Quaternary Climates, Environments and Magnetism

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'Whence is it that nature does nothing in vain; and whence arises all that order and beauty which we see in the world?' I. Newton.

1– Introduction

B. A. Maher, R. Thompson and M. W. Hounslow

The Quaternary geological period, beginning roughly two million years ago, is the most recent, and ongoing, period of Earth's history. It comprises a particularly dynamic timespan, characterized by major shifts in climate, expansion and contraction of continent-sized ice sheets, rises and falls in global sea level, migrations and extinctions of fauna and flora, and not least, the evolution and exponential rise in population of modern humans. These sequences of dramatic changes in the Earth's climate and biosphere have frequently imprinted themselves within natural *proxy records* – as physical, chemical and isotopic variations within sediments or ice. Such proxy records, if they can be retrieved and deciphered, allow us to identify the timing, rate and mechanisms of past changes in climate and environment. This information is increasingly critical. It provides the context and perspective for both our present understanding and future prediction of climate, at a time when human modification of the climate system, via greenhouse gas emissions and pollutant aerosols, appears significantly under way.

This book aims to examine the Quaternary palaeoclimatic and environmental information recorded by *magnetic* proxies. Magnetic grains, dominantly iron oxides and sulphides, occur virtually ubiquitously in Quaternary sediments, soils, dusts and organisms, albeit often in minor or trace concentrations. As is widely known, such grains may act as palaeomagnetic recorders of the Earth's ancient magnetic field. Additionally, however, they may act as sensitive magnetic recorders of palaeoclimatic and palaeoenvironmental change. Changes in climate produce changes in the environment, including sedimentary and soil-forming environments. The mineralogy, concentration, magnetic grain size and morphology of magnetic grains may

all vary according to the origins of the magnetic grains and their subsequent post-depositional sedimentary history. Such variations can result in shifts in the magnetic properties of the material under study, shifts which can be readily and rapidly identified by highly sensitive magnetic instrumentation. Thus, the rationale for magnetic analysis of Quaternary (and older) materials is that environmental processes act to create archives of natural magnetic order, hence providing a window on those processes, past and present. The study of these natural magnetic archives comprises part of the rapidly growing field of Environmental Magnetism.

As magnetic measurements can be made relatively quickly this enables large numbers of samples to be processed, a boon for high-resolution Quaternary studies. In many cases, a relatively small number of carefully selected magnetic measurements of bulk samples can sensitively identify differences between samples. As soils and sediments frequently contain mixtures of magnetic minerals, comprehensive identification of individual magnetic components and their specific environmental origins cannot, as yet, be achieved from magnetic measurements alone (although progress is presently being made in this respect). Hence, independent analysis of smaller numbers of representative sub-samples may be required to 'calibrate' the magnetic data at any one site. Extraction of the magnetic grains from their host samples and mineralogical analysis (e.g. by microscopy and X-ray diffraction) may provide the additional information required to identify their source and environmental significance, and also allow quantitative modelling of their relative magnetic contributions. Another approach is to examine the relationship between sample magnetic properties and independent environmental proxies, such as stable isotope composition, pollen content and geochemical factors.

However, although it is always interesting to demonstrate correlation between magnetic shifts and other environmental indicators or proxies, such as oxygen isotope ratios, mere demonstration of co-variation is *not* the major aim here. Rather, we address the inverse problem: what *new and additional information* can be gained from the magnetic record of Quaternary materials? Thus, the field of environmental magnetism is evolving and using magnetic parameters not as generalized environmental *indicators* but as calibrated, quantified *proxies* of specific environmental processes or of specific components of the climate system. Here, we aim to bring together results, ideas and knowledge gained during rapid expan-

sion of environmental magnetism over the last decade or so, and thus identify the sensitivity and value of the 'magnetic window', for both the magnetist and the Quaternary scientist, across a diverse range of sedimentary contexts.

Having identified the significance and sensitivity of magnetic records as proxy recorders of climate and environment, we briefly outline the inception of the large-amplitude swings in climate that characterise the Quaternary period. For more comprehensive treatments of this area, the reader is referred to the excellent books by Lowe & Walker (1997) and Williams *et al.* (1998). The wide variety of natural and anthropogenic magnetic contributors that are inherited, formed and transformed in the environment is then illustrated by an atlas of optical, scanning and transmission electron micrographs. Finally, we describe magnetic instrumentation, measurement techniques, parameters and methods for discrimination between magnetic minerals.

Evolution of Quaternary climate

The Quaternary provides a wealth of evidence, from oceans to ice-caps and continents, of a whole spectrum of climatic and environmental changes, from full interglacial as at the present day to full glacial conditions (Fig. 1.1 in colour plates section) as at approximately 20 thousand years ago (ka). The Quaternary can be seen as a continuation of climatic deterioration which began some 50 million years ago (Ma), when changes in the configuration of the continents and oceans are thought to have induced key changes in heat transfer around the globe. For example, the opening of the south-east Indian Ocean (around 50 Ma), as Australia drifted north from Antarctica, and subsequently the formation of the Drake Passage (around 38 Ma), as South America and the Antarctic peninsula moved apart, enabled the establishment of the Antarctic Circumpolar Current. This had the effect of virtually isolating the Antarctic from poleward heat transfer by warm ocean currents (Fig. 1.2). This reorganization of land, ocean and energy transfer resulted in progressive development of ice on Antartica, burying the temperate forests that were previously growing in the area. As ice sheets grow larger, they can create further modifications to the Earth's energy budget. The high reflectivity of ice and sea-ice may further cool the region; steepening temperature gradients may result in increased wind

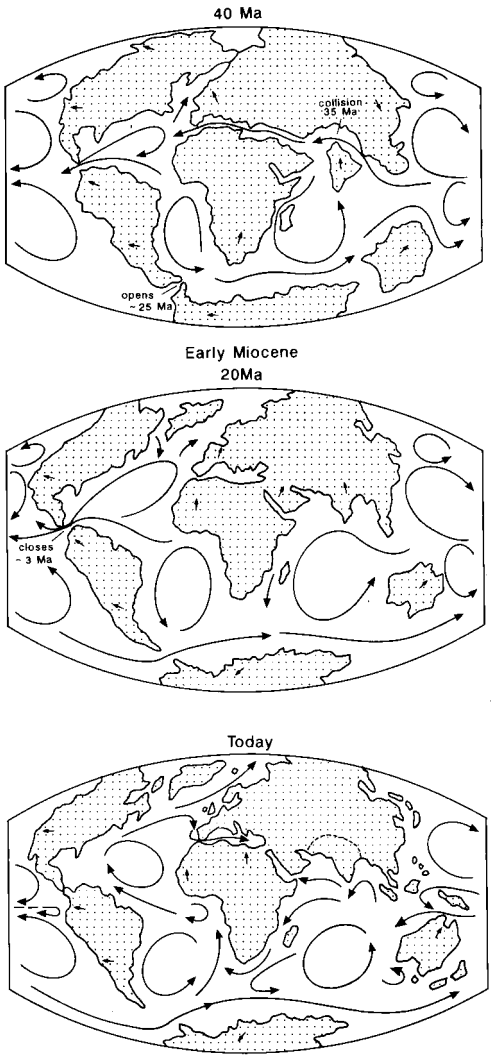

Figure 1.2. Reconstruction of continental configurations and major ocean currents from the Late Eocene to the present day (redrawn from Williams *et al.*, 1998).

strengths; and an ice sheet several kilometres thick may also impinge upon the structure of the atmospheric circulation. Indeed, further major cooling of the planet is evident from the middle and late Miocene (Fig. 1.3). It is speculated that these cooling effects were causally related to changes in the salinity of the Earth's oceans. Around 5.5 Ma, tectonic activity combined with marine regression resulted in the isolation of the Mediterranean Sea and evaporation of its waters – the imaginatively-called 'Messinian salinity crisis'. Other shallow ocean areas, including the Red Sea and the Persian Gulf, subsequently underwent similar dramatic effects, the net result being

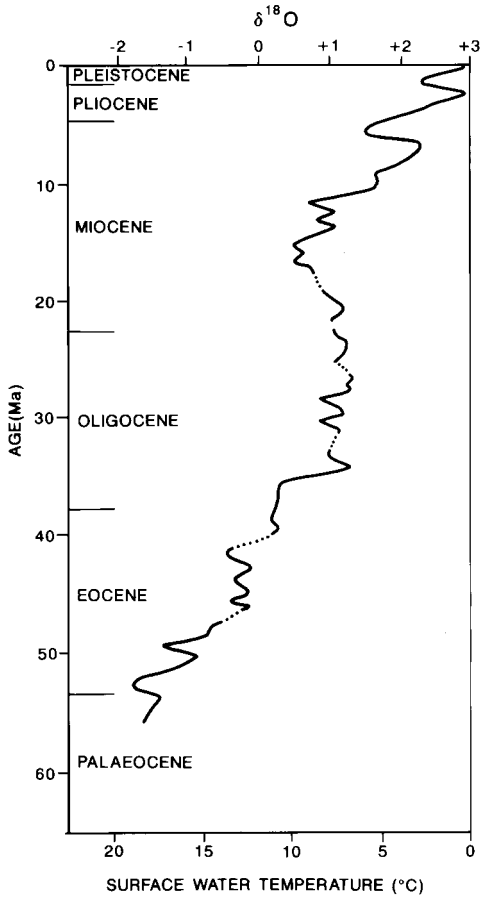

Figure 1.3. Reconstruction of surface water temperatures of high-latitude Southern Hemisphere oceans during the Cenozoic era (redrawn from Shackleton & Kennett, 1975).

a massive increase in the global store of precipitated salt. The accompanying reduced salinity of the oceans (~ –6%) would have enabled increased sea-ice formation at higher latitudes, again with a cooling feedback.

Alongside these late Tertiary tectonic, oceanic and eustatic adjustments, major episodes of mountain-building were initiated. The Tibetan Plateau began a formidable rate of uplift (~10 mm/yr), reaching an average height of 5000 m. In combination with increased Asian continentality due to the final closing of the Tethyan Ocean, this additional high mountain massif provided the driving force for development of the Asian monsoon. Similarly significant uplift along western North and South America produced further topographic obstacles to the global atmospheric circulation. However, here the north–south aligned mountain belts diverted the jet stream into more meridional patterns, thus shifting global climate and

vegetation zones. Furthermore, these episodes of northern hemisphere mountain building may have triggered a shift in the carbon dioxide concentration of the atmosphere, via weathering and erosion. Weathering of the uplifted rocks probably consumed large amounts of atmospheric CO_2. Subsequent erosion of the weathering products and their eventual deposition in the deep oceans could then 'lock-up' the carbon, causing a reduction in the atmospheric CO_2 store and hence diminished greenhouse warming.

Clearly, it is possible to suggest a range of hypotheses, involving mountain building, opening of isthmuses, atmospheric change and geochemical change to account for the causes of the climatic deterioration from mid-Tertiary times. Precision, rather than speculation, is not achievable for this timespan, however, due to the incompleteness of the available geological data and our inability to obtain accurate age control on events, tectonic or climatic. For the Quaternary, in contrast, high-resolution archives exist, which can be dated and deciphered with increasing precision. This can be demonstrated with regard to one widely-used palaeoclimatic proxy, namely, oxygen isotope ratios derived from foraminiferal skeletons preserved in deep-sea sedimentary sequences. The interpretative model for the relationship between past climate and this stable isotope parameter has evolved from the 1940s onwards, when Harold Urey first demonstrated the temperature-dependence of oygen isotope fractionation. Applying these methods and principles to a sequence of Quaternary sediments from the Caribbean Sea, Cesare Emiliani in 1955 identified significant oscillations in the $^{18}O/^{16}O$ ratio of foraminiferal shells through time and interpreted these as a proxy for variations in ocean water temperature (Fig. 1.4). Emiliani's model was subsequently challenged by Shackleton, who argued that the key factor controlling foraminiferal oxygen isotope ratios was the isotopic composition of the ocean water, which varied according to the amount of isotopically light oxygen locked up in continental-sized ice sheets. Hence, he interpreted palaeo-isotopic shifts as evidence of a sequence of glacial, interglacial, stadial and interstadial climate stages, some 30 to 50 such shifts being identified within the Quaternary period (Fig. 1.5). An independent check on this new model was provided by the record of sea level changes, recorded, for instance, by a series of raised coral terraces on the tectonically-rising coast of New Guinea (Chappell & Shackleton, 1986). Since a change of 0.1 parts per thousand (‰) in the marine oxygen isotope ratio

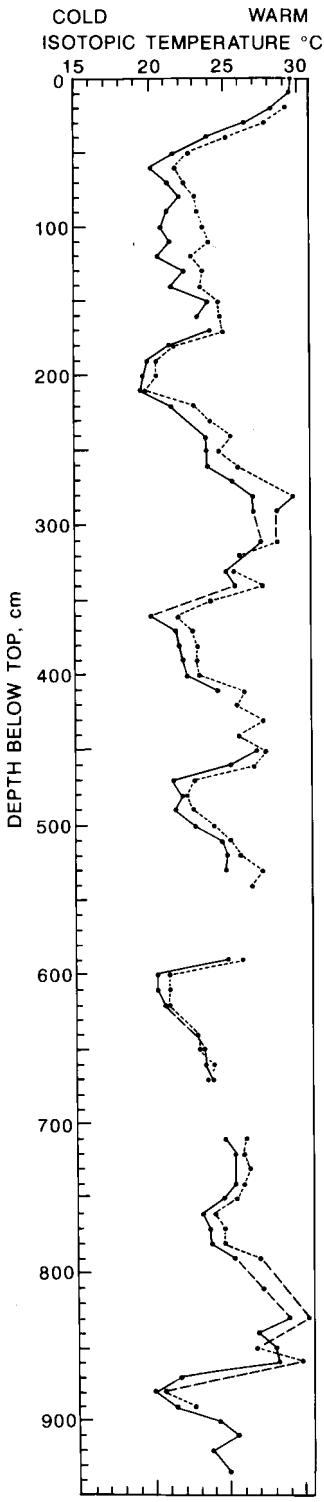

Figure 1.4. 'Isotopic temperatures' calculated by Cesare Emiliani from $\delta^{18}O$ analyses of *Globigerinoides rubra* (dotted line) *and G. sacculifera* (solid line) in sediments from the Caribbean (reproduced from Emiliani, 1955).

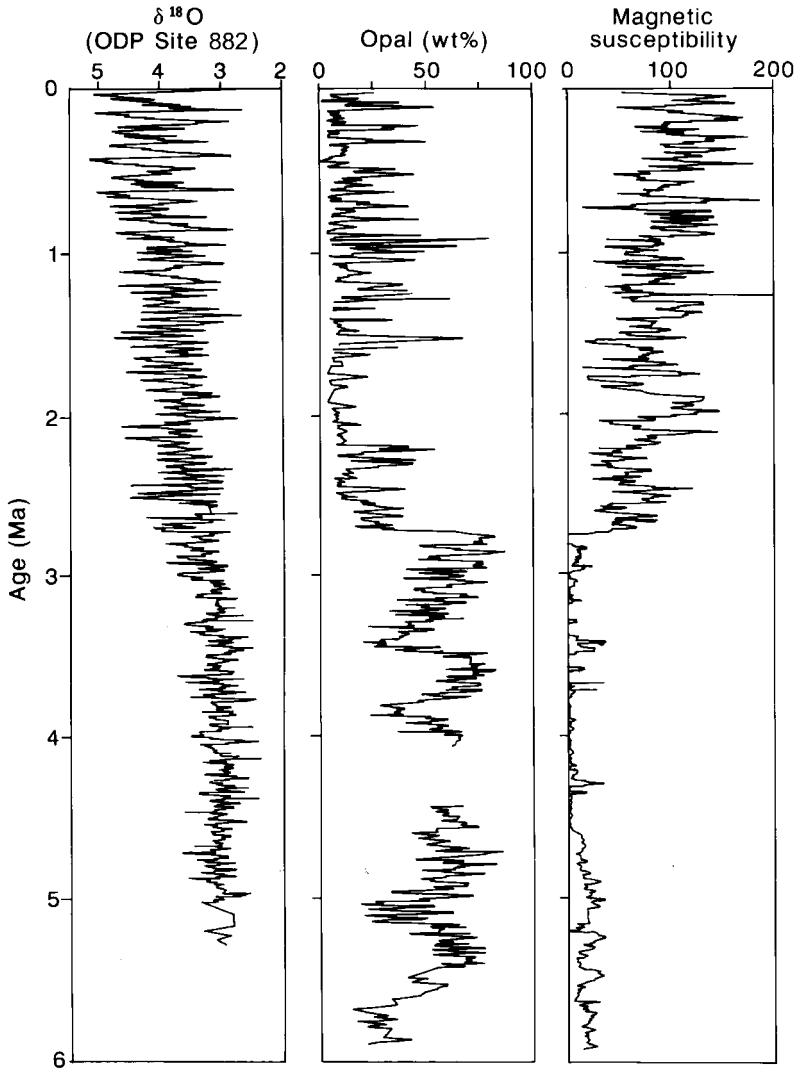

Figure 1.5. Oxygen isotope, opal and magnetic susceptibility records from Ocean Drilling Program Site 882, in the North Pacific (redrawn from Maslin *et al.*, 1996). Here we will consider the synchronous changes in the oxygen isotope and magnetic susceptibility records, at 2.75 Ma, as the time of major climate reorganization associated with the start of the Quaternary.

($\delta^{18}O$) equates to a fall in sea level of approximately 10 m, a direct comparison between the two records can be made. Although there is some general agreement between the two curves, they fail to correspond in detail. Hence, the interpretative model for the oxygen isotope proxy was seen to

require re-evaluation and modification. Shackleton's new model incorporated the effects of glacial–interglacial temperature changes in both the deep ocean and surface waters. Such problems notwithstanding, the development of the oxygen isotope proxy has revolutionized our view of the Quaternary. It has substantiated the Croll–Milankovitch theory of climatic cyclicity induced by variations in the orbit of the Earth. It also provides a remarkably precise method of dating of sediments, via correlation with the astronomical timescale, assuming the Croll–Milankovitch periodicities are stable through time.

Magnetic contributors to sediments, soils, dusts and organic tissues

Until the last 10–15 years or so, palaeomagnetists and rock magnetists concentrated primarily on characterizing the magnetic properties of a relatively narrow subset of natural magnetic minerals. One intensively studied group comprised the titanium-substituted magnetites and maghemites, formed at high temperatures in igneous rocks. These minerals played a key role in palaeomagnetic studies of continental crust and in the development of the sea-floor spreading hypothesis, through the study of marine magnetic anomalies. The importance of these minerals in these contexts is due primarily to *their formation at high-temperatures*; they carry a permanent *stable* magnetization due to cooling through their respective Curie points.

The significance of *low-temperature formation* of magnetic minerals was also recognized, specifically with regard to red-coloured sediments (i.e. terrestrial sediments), dominated magnetically by haematite. In this context, the haematite forms both through transport-related oxidation and the influence of oxidizing pore fluids during burial, modifying the magnetic minerals derived from igneous and metamorphic source rocks.

The development of environmental magnetism, with its focus on sediments ands its application to a wide range of Quaternary environments, has stimulated the recognition and identification of additional processes which produce distinctive and strongly magnetic minerals.

First, a range of ferrimagnetic minerals has been shown to form at ambient temperatures ($< 50\ ^{o}C$) within sedimentary and soil-forming environments. These minerals include the iron oxides, magnetite and maghemite and the iron sulphide, greigite. The pathways of formation of these minerals include soil-forming and weathering processes and intracellular, biogenic

precipitation by magnetotactic bacteria. The resultant magnetic particles frequently occur as distinctively fine and ultrafine grain assemblages, characterized by special magnetic properties. For example, the magnetic grains formed in soils are magnetically particularly *unstable*.

Second, there are two additional high-temperature pathways of magnetic mineral formation. Strongly magnetic particles are formed during heating of iron compounds during fire events (e.g. by the burning of topsoils during forest fires) and also during the combustion of fossil fuels. The magnetic pollutant particles can be released into the atmosphere, to form a significant magnetic source for soils and sediments.

Hence, the application of magnetic techniques to a range of environmental contexts has demonstrated greater diversity both in the *processes* which produce magnetic minerals and in the mineralogy, grain size, morphology and interactions of the resultant minerals. Rock magnetists who are familiar with the variation of magnetic properties with microstructural changes, such as chemical composition (e.g. degree of substitution, or cation vacancy), grain shape (e.g. elongate compared with equidimensional) and magnetic grain size may have been surprised by the amount of additional magnetic order observed and classified from empirical measurements of soils, sediments, dusts and organic tissues. Microstructural magnetic variations in the magnetic components of these natural materials commonly appear to be subordinate to larger-scale changes in their magnetic assemblages, reflecting the wide variety of possible geological, anthropogenic and diagenetic sources. This wide variety of magnetic sources is a boon for the environmental magnetist, since it broadens the potential sensitivity and resolution of the magnetic proxy record of environmental change.

To illustrate the variety and distinction of possible magnetic contributors to natural samples, Plates 1.1–1.35 display a range of magnetic grains produced by different types of environmental processes.

Plates 1.1–1.35: An atlas of micrographs of natural and anthropogenic magnetic grains

Plates 1.1–1.7 Detrital, lithogenic magnetic components

Plate 1.1. Scanning electron micrograph of a detrital, windblown titanomagnetite crystal from the Quaternary loess/palaeosol sequences of north central China (Photo: B. Maher).

Plate 1.2. Scanning electron micrograph of a mixture of detrital, aeolian Ti-magnetites and Ti-free magnetites, from the Chinese loess/palaeosol sequences (Photo: B. Maher).

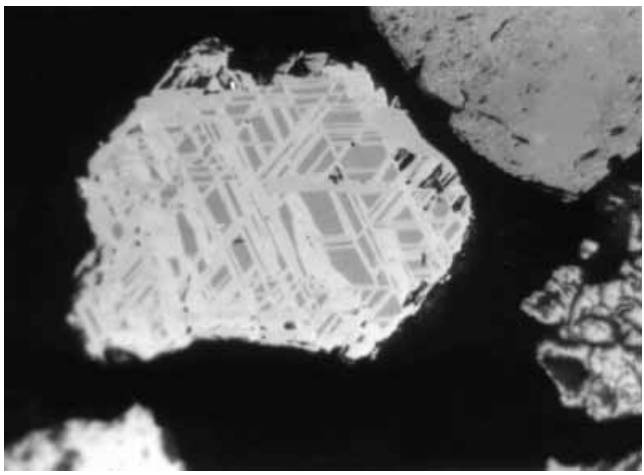

Plate 1.3. Detrital titanomagnetite grain displaying typical high-temperature exsolution texture relict from the original igneous source rock. The titanomagnetite (dark grey) is sub-divided by many lamellae of ilmenite (mid-grey, derived from ulvospinel lamellae). Some patches of haematite (pale) are also present, especially towards the edge of the grain, showing that the magnetite in the grain is undergoing oxidation. Optical, reflected light micrograph, from Miocene Catahoula tuff (Photo: R. Reynolds *et al.*, 1982). Scale: micrograph width = 320 μm.

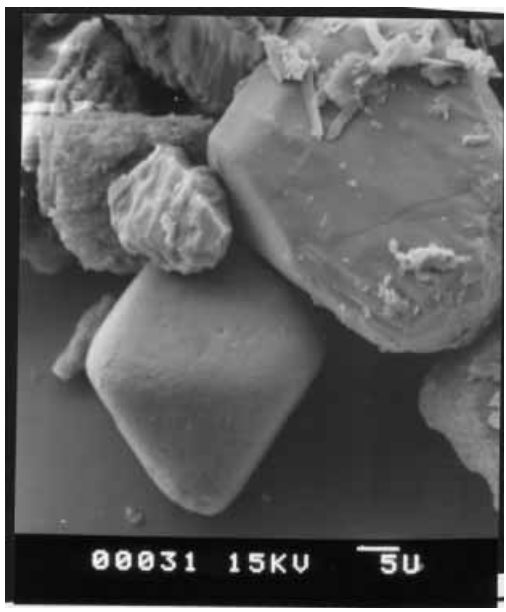

Plate 1.4. Several chromite grains from a magnetic extract. The smooth octahedral grain and the larger smooth grain (top right) are unaffected by the aggressive diagenetic dissolution evident in this sample, whereas the smaller Fe–Cr grain attached to the octahedral particle is showing some etching. Scanning electron micrograph, from late Triassic, Lunde Formation sandstone, northern North Sea (Photo: M. Hounslow).

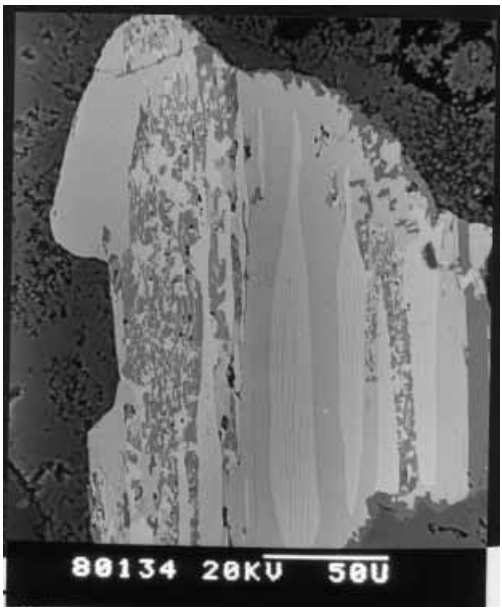

Plate 1.5. A haematite grain (very little Ti) showing texture relict from an original, intergrown magnetite-ulvospinel grain (cf. Plate 1.3). This typical 'martite texture' is a common fingerprint for oxidation either during transport or diagenesis. Back-scattered electron micrograph of a polished section, reefal carbonate, Quaternary Shagara Formation, Egypt (Photo: M. Hounslow).

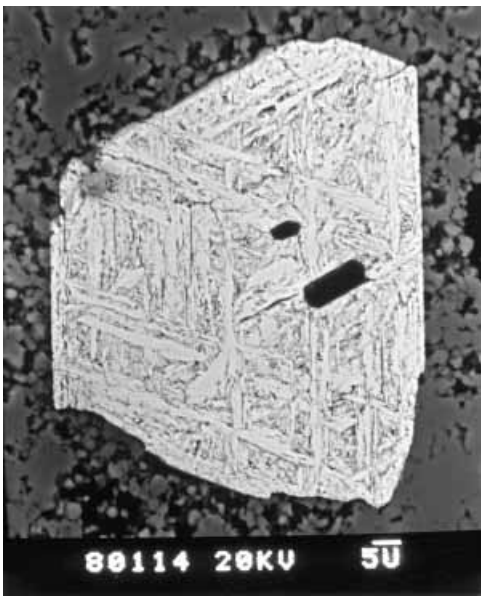

Plate 1.6. Composite grain of Ti-haematite (bright), ilmenite (mid grey) and rutile (dark), showing typical ilmenohaematite high temperature oxidation (tiger-striping), derived from an igneous or metamorphic source. The haematite exsolution is present as several sizes and generations of exsolution lamellae. The rutile-haematite intergrowth has a less organized texture. Back-scattered electron micrograph of a polished section, through a martite, with ilmenite/haematite intergrowths, from Quaternary Shagara Formation, Egypt (Photo: M. Hounslow).

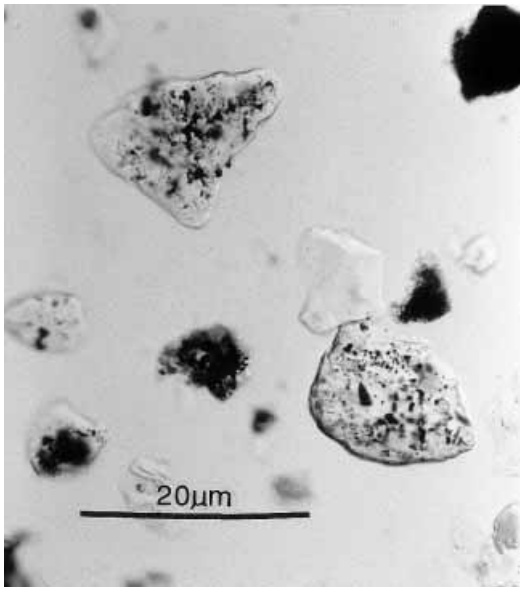

Plate 1.7. Optical micrograph of Fe-oxide particles (inferred to be magnetite) included within host quartz grains. Note the variable size and inclusion density within the different grains; from Quaternary pelagic ooze, Ocean Drilling Program Site 722B, Indian Ocean (Photo: M. Hounslow).

Plates 1.8–1.13 Biogenic magnetic components

Plate 1.8. is in colour plates section.

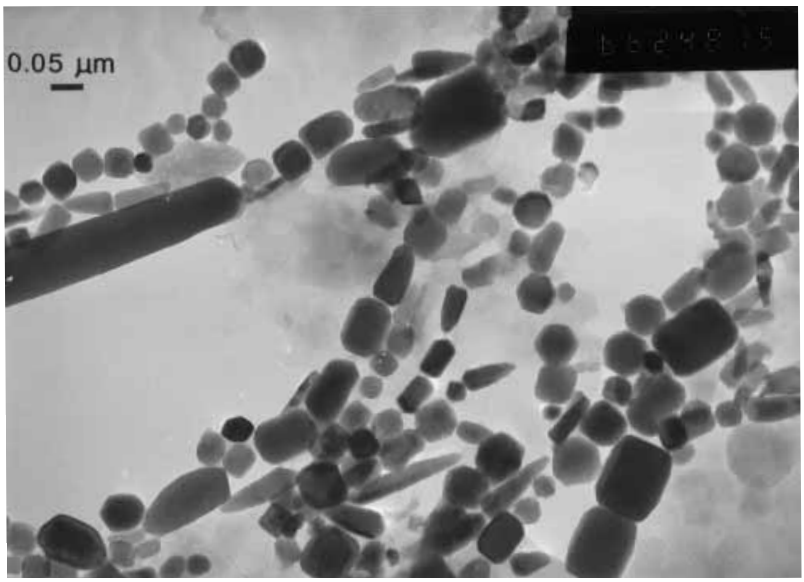

Plate 1.9. Transmission electron micrograph of bacterial magnetosome chains, formed intracellularly by magnetotactic bacteria. This sample contains four-sided, eight-sided and bullet-shaped magnetosomes, as well as rather unusual, highly elongate blade-shaped grains. Note the large range in grain size of the magnetosomes. The smallest grains do not display such well crystalline form (some are irregular), probably as a result of some *in situ* dissolution. Quaternary hemi-pelagic ooze, ODP Site 1006D, the Bahamas (Photo: M. Hounslow).

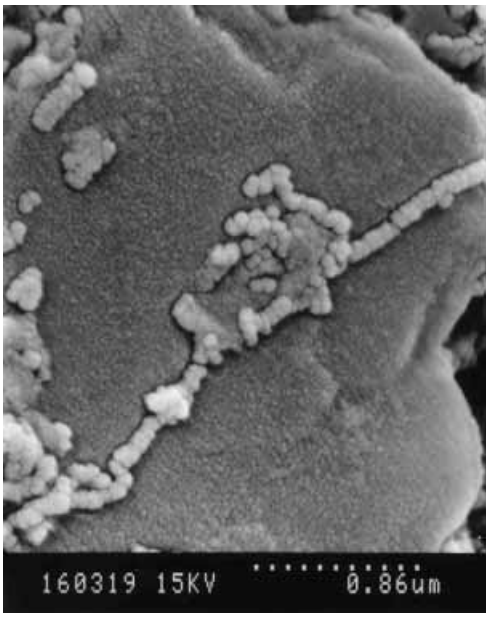

Plate 1.10. Bacterial magnetosome chain (of mostly octahedral grains – confirmed by TEM) on a clay particle. The granularity on the clay particle and on the chain is due to the gold coat on the sample, necessary for the SEM observation. Field emission electron micrograph, Cretaceous Chalk, Culver Cliff, UK (Photo: M. Hounslow).

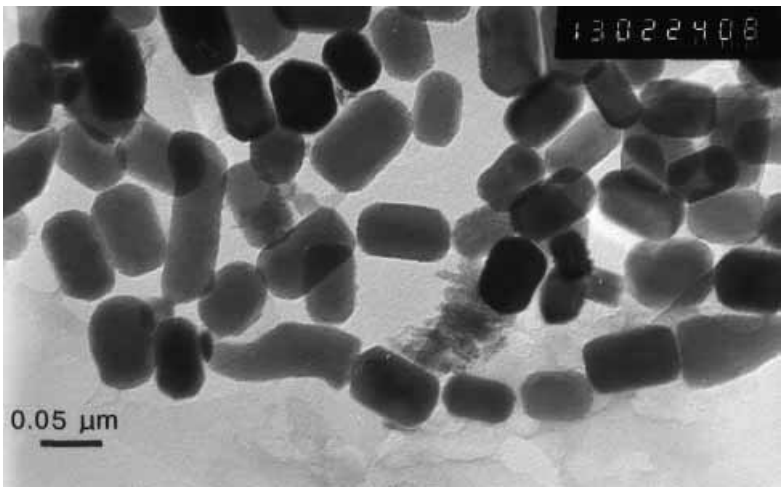

Plate 1.11. Transmission electron micrograph of magnetosomes mostly with eight-sided forms (prismatic), although some have distinctive 'boot' and 'bullet' morphologies. From Cretaceous chalk, Culver Cliff, UK (Photo: M. Hounslow).

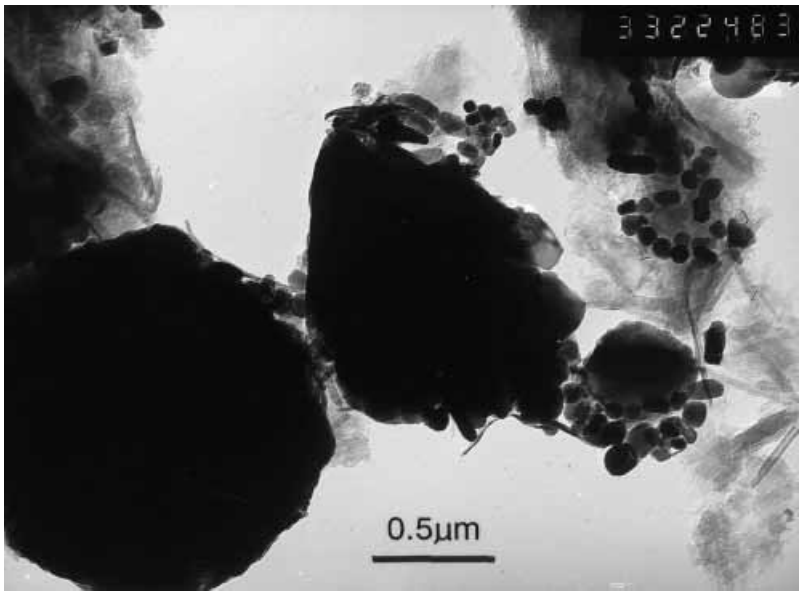

Plate 1.12. Transmission electron micrograph of clastic titanomagnetites (large opaque grains), bacterial magnetosomes (smaller satellite grains) and goethite (?) or clay laths, from Quaternary pelagic ooze, ODP Site 722B, Indian Ocean (Photo: B. Maher).

Plate 1.13. Bacterial magnetosomes (smallest opaque grains), barytes ($BaSO_4$) crystals (large rounded, opaque particles)and siliceous radiolarian spine (large, porous, elongate fragment). This magnetic extract is rich in barytes, which we infer has been extracted due to the presence of magnetic inclusions (which cannot be imaged in TEM) within the barytes crystals. The siliceous fragments are present in the extracts due to enmeshed magnetosome grains. From Quaternary pelagic ooze, ODP Site 709, Indian Ocean (Photo: B. Maher).

Plates 1.14–1.17 Pedogenic (soil-derived) and synthetic magnetic components

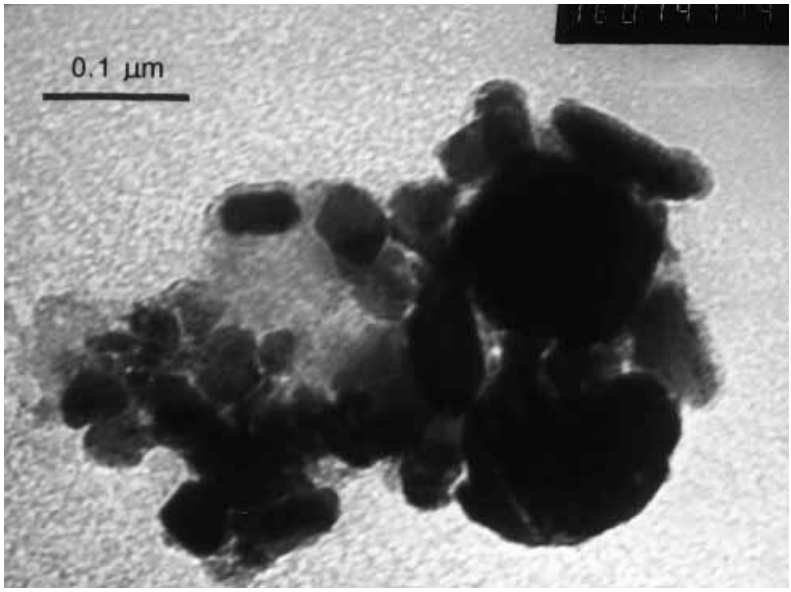

Plate 1.14. Transmission electron micrograph of ultrafine magnetic grains of variable grain size from palaeosol S_1 from the Chinese Loess Plateau (Photo: B. Maher).

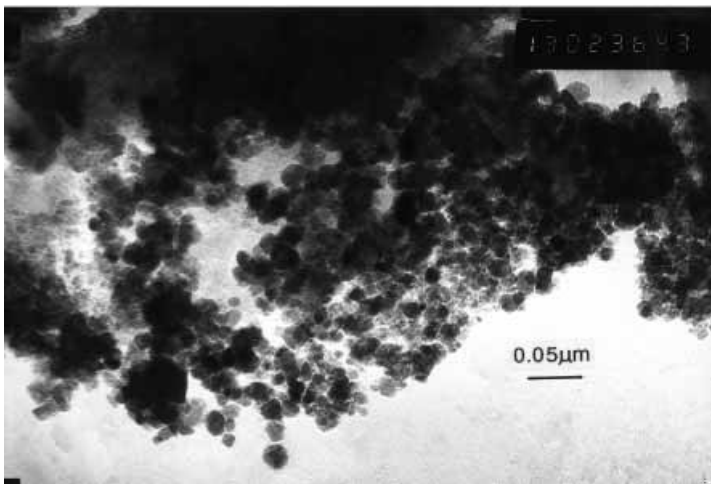

Plate 1.15. Transmission electron micrograph of clusters of ultrafine magnetic grains from a modern soil profile (a cambisol/brown earth), Exmoor, UK (Photo: B. Maher).

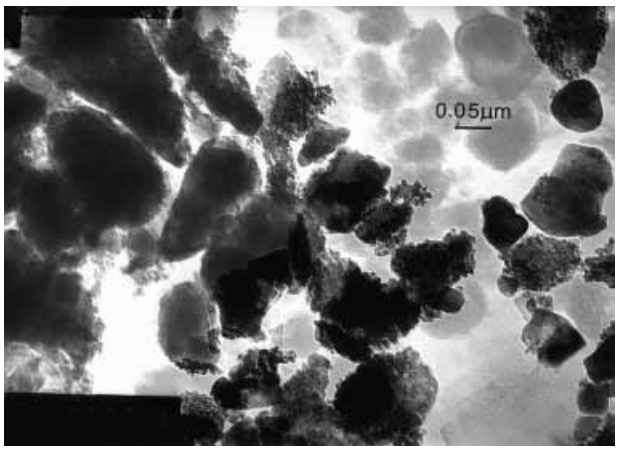

Plate 1.16. Transmission electron micrograph of superparamagnetic grains adhering to slightly larger magnetic grains, from palaeosol S_1, Chinese Loess Plateau (Photo: B. Maher).

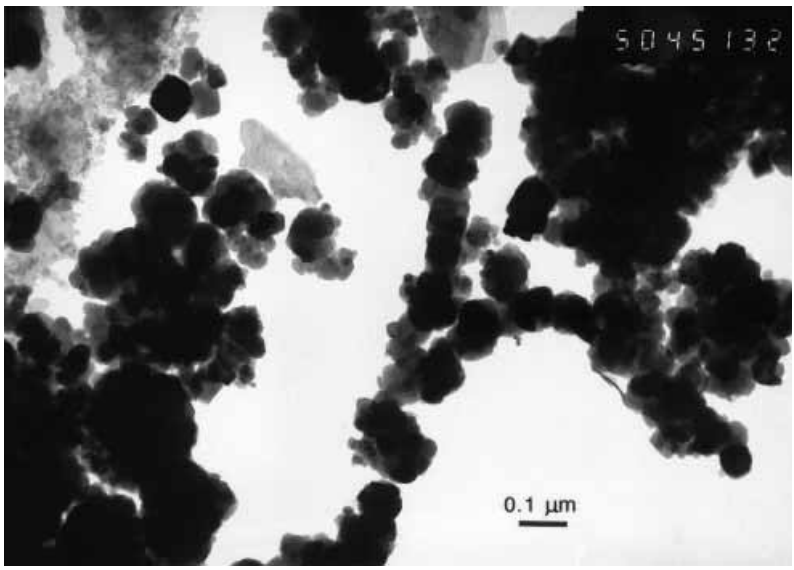

Plate 1.17. Transmission electron micrograph of a synthetic magnetite, formed at room temperature by controlled oxidation of an initially anoxic Fe^{2+}/Fe^{3+} suspension (Taylor *et al.*, 1987) (Photo: B. Maher).

Plates 1.18–1.20 Haematite and goethite

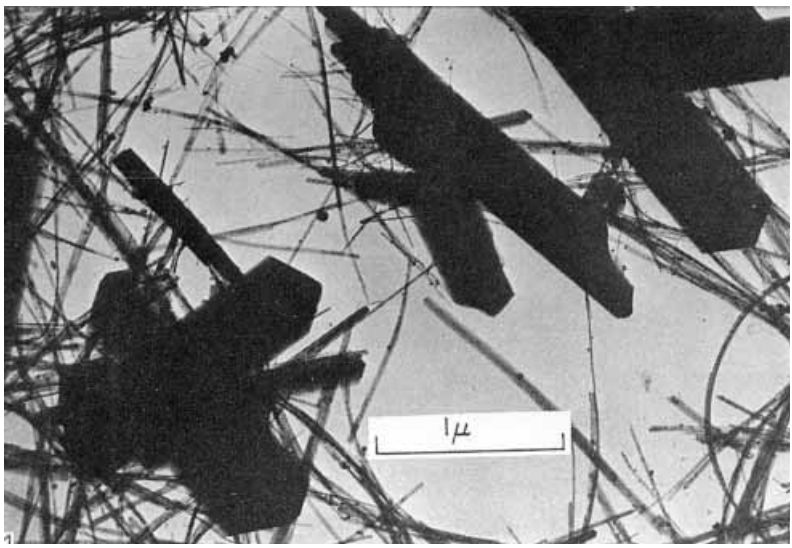

Plate 1.18. Transmission electron micrograph of synthetic goethite (narrow laths) formed from lepidocrocite (Schwertmann & Taylor, 1972).

Plate 1.19. Transmission electron micrograph of synthetic goethite laths formed from controlled oxidation of an initially anoxic Fe^{2+}/Fe^{3+} suspension (Taylor *et al.*, 1987). (Photo: B. Maher).

Plate 1.20. Scanning electron micrograph of specular haematite rosettes on surface of smectite, Cutler Formation, Lisbon Valley, Utah (Photo: R. Reynolds *et al.*, 1985).

Plates 1.21–1.22 Cosmic spherules

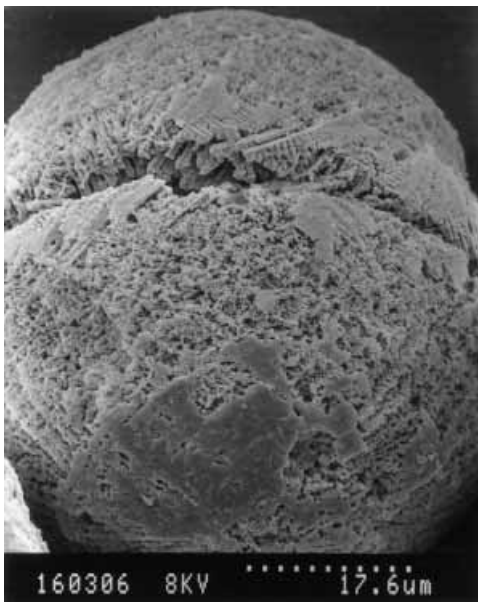

Plate 1.21. Cosmic spherule with extensive and characteristic pitting of the grain surface. The grain is mostly composed of silicate material, with dendrites of Fe-rich material (inferred to be magnetite). The pitted surface is probably due to the progressive dissolution during burial of an original crust of silicate glass (some patches of this still adhering to surface). Scanning electron micrograph, from Quaternary pelagic ooze, ODP Site 709, Indian Ocean (Photo: M. Hounslow).