto-sensory system capable of responding to both magnetic field direction and intensity (Yorke 1979, 1981; Kirschvink 1979, 1981; Kirschvink and Gould 1981).

An X-ray diffraction pattern uniquely identified magnetic particles extracted from the dermethmoid tissue as crystalline magnetite. When viewed in TEM the particles were not completely dispersed but were arranged in linear chains of particles having similar dimensions to those found in the yellowfin tuna (Fig. 3). The particles appear to be bound in some form of organic matrix, which yields an occasional electron-transparent gap between adjacent crystals. The matrix apparently prevents the particles from contacting each other as a result of magnetic attractions but preserves

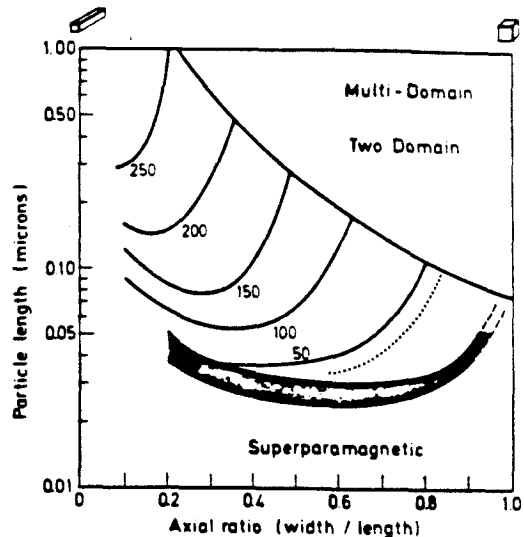


Fig. 2. Approximate contours of equal microscopic coercive force in mT (from McElhinny 1973) superimposed on the size and shape boundaries for single-domain magnetite of Butler and Banerjee (1975). Magnetite particles which spontaneously display single-domain behavior are those which have lengths and widths which plot in the central area of the diagram, between the areas labelled superparamagnetic and multi-domain. Kirschvink (1983) provides a further description of this figure. Single-domain crystals with remanent coercive fields of 46 mT, as measured here for the salmon (Fig. 1), should lie approximately in the region indicated by the dotted line. These inferred crystal sizes and shapes agree well with biogenic magnetite crystals reported from bacteria by Blakemore (1975) and Towe and Moench (1980) and from yellowfin tuna by Walker et al. (1984).

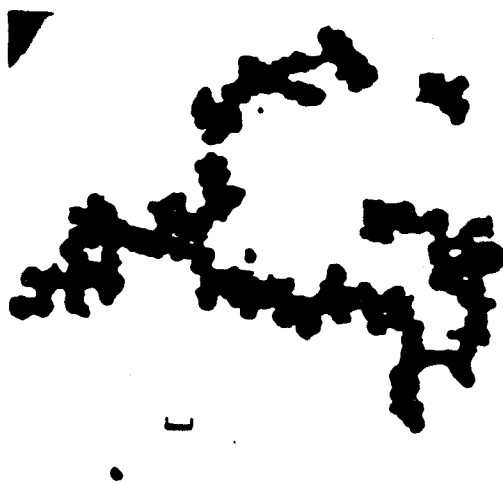


Fig. 3. Chains of magnetite particles isolated from the chinook salmon dermethmoid tissue. Scale bar 100 nm

their linear arrangement. However, folding of the chains, possibly occurring after extraction, is evident.

## Discussion

The experiments reported here clearly show that adult chinook salmon possess large numbers of single-domain magnetite particles suitable for use in magnetoreception. Their narrow coercivity distribution, which indicates a restricted size range, and their presence in linear chains imply that the magnetite particles detected in the dermethmoid tissue of the salmon are produced as biochemical precipitates. As in the yellowfin tuna (Walker et al. 1984), the magnetite particles are too small to be used individually in magnetoreception as their magnetic to thermal energy ratio in the earth's magnetic field is only about 0.5. The inter-particle interaction effects detected in both the tuna and the salmon indicate that the particles are organized into arrays that could attain easily the size required for magnetoreception. Because the magnetite particles extracted from the salmon were dispersed before mounting using the same alternating magnetic field that produced isolated particles in samples taken from the yellowfin tuna, it is unlikely that the chains of particles observed in TEM in this study arose as an artifact. The hypothesis that magnetite particles in the dermethmoid tissues of the salmon and the tuna are organized in chains like those in the magnetosomes of bacteria (Balkwill et al. 1980) therefore seems reasonable. Mechanoreceptors such as hair cells could have the dimensions and sensitivity (e.g. Hudspeth 1983) to monitor the movements of the particle groups accurately.

Final demonstrations that the magnetite particles are organized as we infer can only be achieved by their identification *in situ*. It will be difficult to locate any such structures with normal transmission electron microscopy, however, as our magnetometry study constrains their volume fraction to be less than 5 parts per billion in the dermethmoid tissue. Each particle chain is likely to be no more than a few micrometers in length and a few hundredths of a micrometer wide. There is only a small probability of locating such a structure in a normal 0.1 micrometer thick TEM section.

It is interesting to note that many studies of other vertebrates have converged on regions of the skull close to the ethmoid bones as the likely site of a vertebrate magnetoreceptor organ (Walcott et al. 1979; Mather and Baker 1981; Zoeger et al. 1981; Baker et al. 1983; Beason and Nicholls 1984;

Hanson et al. 1984a, b; Perry et al., *in press*). As in many of these other studies (e.g. Quinn et al. 1981; Presti and Pettigrew 1980; Baker et al. 1983), we also detected magnetic material that was not always in the same place in all individuals sampled. Some of this material, particularly that associated with tissues such as the gills and gut of the salmon, was clearly contamination that could be removed by thorough cleaning, but other magnetic samples could well have contained true biochemical precipitates. If so, the functions of these deposits remain unknown. A magnetoreceptive role seems unlikely, however, since they usually are not reproducible in all individuals (Walker et al. 1984, this study), often are detected from their natural remanent magnetization (e.g. Zoeger et al. 1981), or are magnetically unsuited to magnetoreception (Presti and Pettigrew 1980; Zoeger et al. 1981; Vilches-Troya et al. 1984).

Our results using adult chinook salmon are at variance with those of Quinn et al. (1981) who failed to find magnetic material anywhere except contaminants within the gastrointestinal tract of sockeye salmon fry. The most likely explanation for this discrepancy is that Quinn et al. (1981) carried out their studies on samples at room temperature (T.P. Quinn, personal communication). We have found in both the chinook salmon and the yellowfin tuna (Walker et al. 1984) that the dermethmoid tissue loses remanence on warming from liquid nitrogen to room temperature. Such loss of remanence is understandable based on the assumption that the magnetite particles must be at least partly free to rotate if they are to be used in magnetoreception (Yorke 1979, 1981; Kirschvink and Gould 1981). Thus magnetite suitable for use in magnetoreception can be detected consistently only by using frozen samples. The presence of IRM or natural remanent magnetization in samples at room temperature suggests the presence of magnetic material serving other functions or arising from external sources.

A second possible explanation is that magnetic material is present in salmon fry in quantities sufficient to mediate the observed responses of fry to magnetic field direction but too small to be detected by currently available superconducting magnetometers. Animals respond either to magnetic field direction (the compass response; Wiltchko 1972; Lindauer and Martin 1972; Walcott and Green 1974) or to some feature related to intensity (the inferred map response; Walcott 1980; Gould 1982). Yorke (1979) and Kirschvink and Gould (1981) found that only a few hundred single-domain crystals would be necessary to determine ac-

curately the direction of the geomagnetic field; the small IRM produced by this number could not be detected with present superconducting magnetometers. In contrast, detection of magnetic field intensity during movements requiring the ability to determine both position and direction, as seems to occur in homing pigeons (Walcott 1980; Gould 1982), requires millions of magnetite-based magnetoreceptors. It is possible that magnetite is present in sockeye salmon fry in quantities sufficient to provide them with the ability to determine magnetic field direction but not sufficient to be detected by a superconducting magnetometer. The movements of adult salmon from the ocean to the outlet of their natal stream could require sensitivity to magnetic field intensity, and so require millions of magnetite particles. We suggest the hypothesis that magnetite is produced continuously throughout the life of the organism and so could be detected more easily in adult than in juvenile fish. A controlled magnetometric study of an ontogenetic series to distinguish among these alternative explanations of the different results for sockeye and chinook salmon is presently in progress.

Thus the presence of magnetite can be correlated with magnetic sensitivity in representatives of three orders of fishes: the European eel and yellowfin tuna, which are known to respond to magnetic fields, and a congener of a third magnetically sensitive fish, the sockeye salmon. The critical tests of the magnetite-based magnetoreception hypothesis, however, will be of behavioral constraints on magnetoreception caused by the properties of the magnetite particles themselves. The behavioral assay developed by Quinn et al. (1981) could be used to test the prediction that accuracy of compass orientation should be poor in very weak fields ( $<10 \mu\text{T}$  or 0.1 Gauss), should increase rapidly in fields up to earth-strength, and asymptotically in fields up to a few times earth-strength. This result holds for magnetotactic algae and bacteria (Kalmijn 1981; Lins de Barros et al. 1981) and also for honeybees (Kirschvink 1981). The response of sockeye salmon fry to magnetic field polarity also can be used in a powerful test of ferromagnetic effects on their magnetic orientation. A short magnetic impulse strong enough to reverse the moments of any magnetite particles present will cause the fry to exhibit reversed magnetic field directional preferences in orientation arenas only if the magnetite particles form the basis for their magnetoreceptor system. Thus the opportunity exists to link magnetite suitable for magnetoreception to the behavior of animals that are known to respond to magnetic fields.

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## Magnetic Stratigraphy and a Test for Block Rotation of Sedimentary Rocks within the San Andreas Fault Zone, Mecca Hills, Southeastern California

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A 500-m section of the Palm Spring Formation in the southern Mecca Hills, located within the San Andreas fault zone in southeastern California, has been paleomagnetically sampled to determine possible tectonic rotation in this area and to establish time-stratigraphic control. This work was partly stimulated by the fact that 80 km farther south, previous studies demonstrated 35° of postdepositional rotation in the Palm Spring Formation of the Vallecito-Fish Creek basin east of the Elsinore fault. Several lines of evidence suggest that hematite is the main magnetic carrier of the Mecca Hills samples. Large anhedral hematite grains observed in magnetic extracts and a positive fold test imply a detrital origin of the remanence. The polarity reversal patterns, together with earlier vertebrate paleontologic studies, restrict the time span for deposition of this unit to the middle-late Matuyama chron (2.0–0.75 myr ago), thus of uppermost Pliocene and early Pleistocene age. Characteristic directions of best least-squares fit for 73 samples suggest little or no overall rotation, despite the severe late Quaternary tectonic activity demonstrated by the intense deformation of these strata. © 1987 University of Washington

### INTRODUCTION

The Palm Spring Formation is a widespread Plio–Pleistocene terrestrial deposit exposed at a number of localities in the Salton trough of southeastern California (Fig. 1). In its type area in the Vallecito-Fish Creek basin of the western Imperial Valley, studies of the magnetic stratigraphy and paleontology of the Palm Spring Formation have shown that the unit here spans the middle-Gilbert to late-Matuyama chron (i.e., about 4 to 1 myr ago; Opdyke *et al.*, 1977; Downs and White, 1968; Cunningham, 1984). Recently, Johnson *et al.* (1983) have remeasured all of the samples earlier studied by Opdyke *et al.* (1977). After heating them through the 500°C thermal demagnetization step, they calculated mean polarity vectors for both normal and reversely magnetized paleomagnetic sites. Their improved data set implies a 35° clockwise rotation of the entire basin, which they interpret as a postdepositional phenomenon related to the presence of the

nearby right-lateral Elsinore fault, an active member of the San Andreas fault system. In a somewhat similar study, Seeber and Bogen (1985) have recently claimed 20° to 30° clockwise rotation of 1-myr and younger sediments in blocks close to the San Jacinto fault, 45 km west of the Mecca Hills.

These intriguing results have led us to apply the same type of analysis to the Palm Spring Formation exposed in the Mecca Hills, 80 km north of the Vallecito-Fish Creek basin, and close to the San Andreas fault (Fig. 1). There are, however, two important differences between the two areas: (1) The exposed section of the Palm Spring Formation in this northern area is thinner than that of the same unit in the western Imperial Valley (about 1500 m vs 4000 m, respectively), and it appears to have a different provenance. (2) The Mecca Hills area is localized within the San Andreas fault zone itself, with active branches slicing through the area, and with intense Quaternary folding throughout, whereas

the Vallecito-Fish Creek area is located in a larger and more unbroken block with throughgoing active members of the San Andreas system some distance to the east and west (Fig. 1). The extent of the Vallecito-Fish Creek sampling profile, which is thought to have rotated as a unit, is some 10 km (Opdyke *et al.*, 1977). Thus, it is not clear in which area one might expect the greater rotation—within a very active fault zone itself, or in a relatively stable and larger block sandwiched between two major throughgoing active faults.

### GEOLOGIC SETTING

The Palm Spring Formation, first named and studied by Woodring (1931), is a thick series of terrestrial arkosic conglomerate, sandstones, siltstones, and claystones that crop out over an area of more than 130 km length along both flanks of the Salton trough (Dibblee, 1954). In the Vallecito-Fish Creek basin, the Palm Spring Formation grades downward into the marine Imperial Formation, thought there to be of Pliocene age, and similar relations exist in the Indio Hills north of the Salton Sea (Proctor, 1968). In the Mecca Hills, however, no Imperial Formation is known, and correlation of the Palm Spring units here with those of the other areas has been based mainly on stratigraphic similarities, sparse fossils, and relationships to adjacent units (Dibblee, 1954). Underlying the Palm Spring Formation in parts of the Mecca Hills, with marked angular unconformity, is the terrestrial Mecca Formation, of probable Pliocene age, and it is near this contact that our paleomagnetic sampling commenced (A, Fig. 2).

In the Hidden Spring area of the Mecca Hills, the Palm Spring Formation comprises a number of individual members with very complex interfingering relationships. In the specific area of Figure 2, which is centered about 2 km southwest of Hidden Spring itself, only three of these members (informally named) are exposed: (1) a basal conglomerate of the Sheephole member, which is a discontinuous reddish-

brown boulder conglomerate with markedly varying thicknesses reflecting the relief of the post-Mecca erosional surface, (2) the Sheephole member itself, which comprises about 340 m of predominantly light-brown arkosic conglomerates and sandstones, and (3) the Box Canyon member, more than 130 m thick, made up mainly of white to varicolored arkosic sandstones and siltstones which are transitional with the underlying beds of the Sheephole member. Stratigraphic and structural relationships within the Palm Spring Formation are so complex that it is difficult to say where the oldest strata of the formation may be exposed, but we have no reason to think that the base of the section sampled in our paleomagnetic study (A, Fig. 2) is not roughly comparable in age to the bases of other Palm Spring sections in the southern Mecca Hills area. Near Hidden Spring, 2 km northeast, basal Palm Spring strata lie directly on crystalline rocks (Dibblee, 1954; Crowell, 1975).

Upward in the section, we have sampled only as far as we are reasonably confident of stratigraphic continuity, but clearly more rocks of the Palm Spring Formation lie stratigraphically above our uppermost sample locality. We estimate, however, that our 500-m-thick section represents the bulk of the local Palm Spring section. It should be noted that Dibblee (1954) reported 1500 m of Palm Spring rocks elsewhere in the Mecca Hills, and some 750 m of strata are well exposed along the road in Painted Canyon, 9 km northwest of our sample area (Sylvester and Smith, 1976). Babcock (1974) reported 765 m of Palm Spring equivalent strata in the Durmid area 19 km to the southeast, there overlain with angular unconformity by the Pleistocene Borrego Formation. Hays' (1957) cross sections suggest that it is primarily the uppermost units of the Palm Spring section that are missing or greatly thinned in the Hidden Spring area.

The two principal neotectonic features of the Hidden Spring area are the San Andreas fault, whose most active trace lies

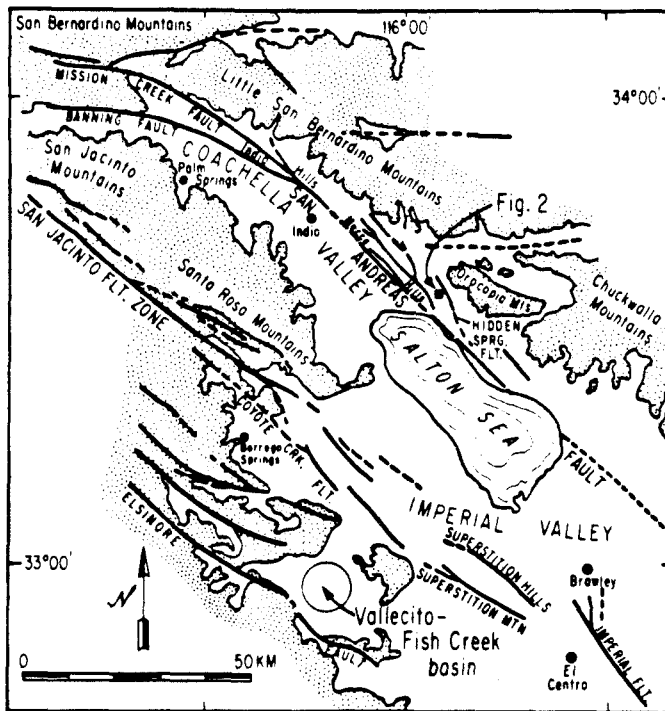


FIG. 1. Map showing the location of the field area of this study (Fig. 2) and that of Opdyke *et al.* (1977) and Johnson *et al.* (1983) in the Vallecito-Fish Creek basin. Areas underlain by crystalline rocks are stippled.

some 5 km to the southwest of the sampling profile, and the subparallel Hidden Spring fault, 3 km to the northeast (Crowell, 1975; Babcock, 1974). The activity of the San Andreas fault is, of course, well known, and recent field studies by the authors near Hidden Spring indicate about 1 km of post-Palm Spring right slip on the Hidden Spring fault. Although the Hidden Spring fault does not appear to be a major, through-going member of the system at this time, the entire area between the San Andreas and Hidden Spring faults could be considered to be within the San Andreas fault zone, and the spectacular evidence of intense Quaternary deformation over a wide zone tends to support this view (e.g., Sylvester and Smith, 1976; Babcock, 1974).

#### SAMPLING AND ANALYSIS

Palm Spring strata in the Hidden Spring area are so highly folded and faulted that it is difficult to identify an appropriate sec-

tion for paleomagnetic sampling, but line A-B (Fig. 2) appears to traverse an unbroken homoclinal sequence. At the base of the section, the 26-m-thick basal conglomerate of the Sheephole member lies with 80° dip on still more highly deformed beds of the Mecca Formation, here exposed in a narrow window through the unconformity, along a very sharp anticlinal axis. (Most faults and folds in the Mecca strata are truncated by the unconformity, but this particular fold was reactivated following Palm Spring deposition.) Upward in the Palm Spring section, dips gradually decrease and then rapidly become less than 10° at the very northern end of the traverse (B, Fig. 2). In order to test the magnetic polarity of rocks still higher in the Palm Spring section, an additional 37 m of section, herein termed section D, was sampled at a locality across Box Canyon wash to the north, 1.3 km N 35° W from Sheephole Oasis (Fig. 2). Although this additional sec-



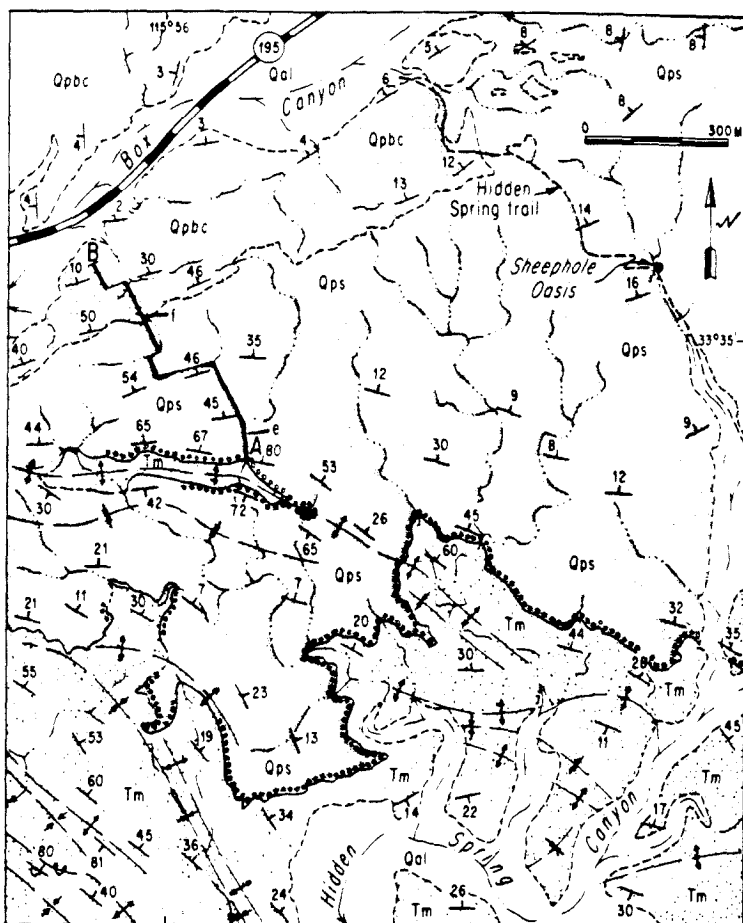


FIG. 2. Geologic map showing the location of the paleomagnetic sampling traverse A-B. Locality C, off the map, is 1.2 km S 74° E from Sheephole Oasis, and Section D, also off the map, is 1.3 km N 35° W from Sheephole Oasis. Tm, Mecca Formation; Qps, Sheephole member of Palm Spring Formation; Qpbc, Box Canyon member of Palm Spring Formation; Qal, Quaternary alluvium. Small circles above Tm-Qps contact (an angular unconformity) indicate locations of the distinctive basal conglomerate of the Sheephole member. See the text for discussion of stratigraphic units and their ages. Geologic mapping is by the authors, with additions by J. A. Nourse in the extreme southwest corner.

tion is shown in the stratigraphic column of Figure 5, it is obviously not part of a continuous measured section, and its stratigraphic correlation with section A-B of Figure 2 is only approximately constrained.

We used the impact coring technique for soft sediments described by Weldon (1985), in which a nonmagnetic stainless tube is gently pounded into the exposure. The *in situ* orientation of the tube was then measured by conventional means, and an orientation mark put on the end of the sample.

The sample was extruded into a quartz glass holder by a plastic bar and sealed with Parafilm. In this manner, we collected 46 oriented samples for paleomagnetic analysis from profile A-B (Fig. 2) and 9 additional samples from locality D north of Box Canyon wash. For comparing possible rotational effects as a function of distance from the San Andreas fault, we also collected 18 samples (including 5 for a fold test), but not in stratigraphic order, from basal Palm Spring strata at locality C at the

entrance to Hidden Spring gorge (not within Fig. 2, but 1.2 km S 74° E from Sheephole Oasis, shown on Fig. 2).

Ten pilot samples were progressively demagnetized at 100°, 200°, 300°, 400°, low alternating fields (75 mT), 500°, 535°, 565°, 580°, and 630°C steps and measured using a SQUID magnetometer. Typical progressive demagnetization plots (Fig. 3) generally reveal a simple characteristic component in these samples after removal of a relatively soft recent overprint. For some samples, a minor direction change occurred after the 300°C demagnetization step, whereafter the magnetic moment remained stable. All of the other samples were demagnetized at low alternating fields (75 mT), 200°, 300°, 400°, and 500°C steps. Principal component analysis (Kirschvink, 1980) was used to find the directions of best least-squares fit to the demagnetization data for each sample.

#### MAGNETIC MINERALOGY AND ORIGIN OF REMANENCE

Figure 4 shows the results from a typical impulse isothermal remanent magnetization (IRM) acquisition vs alternating fields

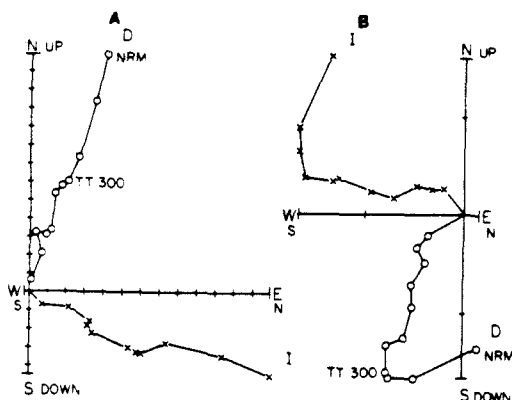


FIG. 3. Typical orthogonal projections of the progressive demagnetization data for two pilot samples: (A) MH 3 and (B) MH 4. Notice the slight direction change after the 300°C demagnetization step for MH 4. Otherwise, magnetic components are quite stable in both samples. One division =  $10^{-6}$  Am<sup>2</sup>.

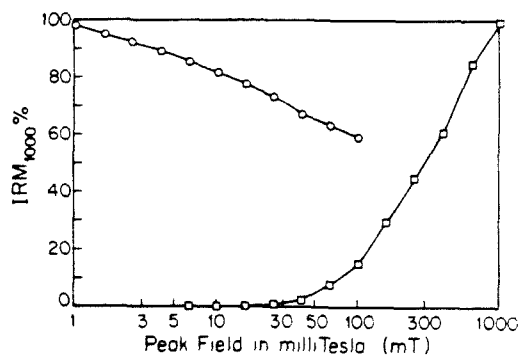


FIG. 4. Isothermal remanent magnetization acquisition vs alternating fields demagnetization curves for sample MH 1. IRM<sub>1000</sub> is the isothermal remanent magnetization acquired at 1000 mT peak field; for this sample, the value is  $7.4 \times 10^{-6}$  Am<sup>2</sup>/g.

(AF) demagnetization experiment (Cisowski, 1981; Kirschvink, 1982) on one of these samples from the Sheephole member of the Palm Spring Formation. The major IRM increase takes place between the 100- and 1000-mT steps and does not reach saturation. The moment gained after the 1000-mT step has a similarly high coercivity. Both features suggest that the main remanence carrier in the sample might be either hematite or goethite (Lowrie and Heller, 1982). From Curie temperature analyses on the magnetic extracts, and the IRM acquisition experiments on bulk samples, Opdyke *et al.* (1977) concluded that the major remanence carrier in their samples was either magnetic or maghemite. However, several lines of evidence suggest that the principal remanence carrier in our samples is hematite, rather than magnetite, maghemite, or goethite. First, the magnetic moment measured in most of the pilot samples is still at or above 25% of the nonmagnetite remanent magnetization (NRM) level after the 580°C demagnetization step, which should destroy all portions of the magnetic remanence carried by magnetite, maghemite, or goethite. Second, we identified very little magnetite in a magnetic extract obtained from these samples by X-ray analysis, and a dithionite-citrate dissolution experiment, which removes virtually all

nonmagnetite magnetic phases (Chang and Kirschvink, 1985), destroyed almost all phases present. Finally, we observed detrital grains of specular hematite in the magnetic extract using petrographic microscope.

In addition to the magnetic mineralogy, the question also needs to be answered as to whether the main magnetic remanence is of primary or secondary origin. Postdepositional oxidation of iron oxides will often produce a chemical remanent magnetization (CRM), and Ozdemir and Banerjee (1981) have shown that magnetic viscosity is similarly correlated with the degree of oxidation. Because hematite is a common oxidation product in sediments, the remanence carried by hematite grains could therefore be of secondary origin. However, Steiner (1983) has argued strongly, based on petrologic and magnetic evidence, that the remanence carried by hematite in red sandstones of the Morrison Formation on the Colorado Plateau is a primary detrital remanent magnetization (DRM). Two observations from our samples from the Palm Spring Formation lead us to conclude that we, too, are dealing with a hematite-carried DRM. First, petrologic examination of the bulk samples reveals large amounts of anhedral hematite grains of probable detrital origin, with only a trace of fine-grained hematite pigments detected. Second, the characteristic components of magnetization pass the fold test at the 95% confidence level ( $(k_1/k_2) = 4.24$  with five samples; Table 1B).

### STRATIGRAPHIC CORRELATION

Figure 5 shows the declinations of samples from section A-B (and the additional 37 m of higher section across Box Canyon to the north, Section D) after correction for the tilt of the bedding, and these are plotted together with the stratigraphic column and the magnetic polarity interpretation. This section is dominated by an interval of reversed polarity and two normal intervals, one near the bottom of the sec-

tion ("e" in Fig. 2) and another near the middle ("f" in Fig. 2). Interpretation of exactly how these events fit into the polarity time scale requires further discussion.

Hays (1957) reported two occurrences in this part of the Mecca Hills of tooth fragments of the horse genus *Equus* in the Mecca Formation (his "Painted Canyon Formation"), unconformably underlying the Palm Spring formation. The earliest appearance of *Equus* in North America has been judged by Lindsay *et al.* (1984) to be at 3.7 myr (the uppermost Gilbert magnetic chron), based on the magnetic stratigraphy of selected Neogene vertebrate fossil sites. Accordingly, the base of the Palm Spring Formation in the Mecca Hills cannot be older than 3.7 myr (mid-Pliocene). Only one reversed chron, the Matuyama, is younger than the Gilbert chron and is compatible with the dominantly reversed polarity period recorded in the Palm Spring section in the Mecca Hills. Thus the two relatively short normal-polarity events recorded in section A-B must correspond to

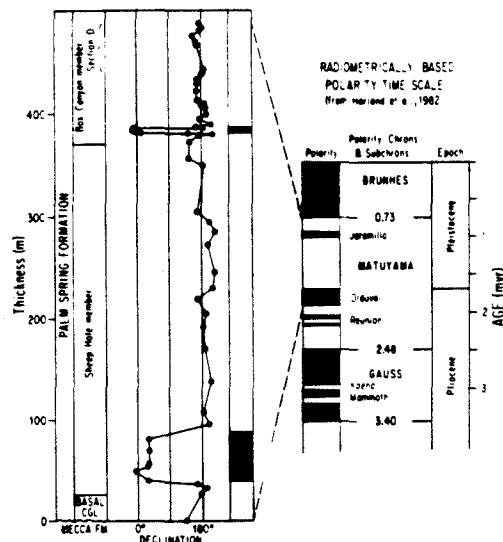


FIG. 5. Magnetic polarity stratigraphy of the Palm Spring Formation in Mecca Hills. The magnetic polarity time scale from Harland *et al.* (1982), with the Pliocene-Pleistocene boundary replaced at right above the Olduvai Normal Subchron following the recent proposal of the ICS (International Commission on Stratigraphy) Quaternary Subcommission (Aquirre & Pasini, 1985), is attached for comparison.

TABLE 1. CHARACTERISTIC COMPONENT MEAN DIRECTIONS OF (A) SAMPLES COLLECTED FROM SECTION A-B, LOCALITY C, AND SECTION D, AND (B) SAMPLES COLLECTED FROM LOCALITY C FOR THE FOLD TEST

(A) Sample description	Number of samples	Tilt corrected					
		Declination	Inclination	Kappa	Alpha-95	DM	DP
Normal samples from the bottom of section A-B	6	27.74	17.58	14.48	18.21	18.87	9.78
Normal samples from the middle of section A-B	4	355.87	20.11	53.51	12.68	13.28	6.95
Reversed samples from section A-B	36	187.19	-44.84	12.40	7.07	8.93	5.64
Reversed samples from section D	9	174.24	-39.28	26.09	10.27	12.28	7.34
Samples from sections A-B and D	55	6.68	39.5	11.35	5.96	7.14	4.28
Normal samples from locality C	8	5.99	35.48	14.44	15.08	17.45	10.09
Reversed samples from locality C	10	172.41	-33.01	13.69	13.54	15.36	8.71
Samples from locality C	18	358.36	34.3	13.87	9.63	11.03	6.32
Normal samples from three sites	18	11.20	26.59	12.05	10.39	11.27	6.11
Reversed samples from three sites	55	181.87	-41.94	13.01	5.53	6.78	4.16
Samples from three sites	73	4.49	38.26	11.76	5.05	5.99	3.55

(B) Number of samples	<i>In situ</i>				Tilt corrected			
	D	I	Kappa ( $k_1$ )	Alpha-95	D	I	Kappa ( $k_2$ )	Alpha-95
5	227.72	-54.62	3.9	44.58	174.29	-34.42	16.52	19.39

Note. Kappa is the best estimate of the precision parameter and alpha-95 is the semiangle of the cone of 95% confidence (Fisher, 1953). The errors DM and DP are the semiaxes of the elliptical error around the pole at a probability of 95%. DP in the colatitude direction and DM perpendicular to it (McElhinny, 1973).

the Olduvai and Jaramillo subchrons. The Reunion events are of such short duration that they are not likely to be found in this section (Hammond *et al.*, 1979).

The fact that the uppermost sample in our section is of reversed polarity indicates that we have not yet reached the Matuyama-Bruhnes boundary, and that the Bishop Tuff, of 0.73-myr age (Mankinen and Dalrymple, 1979), must occur still higher in the section. No tuff has been identified locally in the Palm Spring section, although the clastic nature of the deposits might well make such preservation unlikely. The Bishop Tuff has been identified, however, 25 km southeast (Sarna-Wojcicki *et al.*, 1984) in the lacustrine Bor-

rego Formation, which there overlies the Palm Spring Formation with angular unconformity (Babcock, 1974). In the northernmost Mecca Hills, Merriam and Bischoff (1975) identified the Bishop Tuff in lacustrine beds that had been mapped Ware (1958) as questionably part of the Brawley Formation, which he considered to overlie middle Palm Spring strata unconformably in this area. Thus it appears that the bulk of the Palm Spring Formation in the Mecca Hills, and perhaps all of it, lies stratigraphically below the Bishop Tuff and is older than 0.73 myr; it is therefore of Pleistocene and very uppermost Pliocene age. This suggests that the Palm Spring Formation in the southern Mecca Hills correlates with

only the uppermost part of the much thicker Palm Spring section in the Vallecito-Fish Creek area, where the Pliocene-Pleistocene boundary lies in the "upper part" of the section (Cunningham, 1984). Furthermore, if our uppermost sample is indeed near the Matuyama-Bruhnes boundary, the uppermost part of the Mecca Hills section of the Palm Spring Formation is younger than that in the Vallecito-Fish Creek area.

An average sedimentation rate of 0.4 mm/yr can also be calculated on the basis of the suggested magnetic-polarity correlation. This is consistent with that for the upper part of the Vallecito-Fish Creek section reported by Johnson *et al.* (1983).

#### SEDIMENTATION HISTORY

Merriam and Bandy (1965) and Muffler and Doe (1968) have shown that many of the late-Cenozoic fine-grain clastic deposits of the Salton trough, including parts of the Palm Spring Formation, were derived as sediment from the Colorado River drainage. However, several lines of evidence suggest that the source of the Palm Spring Formation in the southern Mecca Hills is more local, as was first suggested by Sylvester and Smith (1976). First, mineral composition of the Palm Spring sediments here is very different from that of the Palm Spring strata in the western Imperial Valley, where Muffler and Doe (1968) argued that the mineral composition supported a Colorado River derivation. Second, sedimentary structures indicate that the main flow directions for the Palm Spring rocks in the southern Mecca Hills were from the north and east (R. Ripperdan, personal communication, 1986), not from the south and west. And finally, interlayered conglomerates and coarse sandstones in the southern Mecca Hills contain abundant anorthosite and Orocopia schist fragments that are clearly of very local origin. Recent studies by Cunningham

(1984) in the Vallecito-Fish Creek area indicate that, although the lower Palm Spring units there were indeed derived from the Colorado River drainage, upper units near the Plio-Pleistocene boundary were locally derived from the adjacent Peninsular Ranges. It therefore seems that by the time of deposition of the Palm Spring Formation in the Mecca Hills, the eastern and western Palm Spring sites had very different sediment sources. Thus, the two units may be correlative in time only, and then only in small part, and perhaps they should eventually be assigned different stratigraphic names.

#### TECTONIC ROTATION?

Figure 6A is an equal-area plot for the tilt-corrected least-squares data of all 73 samples collected, from section A-B, locality C, and section D. The mean stratigraphic inclination shows the typical shallowing effect for DRM (Versoub, 1977). The mean stratigraphic declination for all sites is  $4.5^\circ \pm 5.1^\circ$  at the 95% confidence level; thus the average rotation is small, if any. When samples from section A-B and locality C are considered separately (Figs. 6B, 6C), it is seen that the mean rotation may be greater at section A-B than at locality C,  $6.7^\circ$  vs  $-1.6^\circ$  (Table 1). Considering the associated  $\alpha_{95}$  values, however, the statistical significance is weak.

The normal-polarity samples from near the bottom of section A-B (mean declination =  $28^\circ$ ) may show somewhat more rotation than both the normal-component samples from the middle of section A-B (mean declination =  $-4^\circ$ ) and the reversed-component samples higher in the column (mean declination =  $7^\circ$ ; Table 1). This could indicate continuing rotation with time, although the statistical significance is again weak. Johnson *et al.* (1983), moreover, rule out the possibility of progressive rotation during deposition of the Imperial and Palm Spring formations in the Vallecito-Fish Creek area, so that any pos-

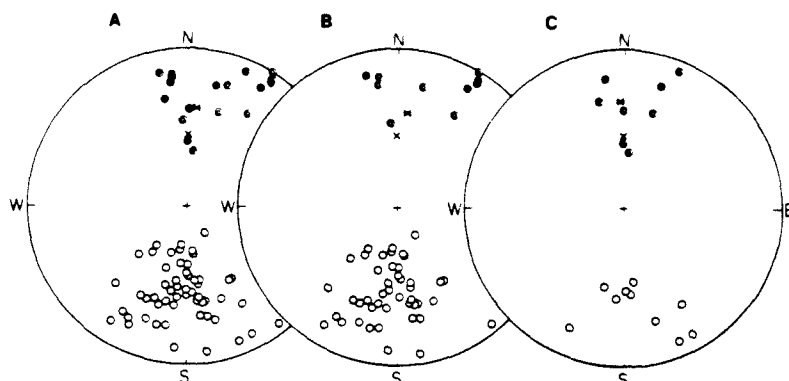


FIG. 6. Equal-area plot for best least-squares fit of tilt-corrected directions for samples collected from (A) all sampling sites, (B) sections A-B and D (together henceforth referred as section A-B in the text), and (C) locality C. The principal component direction of the normal sample is symbolized by double circles and that of the reversed sample by single circles. The "x" shows the present field direction. The double triangle represents the mean direction with the vector value and all the related statistical data listed in Table 1.

sible rotation in the Mecca Hills area cannot be viewed as merely representing the final stage of a  $35^\circ$  regional rotation that affected the accumulating sediments in the Vallecito-Fish Creek area over a longer period of time.

Considering how highly deformed the rocks are throughout the Mecca Hills (e.g., Fig. 2), reflecting the wide and very active underlying San Andreas fault zone, we are surprised that the rotation at any of the sites is so low. Evidently deformation has taken place by local intense folding and faulting rather than by rotation of individual discrete blocks within the fault zone, although our sampling has admittedly been sparse. In the Vallecito-Fish Creek area, on the other hand, a large block—more than 10 km on a side—is sandwiched between two major throughgoing faults and has apparently rotated a relatively rigid unit.

## CONCLUSIONS

The Palm Spring Formation in the southern Mecca Hills was deposited in the very latest Pliocene and early Pleistocene epochs, mainly during the Matuyama reversed chron, between about 2.0 and 0.75 myr ago. Although we have not paleomag-

netically sampled the entire Palm Spring section here, most of the remaining unsampled section appears to be still higher stratigraphically. On the other hand, previous paleomagnetic studies of the Palm Spring Formation in its type area in the Vallecito-Fish Creek basin 80 km to the south (Johnson *et al.*, 1983) suggest that the base of the section there is at least 2 myr older than in the southern Mecca Hills, and the section does not include rocks as young as some of those in the Mecca Hills. This difference, taken together with the completely different provenances of the two units, raises questions as to whether they should be considered parts of the same formation. Despite the location of the southern Mecca Hills virtually within the San Andreas fault zone, only a small amount of average rotation, if any, has taken place at our sample sites since deposition, in contrast to  $35^\circ$  of clockwise rotation in the Vallecito-Fish Creek area.

## ACKNOWLEDGMENTS

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## APPENDIX IV

# Magnetostratigraphic dating of shallow-water carbonates from San Salvador, Bahamas

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## ABSTRACT

Magnetostratigraphic results are reported here from a sequence of late Neogene-Quaternary shallow-water carbonate sediments from a continuous core drilled on the island of San Salvador, Bahamas. On the basis of the remanent magnetism of 136 samples from a 91-m measured section of core, the polarity sequence can be correlated with the magnetic polarity time scale from the Gilbert chron (early Pliocene) through the late Brunhes chron (late Pleistocene-Holocene). Magnetic polarities were determined on the basis of relative up-down direction in the unoriented core. Extraction studies of the magnetic particles reveal the presence of single-domain crystals of magnetite resembling those produced by the magnetotactic bacteria and algae. The sequence of reversals provides a minimum of six new major chronostratigraphic markers for the Pliocene-Pleistocene of the Bahamas; it confirms and refines the local timing of both the lithologic change from skeletal to nonskeletal sediments and the disappearance of coral and molluscan species from the Bahamas as upper late Pliocene (between 2.6 and 2.7 Ma). That the primary magnetic remanence is preserved in shallow-water carbonates, including replacement dolomites, suggests that this technique could be used to date similar Tertiary and possibly even older carbonate sequences. The establishment of a reliable magnetostratigraphy provides refined dating of shallow-water carbonates and regional faunal appearances or disappearances, sediment accumulation rates, subsidence, and depositional events.

## INTRODUCTION

Magnetostratigraphy, the use of an established reversal pattern of remanent magnetism for dating, is well established for siliciclastic deposits and pelagic carbonates, but there have been few similar applications to shallow-water carbonates. Encouragement for this application has now come from a combination of three developments: (1) superconducting magnetometers capable of accurate determinations of extremely weak magnetic signals, (2) a few reports of remanent magnetism in shallow-water carbonates, and (3) the identification of living magnetite-precipitating bacteria in shallow-water carbonate environments in sufficient number to provide a source for a measurable remanent magnetism. As a first test for the existence of a reversal stratigraphy, we made a pilot study of a continuous core nearly 100 m deep from the Bahamas. Here we report successful results of the study and show how the new magnetostratigraphy adds significantly to the dating of major depositional events in pure carbonates.

Until recently, there were only a few reports of remanent magnetism in shallow-water carbonates (Jowett and Pearce, 1977; Kent, 1979; Smith et al., 1980; Hurley and Van der Voo, 1987; Stolz et al., 1987; Chang et al., 1987). This limited attention stemmed from the general consensus that remanent magnetism required the presence of terrestrial magnetic material that is

rare or absent in pure carbonates. The discovery of an indigenous source of single-domain magnetite produced by bacteria (Blakemore, 1975; Kirschvink, 1980a; Kirschvink and Chang, 1984) obviated this limitation. Subsequent research has demonstrated that magnetite pro-

duced by bacteria is common in modern shallow-water environments of south Florida (Stolz et al., 1987; J. L. Kirschvink, 1987, personal commun.).

There are several reasons for choosing the late Cenozoic carbonates of the Bahamas as a test case for magnetostratigraphy. First, continuous cores of these young carbonates that have been studied and dated biostratigraphically (Beach, 1982; Williams, 1985) are available; second, these carbonates have no detectable siliciclastic components; and third, although they are young, they have already undergone some major diagenetic changes, including cementation, dissolution, and dolomitization, any or all of which might modify original magnetism.

## CORE LOCATION, SAMPLING METHODOLOGY, AND MAGNETIC DATA

A continuous core 8 cm in diameter from the northern end of San Salvador, Bahamas (Fig. 1), was sampled to determine magnetic polarities. The core was drilled in the late 1960s by Peter Supko, who described and interpreted the carbonate rocks recovered (Supko, 1977). The re-

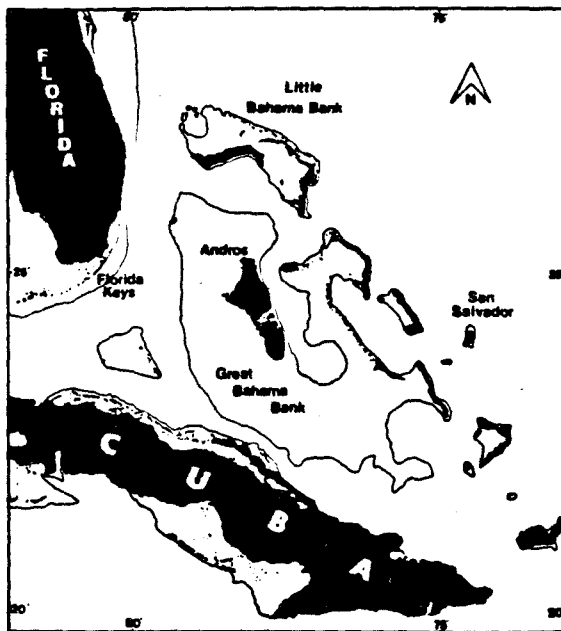


Figure 1. Regional location map of Bahamas archipelago. Core was collected from northern end of San Salvador.

covered core section is nearly complete except for the very top 2 m and small (<1 m) intervals which were very friable. The upper 91 m of the 168-m core was used for this study. From this section, a total of 174 samples were taken, averaging 1 per 0.5 m. The actual sampling interval varied depending on the condition of core sections and the presence of a geopetal structure confirming the up-down orientation.

Each sample for paleomagnetic analysis was a plug about 3 cm long and 2 cm in diameter, drilled from the core with a hollow, nonmagnetic diamond-studded drill bit mounted on a standard drill press. Orientation was marked by a small saw-cut groove on the top of the plug. All samples were briefly submerged in 25% hydrochloric acid and rinsed to remove residual metallic particles from the drill or core barrel.

The remanent magnetism of the samples was measured with a SQUID (Superconducting Quantum Interference Device) moment magnetometer (Fuller et al., 1985). After measuring natural remanent magnetism (NRM), all samples were demagnetized by using alternating fields (AF 2.5, 5.0, 7.5, 10.0, and 12.5 mT) and thermal demagnetization (150, 200, 233, 266, and 300 °C) to isolate characteristic components of remanent magnetization. Magnetic polarities were determined on the basis of relative up-down directions in the core.

The paleomagnetic results used for the polarity sequence included 136 of the 174 samples. The results from 38 samples were omitted because of extremely weak and unstable remanent magnetism ( $<1.0 \times 10^{-9}$  A m<sup>2</sup>/kg).

Because the core was not oriented with reference to magnetic north, only the inclination could be used to identify periods of normal and reversed polarity. Polarity interpretations were not made on samples with very shallow inclinations ( $<10^\circ$ ). The true inclination for normal and reversed samples of  $32.4^\circ$  ( $\alpha_{95} = 12.1^\circ$ ) (calculated by using the inclination-only method of Kono, 1980) is slightly shallower, but still comparable to the expected geocentric axial dipole inclination of  $46.3^\circ$  at the sampling site. The inclination angles from the San Salvador core have a modal class between  $35^\circ$  and  $40^\circ$ . Of the 136 samples used, 83 had a normal polarity and 53 reversed.

The demagnetization steps were plotted as Zijderveld diagrams (Zijderveld, 1967), and a least-squares analysis of the data was used to estimate average remanence direction Kirschvink, 1980b). As demagnetization progressed, measurements not reproducible to within  $15^\circ$  were not included from estimates of the characteristic remanence direction. Typical thermal demagnetization ceased at 300 °C because most samples became too weak to measure accurately (Fig. 2). NRM intensities ranged from  $1.63 \times 10^{-9}$  to  $1.99 \times 10^{-7}$  A m<sup>2</sup>/kg, with a mean intensity of  $2.75 \times 10^{-8}$  A m<sup>2</sup>/kg. Most NRM values fell within the  $6.0 \times 10^{-9}$  A m<sup>2</sup>/kg to  $6.2 \times 10^{-8}$  A m<sup>2</sup>/kg range from the top of the core through 56 m. From 56 to 83 m, a zone of lower intensity was encountered (Fig. 3).

Sampling deficiencies in this study, which include irregular sampling intervals and single-point reversals, are often controlled by core

recovery. Poor core recovery is evidenced by the decreased sampling interval in the lower section of the core. The single-point reversals in this study are preliminary and need verification by additional analyses.

## RESULTS

### Reversal Chronology

The chronology of reversals is based on the comparison of the measured sequence of polarities with the dated geomagnetic polarity time scale, fixed by a biostratigraphic datum. Boundaries for magnetic polarity zones reported here for the core have been approximated on the basis of mid-point distance between two adjacent samples of opposite polarity and are usually constrained in position to within 1 m. To match these polarity zones with the standard geomagnetic polarity time scale (Harland et al., 1982), we used a well-established late Pliocene biostratigraphic datum (disappearance of *Bowden assemblage molluscs* and coral *Stylophora affinis*) as the starting point for age determinations (Beach and Ginsburg, 1980; Beach, 1982; Williams, 1985). On the basis of the biostratigraphic age and the presence of this datum in a normal zone, we interpret this to be the upper part of the Gauss normal chron. This interpretation implies that the major reversed section above the datum is the Matuyama chron. By extrapolation, the four major magnetic zones recognized throughout the sampled core include the normal Brunhes chron, the reversed Matuyama, the normal Gauss, and the upper part of the reversed Gilbert chron (Fig. 3).

When compared to the standard reversal time scale, however, differences in relative thickness of the chrons are likely the result of variations in the amount of subaerial exposure and rates of accumulation (Fig. 4). The Matuyama reversed

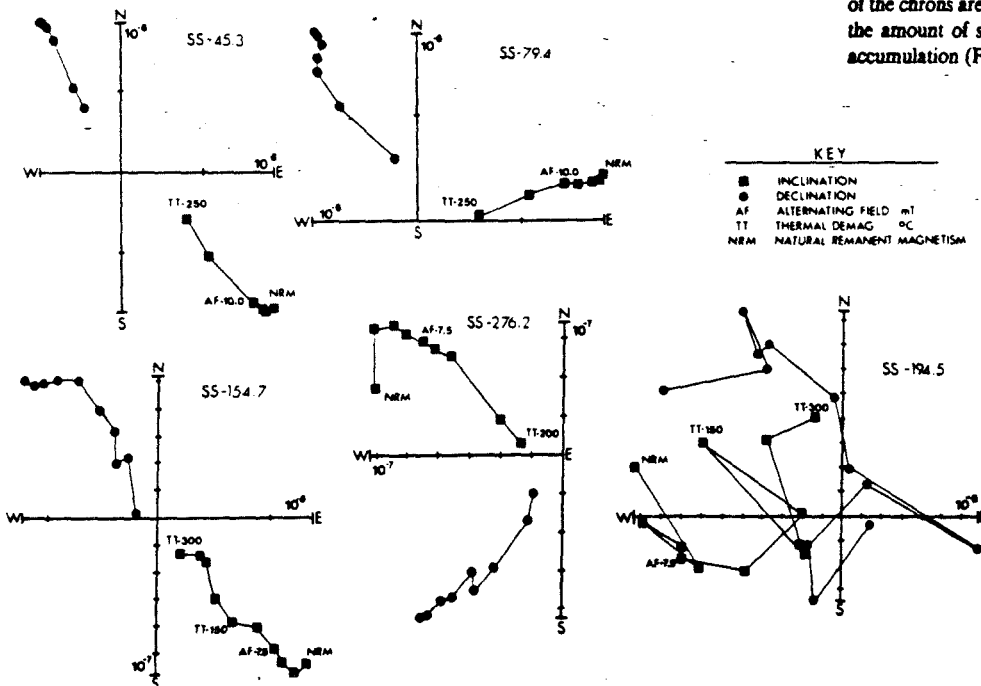


Figure 2. Typical Zijderveld plots from San Salvador core. Sample SS-45.3 (13.8 m depth) is from normal Brunhes chron; SS-79.4 (24.2 m depth) is from reversed Matuyama chron; SS-154.7 (47.2 m depth) is part of normal Gauss chron; SS-276.2 (84.3 m depth) is from Gilbert chron. Sample SS-194.5 (89.3 m depth) is typical of unusable sample exhibiting extremely weak and unstable remanent magnetism.

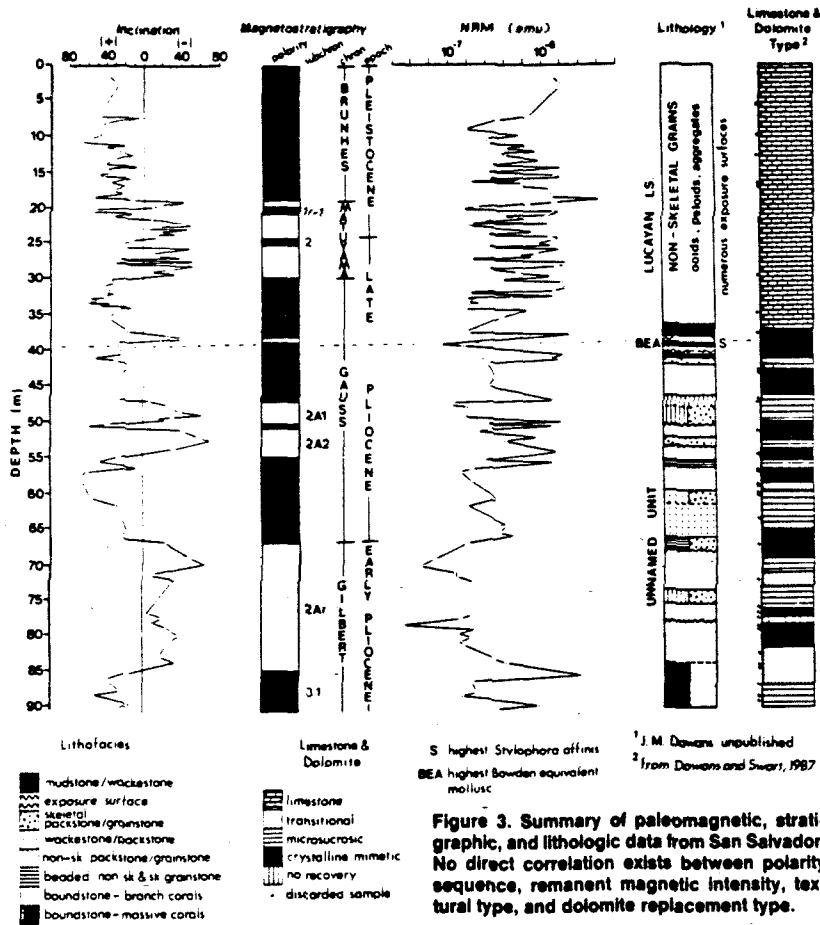


Figure 3. Summary of paleomagnetic, stratigraphic, and lithologic data from San Salvador. No direct correlation exists between polarity sequence, remanent magnetic intensity, textural type, and dolomite replacement type.

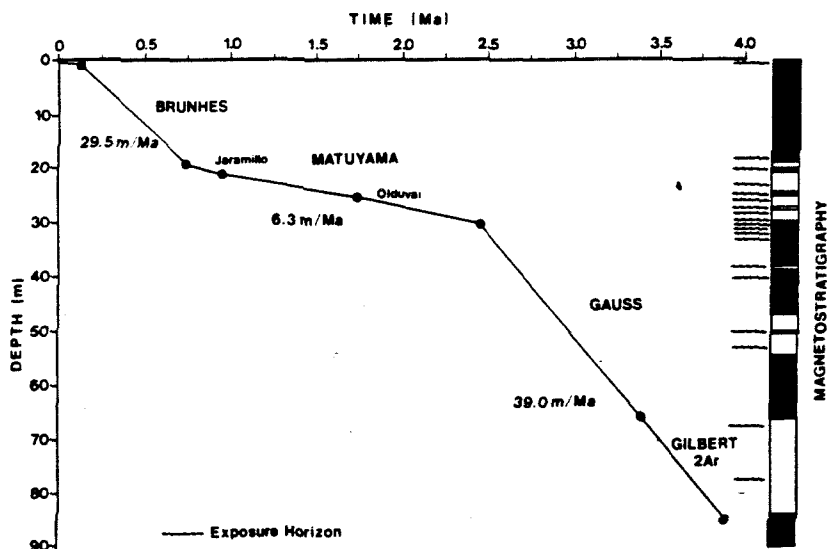


Figure 4. Age/depth curve for 91-m San Salvador core based on magnetostratigraphy (Harland et al., 1982). Matuyama reversed zone in core is relatively short, most likely result of prolonged subaerial exposure during late Pliocene and early Pleistocene. Increased frequency of subaerial exposure horizons during this period is consistent with estimated global eustatic lowering of sea level.

zone is particularly short, but the unrecorded time could easily have been lost in the several exposure horizons that were recognized previously (Fig. 3) (Supko, 1977; Dawans and Swart, 1987).

These new magnetic results seem to permit a detailed correlation with the standard magnetic time scale (Harland et al., 1982). The top of the core has a normal polarity that we have equated to the Brunhes chron. The underlying Matuyama chron is punctuated by two normal-polarity units from about 20.1 to 21.3 m and 24.7 to 25.6 m, possibly representing the Jaramillo and Olduvai events, respectively. At 27.4 and 28.4 m, normal polarity was encountered in single samples from the same section of core containing reversed polarity. These thin polarity reversals may represent part of the Reunion (2r-1 and 2r-2) events, although we realize that these events are of short duration and are rarely encountered in magnetostratigraphic sections. The Gauss chron exhibits a long normal section from about 30.2 to 66.4 m. Within the Gauss, the two reversed sections can be correlated to the 2A1 and 2A2 subchrons. A long reversed section measured in the core from 66.4 to 84.7 m is matched to the upper section of the Gilbert chron (2Ar).

**Source of Remanent Magnetization**

Examination of the magnetic mineral separates from a typical sample at 20.1 m below the top of the core was made with the transmission electron microscope (TEM) and revealed crystals about 0.05–0.3 μm in diameter (Fig. 5). X-ray and electron diffraction studies on these particles showed that they are composed of magnetite or maghemite; the black color suggests that mainly magnetite is present. Kirschvink and Chang (1984), Petersen and von Döbenek (1986), and Stolz et al. (1987) have shown that biogenic magnetites, especially those from magnetotactic bacteria, can be recognized on the basis of particle size and crystal morphology. The magnetite crystal dimensions were plotted on a grain-size stability diagram (Butler and Banerjee, 1975). The crystals measured are within the single-domain field (Fig. 6), similar in size and morphology to those produced by a variety of magnetotactic organisms. In particular, there are two distinct types of single-domain magnetite present: (1) teardrop-shaped particles, shown in Figure 5B and plotted as the triangle of Figure 6, which match those from the magnetotactic algae (Torres de Araujo et al., 1986), and (2) cuboidal, plotted as a small cross in Figure 6. It is important to note that we did not observe any of the large framboidal magnetite spheres that are often linked to the presence of secondary magnetite components in organic-rich sediments (e.g., McCabe et al., 1987; Elmore et al., 1987).

Although the Curie temperature of magnetite is near 580 °C, well above the 300 °C level

Figure 5. Transmission electron microscope photomicrographs of magnetic mineral separates from 20.1 m depth in San Salvador core. A: Cubic to spherical magnetite particles in short chain; grains are similar in size to bacterial magnetite. B: Oblate spherical magnetite crystals in elongate sheaths of unknown origin, but resembling blunt, elongate crystals from recently discovered magnetotactic eukaryotic algae (Torres de Araujo et al., 1986). C: Abundant magnetite crystals within unknown matrix material, similar to particle aggregates found in colonial magnetotactic organisms (Lins de Barros and Esquivel, 1985). Scale bar in all three micrographs = 0.1  $\mu$ m.

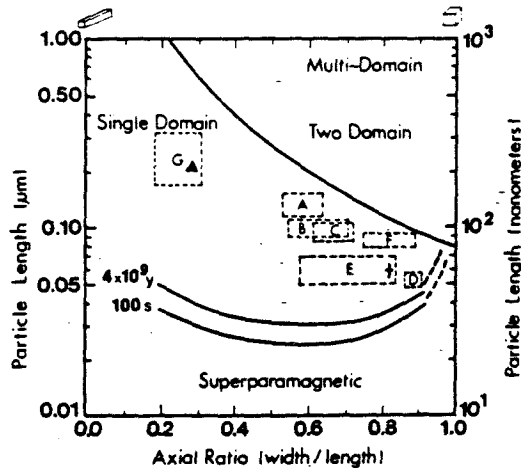


Figure 6. Grain-size/stability field diagram of Butler and Banerjee (1975) showing position of magnetite crystals from magnetotactic organisms of different environments. Mean length and axial ratios from Figures 5B (triangle) and 5C (cross) are within single-domain field, similar to known magnetotactic algae and bacterial crystals, respectively.

where most of our samples become unmeasurable, these TEM observations of the magnetic particles are consistent with the alternating-field and thermal-demagnetization results from the core samples. Two observations support this conclusion. First, extremely small crystals that plot near the bottom margin of the single-

domain stability field shown in Figure 6 will become superparamagnetic at temperatures well below the Curie point, and many of the magnetic particles extracted from the samples fall within this size range. Second, many of the ultrafine-grained magnetites extracted from deep-sea carbonates have been partially oxidized

to maghemite, as deduced by the partial dissolution of their surface features during treatment with Na-dithionite (Kirschvink and Chang, 1984). Maghemite is known to invert to hematite at temperatures between 300 and 600 °C, and for any magnetofossil with a magnetite core and maghemite rim, this conversion would similarly yield a superparamagnetic particle. Note, however, that both maghemite and magnetite share the same electronic crystal lattice superstructure, and therefore the solid-state oxidation of single-domain magnetite to maghemite does not alter the direction of the primary remanent magnetization.

In summary, the presence of an internally consistent magnetic polarity stratigraphy, the discovery of bacterial magnetofossils, and the lack of obvious diagenetic magnetites all indicate that we are dealing with a primary or early diagenetic magnetic remanence.

## DISCUSSION

### Remanent Magnetism Unaffected by Variations in Depositional and Diagenetic Textures

There are significant variations in depositional and diagenetic textures in the core, but these do not appear to have any detectable effect on the preservation of the remanent magnetism established during deposition. The upper 37 m of the core is limestone that is a mix of packstones and wackestones composed of ooids and peloids; the lower 54 m, now all dolomite, was originally skeletal debris of varying grain sizes and composition. These differences in composition and grain size do not correlate with changes in magnetic polarity. Similarly, the variations in mineralogy have no major discernible effect on the preserved magnetism. From the top of the core to a depth of 10.7 m, the prevailing (>50%) mineralogy is aragonite. From 10.7 to 33.5 m, the core is all calcite. From 33.5 to 91.4 m, the core is almost entirely dolomite. The upper section shows the least postdepositional modification, judging from the presence of original aragonite and the sparse cementation (Supko, 1977). In the middle calcitic section, there is much evidence of dissolution and cementation that probably occurred in meteoric environments (Supko, 1977; Beach, 1982; Williams, 1985). The lower section of almost pure dolomite has significant variations in texture, from microcrystalline to coarse-crystalline varieties that preserve original fabric elements. These variations in diagenesis and especially the dolomitized interval have no detectable effects on magnetic polarities; long normal and reversed intervals traverse changes in dolomite texture. However, the microcrystalline dolomites consistently exhibit a slightly weaker NRM intensity (Fig. 3). This weaker signal may be indicative of sediments that were inverted to calcite prior to dolomitization (Dawans and Swart, 1987). The slightly weaker signal in these zones is still well

- A. Fresh-water sediments of New Zealand (Blakemore et al., 1980)
- B. Complex simulated natural environment (Tove and Noenck, 1981)
- C. Fyshwick sewage pond, Australia (Kirschvink, 1980a)
- D. Salt marshes of Cape Cod, Massachusetts (Blakemore, 1975)
- E. Santa Barbara basin (Stolz et al., 1986)
- F. Laguna Figueroa, Baja California, and Sugarloaf Key, Florida (Stolz et al., 1987)
- G. Magnetotactic algae (Torres de Araujo et al., 1986) and teardrop-shaped magnetite in magnetotactic bacteria from New Zealand (Blakemore et al., 1980)

within the range of measurement. The preservation of remanent magnetism established during deposition, despite the significant diagenetic modifications, is quite remarkable and, if reproduced elsewhere, will indicate that dissolution, recrystallization, and even pervasive dolomitization can proceed at such a fine scale as to not reorient the original remanent magnetism.

#### APPLICATIONS OF MAGNETOSTRATIGRAPHY

The magnetostratigraphy confirms and refines the dating of two major events in the Pliocene-Pleistocene history of the Bahamas archipelago: a change in depositional facies and the local extinction of bivalves and a common coral. Beach and Ginsburg (1980) used biostratigraphy to date (boundary between early and late Pliocene, ca. 3.4 Ma) the base of their Lucayan Formation, which marks both the disappearance of a distinctive coral and a change from skeletal to nonskeletal limestones. Williams (1985) identified the upper limit of a diagnostic molluscan assemblage equivalent to that of the Bowden Formation in Jamaica at 39.6 m in the San Salvador core. This biostratigraphic datum further refined the timing of the faunal and lithologic change to the middle of the late Pliocene. By using the magnetostratigraphy (Fig. 3), these events can now be dated at between 2.6 and 2.7 Ma.

The refined dating of the major changes in lithology and fauna in the Bahamas may also be applied to the regional mass extinction of bivalves from the southeastern United States and Caribbean discussed by Stanley (1986). The last appearance of the molluscan assemblage (2.6 to 2.7 Ma) on San Salvador is perhaps correlative with oceanic cooling in the late Pliocene and subsequent early Pleistocene cooling pulses (Shackleton, 1985).

The reversals provide a minimum of six new chronostratigraphic markers for the Bahamas which can be used to calculate island subsidence. The age/depth curve (Fig. 4) shows significant variations in the rate of subsidence that may be related to hydro-isostatic effects. Rates of accumulation are variable, slow periods corresponding to an increased frequency of subaerial exposure horizons. The age/depth curve in Figure 4 is similar to age-depth curves from periplatform sediments cored in Exuma Sound during Ocean Drilling Program Leg 101 (Austin et al., 1986). The similarity of these curves provides confirmation of highstand sediment shedding.

#### CONCLUSIONS

The results establish that a legible magnetostratigraphy that is based presumably on a biogenic magnetite signal can occur in shallow-water carbonates. It is especially significant that the original remanent magnetism is preserved

even in recrystallized and dolomitized carbonates. If this first indication of a magnetostratigraphic record in pure shallow-water carbonates can be replicated elsewhere and extended to older strata, a valuable new technique for stratigraphic correlation, dating events, rates of accumulation, and subsidence would be available.

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#### Reviewer's comment

This paper is quite important; first, because it provides the first evidence for the timing of Ice Age extinction in the Bahamas; second, because it demonstrates the value of undertaking magnetostratigraphic studies in limestone borings; and third, because it raises the possibility that bacteria may have produced the magnetic material.

Steven Stanley