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 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 work of Opdyke et al. (1966). 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 microfossils and nannofossils (e.g., Alvarez et al., 1977; Tauxe et al., 1983; Lowrie and Channell, 1984). 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 km across) as the carrier 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 samples, small proportions of the total magnetic material have been isolated, and the particles that 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 particles. With SEM it is easy to identify grains larger than 0.5 µm (i.e., the pseudo-single-domain to multidomain 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 sub-0.1 µm 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, 1981). The dimensions of all bacterial magnetite crystals measured with the TEM and published to date plot within the boundaries of singledomain stability field as determined by Butler and Banerjee (1975) and shown here in Figure 1 B. This property apparently results from natural selection for magnetotaxis on the size, shape, and number of the crystals in each bacterium (Kirschvink, 1982). Three distinctive particle morphologies have been reported to date, including subrounded 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 that commonly form through igneous, cosmic, and authigenic processes in nature.

We report here results from new extraction, purification, and TEM sample preparation techniques that result in a higher yield of the fine-grained fraction and permit classification based on crystal morphology. Single-domain magnetite crystals of both biogenic and inorganic affinities appear to be present in varying amounts, but the biogenic fraction dominates the calcareous oozes. These objects appear to be the smallest mineral fossils yet found in the sedimentary record, are bioinorganic particles of presumed prokaryotic origin, and may be of use for measuring paleo-oxygen levels.

MATERIALS AND METHODS

Deep-sea piston-core samples of various sedimentary types were obtained from the Scripps Institution of Oceanography and the LamontDoherty Geological Observatory. The sample sites range from the equator to mid-latitudes of the Pacific, Atlantic, and Indian Oceans, and they vary in age from early Oligocene to Holocene. Various properties of samples examined to date are shown in Table 1. The extraction and sample-preparation procedures are the same as those described by Chang and Kirschvink (1984). X-ray analysis was made with the Debye-Scherrer method on magnetic separates.

RESULTS AND DISCUSSION

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, and we found that 90° of the magnetic particles in the samples have been removed, a figure that is much higher than the 50% reported by Lovlie et al. (1971). X-ray diffraction analysis on the final magnetic 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 µm) 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 nonmagnetite 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 decrease in saturation isothermal remanent magnetization (sIRM) after this treatment measures the moment carried by minerals other than magnetite. About 40% of the sIRM of our sample is removed with this treatment, indicating that about 60% of the sIRM is carried by magnetite; the remainder presumably is maghemite. Although we have studied samples from only two deep-sea cores in this detail, other work on the magnetic minerals in pelagic and hemipelagic sediments reveals that fine-grained magnetite is also the main

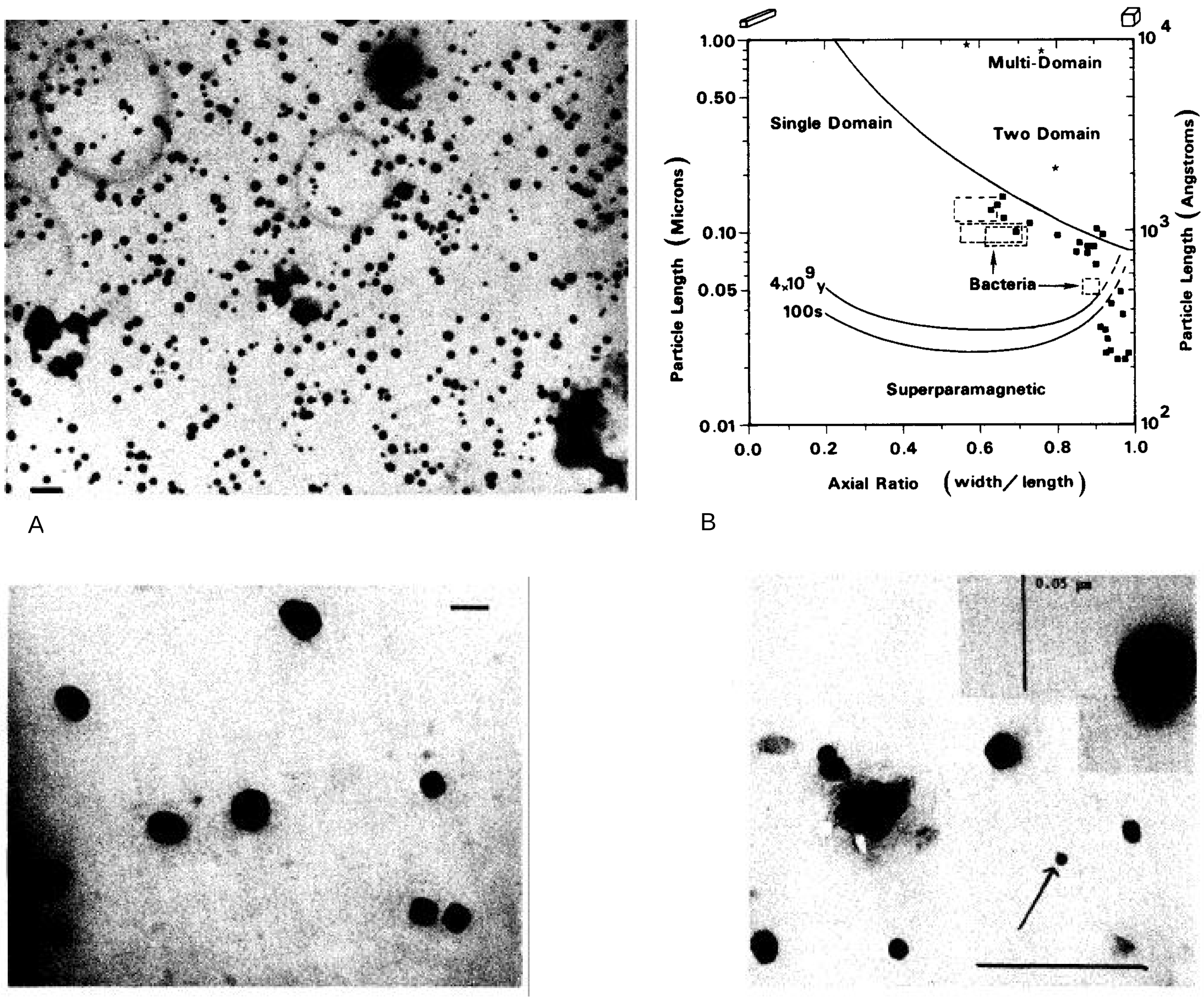

Figure 1. A: Low-magnification (22 400 X) electron micrographs of magnetite extracts from sample core 31, sec. 3, 9-11 cm, of DSDP Leg 73. Scale bar = 0.5 µm. B: **Plotted into single-domain stability field diagram for magnetite (Butler and Banerjee, 1975), size and shape distribution of grains shown in A range from superparamagnetic to multidomain. Each solid square represents average of 50 grains. Each asterisk represents 1 Individual grain.** C: **Electron micrograph of magnetite extract for sample core 31, sec. 2, 129 cm, showing typical single-domain particles. Scale bar = 0.1 µm.** D: **Electron micrograph of magnetite extracts from sample core 2, sec. 2, 70 cm depth. Scale bar = 0.5 µm High magnification image of 1 paramagnetic (SPM) grain (indicated by arrowhead) is shown in right upper corner (scale bar = 0.05 µm). Fuzzy outlines of SPM grains imply that they are remaining cores of surficially oxidized grains after the dissolution treatment.**

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, many minerals that are precipitated biochemically under matrix-mediated control have crystal shapes that 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. TEM examination of our separates reveals three general classes of fine-grained magnetite particles that we designate as A, B, and C as follows: Type A grains are 0.02 to 0.05 'µm in length, and their aspect ratios vary from 0.9 to 1.0 (e.g., superparamagnetic); type B grains are 0.06 to 0.15 µm in length, and their aspect ratios vary from 0.6 to 0.9 (single-domain); type C grains are pseudosingle-domain and multidomain particles longer than about 0.2 µm.

As can be seen in Figure 1 B, the sizes and shapes of particles measured from the final magnetite extract of one sample from the South Atlantic fall mainly in type B, which overlaps with those of typical single-domain grains from magnetotactic bacteria. They also share some of the same cuboidal and hexagonal forms as those of bacterial magnetite (Fig. 1, C and D).

The presence of numerous type-A grains (superparamagnetic size) is probably an artifact of our magnetite extraction procedure, particularly the DCB treatment that removes all iron minerals except magnetite. We have not observed many of these particles in extracts prior to the DCB dissolution step, and all that we have observed after treatment show fuzzy outlines (Fig. 1D). It seems probable that these are the remaining cores from larger type-B grains that 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 that 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, On the basis of observed population densities and growth rates, Kirschvink and Lowenstam (1979) and Towe and Moench (1981) 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 that are known to produce magnetite crystals (tuna, salmon, cetaceans, etc.) are found in large enough numbers to contribute a significant amount to the sediments. Yellowfin tuna, for example, make only about 20 ng of magnetite in a small tissue within the dermethmoid bone, but the crystal morphology strongly resembles the morphologies of the bacteria (Walker et al., 1984). 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 the marine plankton.

We have found abundant particles of single-domain magnetite in all sediments with medium to high $CaCO_3$ content and with relatively high

TABLE 1. MAGNETIC GRANULOMETRY AND OTHER PROPERTIES OF DEEP-SEA SAMPLES

	RC 16-138	RC 16-150	14 PV	35 PV	35 PV	103 P	DSDP Leg 73, Site 522* Core 2 Pleistocene	DSDP Leg 73, Site 522* Core 15 Early Miocene	DSDP Leg 73, Site 522* Core 31 Early Oligocene
Locality	Southwest Atlantic (27°03'S, 40°10'W)	Southwest 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	Foram marl	Sandy foram	Siliceous clay	Foram rad. marl	Marl	Foram 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
NRM (10^{-7} Am^2/kg)	8.31	1.59	0.32	2.90	3.32	6.91 (Sec 2,70cm)	7.21 (Sec 3,40cm) 6.35 (Sec 3,82cm)	33.40 (Sec 3,9cm) 22.10 (Sec 2,120cm)	7.52 6.10 (Sec 2,129cm)
IRM at a 0.720 Tesla impulse (10^{-4} Am^2/kg)	32.90	1.97	2.06	4.05	3.15	28.10 (Sec 3,82cm)	12.60 (Sec 2,90cm) 7.80 (Sec 2,120cm)	34.20 (Sec 3,40cm) 29.30	12.10 (Sec 3,9cm) 9.95 (Sec 2,129cm)
Sedimentation rate (m/m.y.)						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

*All cores examined by Tauxe et al. (1983).

sedimentation rates (>8 m/Ma) examined so far. They are extremely rare or nonexistent in silty clay, siliceous marl, and sediments with low deposition rates (< 5 m/Ma). 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 described 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 that 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 postdepositional remanence (pDRM) from Brownian motion. This could explain why some deep-sea cores preserve high-resolution records of geomagnetic transitions (Opdyke et al., 1974; Clement 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, 1984).

CONCLUSIONS

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 recovered, and could justifiably be called either picofossils or magnetofossils. 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.

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