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Iron oxide formation in the active oxidation front above sapropel S1 in the eastern Mediterranean Sea as derived from low-temperature magnetism

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SUMMARY

Low-temperature magnetic properties of eastern Mediterranean sediments from a box-core have been investigated. This box-core contains the present-day oxic–suboxic boundary that is situated at the top of the relic of the youngest sapropel (S1). The upper half of sapropel S1 has been oxidized, and Fe oxides have precipitated in the oxidized sapropel. Zero-field-cooling (ZFC) and field-cooling (FC) saturation remanent magnetization (M_r; induced in a field of 2.5 T at 20 K after cooling from 300 K with or without the 2.5 T field) was measured during warming to 300 K. An M_r imparted at room temperature (RTSIRM) was cycled to 20 K as well. The difference between ZFC and FC curves around the Verwey transition, as estimated by the parameter $\delta_\mathrm{FC}/\delta_\mathrm{ZFC}$, suggests the presence of magnetosomes in the oxidized part of the sapropel. We propose a new parameter $D = (\bar{M}_\mathrm{r,FC}^{150-300\,\mathrm{K}} - \bar{M}_\mathrm{r,ZFC}^{150-300\,\mathrm{K}})/M_\mathrm{r,FC}^{300\,\mathrm{K}}$, where $\bar{M}_\mathrm{r,(Z)FC}^{150-300\,\mathrm{K}}$ represents the average remanence between 150 and 300 K, to estimate the difference between ZFC and FC curves above the Verwey transition. This is interpreted as being indicative of the number of defects and the extent of partial maghemitization. At the oxic–suboxic boundary where Fe oxides actively precipitate, the magnetite appears to be least maghemitized as inferred from low values for D. Further upward in the oxidized sapropel, in older precipitates, the magnetite is slightly more maghemitized. Just below the sapropel, maghemitization is most pronounced. In addition, the initial slope of ZFC and FC curves indicates that small grains or grain coatings that are superparamagnetic at room temperature (SP), are enriched at the oxic–suboxic boundary. Higher in the oxidized sapropel, the relative contribution of SP grains decreases, presumably because they age to larger grains.

Key words: geochemistry, low-temperature magnetism, magnetite, marine sediments, oxidation, sediment magnetism.

1 INTRODUCTION

The natural remanent magnetization (NRM) carried by marine sediments is controlled by several physical and chemical processes that act during and after deposition. The intensity of NRM depends not only on the ambient magnetic field, but also on the mineralogy, grain-size distribution and concentration of magnetic particles in the sediments. The type of magnetic grains in a sediment can be diagnosed by its magnetic properties, which provides information on the environment during and after deposition. Detailed knowledge of the factors and processes that influence sedimentary magnetic records is essential to understanding these archives of Earth's history.

Iron oxides are the primary magnetic carriers in sediments. These minerals are particularly affected by diagenetic redox reactions in the sediment. A number of different redox processes are important for the iron mineralogy of cyclically deposited organic-rich/organic-poor sediments such as those in the eastern Mediterranean. In this basin, organic-rich layers (sapropels) formed periodically (Fig. 1). Sapropels were anoxic/sulphidic during deposition, and reductive dissolution and subsequent pyritization of Fe oxides in this period caused a decrease of magnetic intensities, in particular, below sapropels (Dekkers *et al.* 1994; Langereis *et al.* 1997; van Santvoort *et al.* 1997; Passier *et al.* 1998; Roberts *et al.* 1999). In addition, formation of a ferrimagnetic Fe sulphide may have caused an increase of magnetic intensities in some sapropels (Roberts *et al.* 1999). Reoxygenation of the bottom water marks the end of sapropel formation, and the sapropel becomes buried under oxic sediments. Directly after burial, oxidation starts to affect the top of a sapropel. Fe oxides precipitated during this oxidation cause higher magnetic intensities (Fig. 1; Dekkers *et al.* 1994; Langereis *et al.*

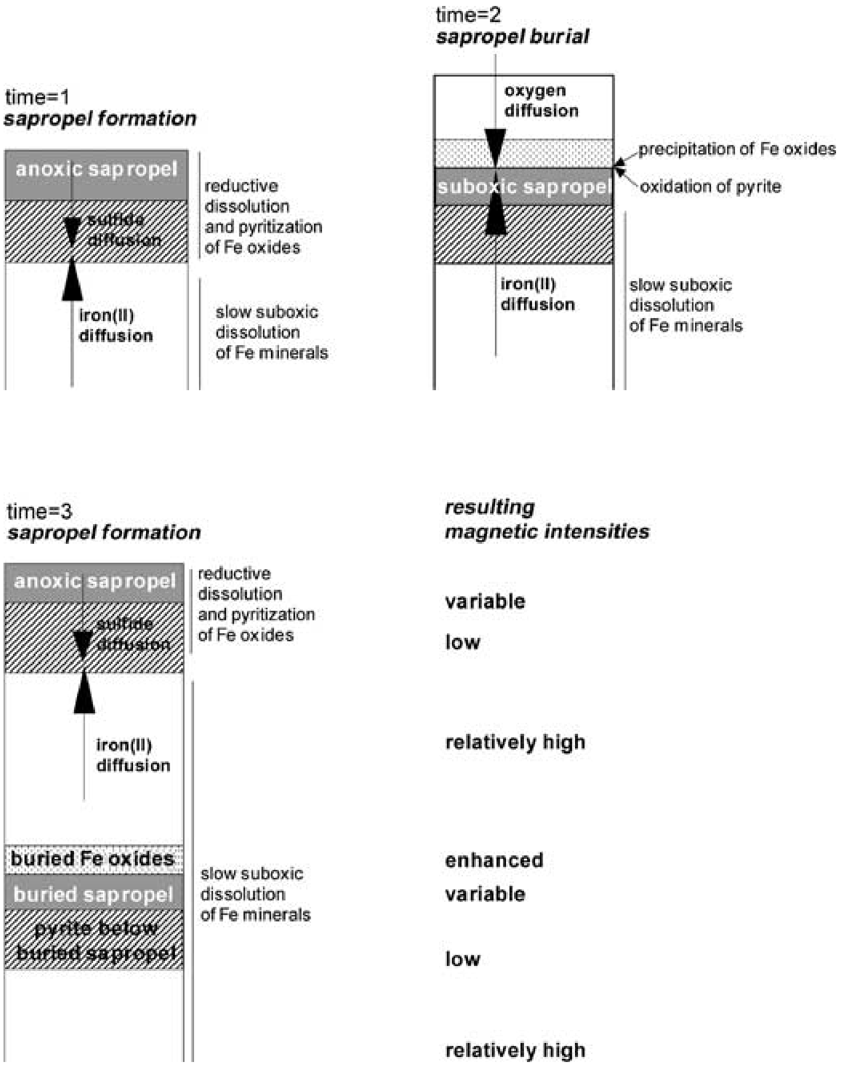


Figure 1. Schematic representation of the most important diagenetic processes for the magnetic mineralogy during sapropel formation (Passier *et al.* 1996, 1997), sapropel burial (Higgs *et al.* 1994; van Santvoort *et al.* 1996), formation of a new sapropel on top of a buried sapropel and the resulting magnetic intensities. Sapropels were anoxic/sulphidic during deposition, and reductive dissolution and subsequent pyritization of Fe oxides in this period caused a decrease of magnetic intensities in and below the sapropel. Directly after burial, oxidation can affect the top of a sapropel, and Fe oxides precipitated during oxidation cause higher magnetic intensities (Dekkers *et al.* 1994; Langereis *et al.* 1997; van Santvoort *et al.* 1997; Passier *et al.* 1998). In addition, formation of a ferrimagnetic Fe sulphide in sapropels may have caused an increase of magnetic intensities (Roberts *et al.* 1999). This figure is adapted from Langereis & Dekkers (1999).

1997; van Santvoort *et al.* 1997; Passier *et al.* 1998). Oxidative diagenesis following reduced conditions has also been reported for Madeira and Cape Verde abyssal plain sediments in turbidites that are enriched in organic carbon (e.g. Sahota *et al.* 1995; Robinson *et al.* 2000; Robinson & Sahota 2000; Robinson 2001). This type of diagenetic sequence is termed redoxomorphic diagenesis by the aforementioned authors. A geochemical study by Thomson *et al.* (1998) also revealed resemblances between the turbidite setting and the sapropel setting discussed here. Biological mediation to explain distinct magnetic properties in confined zones directly above the iron redox front has been put forward by Karlin *et al.* (1987) and Robinson *et al.* (2000). Also Schwartz *et al.* (1997) infer magnetotactic bacteria in carbonate-rich surficial sediments of the Blake/Bahama outer ridge that show high magnetic intensities. In the Bahama/Blake environment, Schwartz *et al.* (1997) argue that the magnetosome-derived magnetite would be less important in deeper carbonate-poor sediments. The authors argue that magnetosomes would be unimportant in the clastic sediments but dissolution of the magnetosomes is not ruled out. The presence of magnetosome-derived magnetite is inferred in open ocean settings as well, referred to by Tarduno & Wilkison (1996) as chemical lock-in. Sediment ages vary from a few tens of thousands to a few hundred thousand years, testifying to the significance of recognizing redox fronts for paleomagnetic interpretation (Tarduno & Wilkison 1996; Tarduno *et al.* 1998).

A detailed study of the magnetic properties at and above room temperature within and around the youngest sapropel (S1; Passier *et al.* 2001) showed that the magnetic properties of the sediments have been considerably affected by reductive dissolution and precipitation of Fe oxides. Oxidation after sapropel deposition has produced Fe oxides that have relatively high coercivity and that carry a relatively high anhysteretic remanent magnetization (ARM). High coercive phases associated with redox fronts were also reported by, for example, Tarduno (1995), Tarduno & Wilkison (1996) and

Robinson & Sahota (2000). Several down-core changes in magnetic properties are associated with variations in grain size and mineralogy, suggesting that there is a sequence of processes leading to the formation of Fe oxides in the oxidized sapropel.

Low-temperature measurements of magnetic remanence can provide detailed information on the presence of minerals that undergo magnetic transitions at low temperatures: magnetite (Verwey transition at 110–120 K; Verwey 1939), pyrrhotite (34 K transition; Dekkers *et al.* 1989), hematite (Morin transition at 250–260 K; Morin 1950), and siderite and rhodochrosite (Néel temperatures 30–40 K; Housen *et al.* 1996). In addition, low-temperature measurements reveal information on the distribution of grains that are superparamagnetic (SP) at room temperature (Banerjee *et al.* 1993), the presence of fossil magnetosomes (Moskowitz *et al.* 1993), and possibly on the extent of partial maghemitization of magnetite (Smirnov & Tarduno 2000, 2001). Smirnov & Tarduno (2001) propose that measurement of the time dependence of remanent coercivity at room temperature with an alternating gradient magnetometer would yield a better estimate of the content of SP particles than low-temperature measurements. However, while it is true that room-temperature measurements are not influenced by low-temperature unblocking of phases that are paramagnetic at room temperature, the measured viscosity effect is entirely modelled in terms of superparamagnetism of discrete particles. This approach may not always be fully justified since magnetically coupled cores and rims with a different composition could produce viscous effects as well. As already noted by Smirnov & Tarduno (2001) small SP particles with a relaxation time smaller than the measurement time would escape detection.

Previous studies of low-temperature magnetic remanence around the oxic–suboxic redox boundary in marine sediments have mainly focused on relatively homogeneous (hemi)pelagic settings with the oxic–suboxic boundary at a few metres below the seafloor (Torii 1997; Urbat & Dekkers 1999; Smirnov & Tarduno 2000). In the western Mediterranean Sea (Torii 1997) and in the western equatorial Pacific Ocean (Tarduno 1995; Tarduno & Wilkison 1996; Tarduno *et al.* 1998; Smirnov & Tarduno 2000), the main conclusion of these studies was that the Verwey transition is only evident below the oxic–suboxic boundary. It is argued that primary magnetite is partially maghemitized by low-temperature oxidation processes in the uppermost sediments, so that no Verwey transition is observable there. Further down, in the suboxic zone, the maghemite coatings dissolve and the Verwey transition is observable again. Tarduno (1995) observed that at the Fe redox boundary enhanced superparamagnetism coincides with a decrease in coercivity, which is interpreted as coarsening of the remanence-carrying grains. Deeper in the core of that study, he noted a gradual increase in superparamagnetism below the HS^- front where sulphate reduction becomes active. Size reduction of coarse magnetite grains leads to enhanced superparamagetism just before complete removal of these grains. In Peru Basin sediments, an NRM overprint was reported from secondary magnetite formed below the oxic–suboxic boundary, which showed the Verwey transition (Urbat & Dekkers 1999).

Here we discuss the low-temperature remanence properties of eastern Mediterranean sediments that contain sapropel S1 and the present-day boundary between oxic and suboxic sediments. In contrast to the (hemi)pelagic sediments discussed above, the present-day suboxic sediments were previously anoxic during deposition of S1. Thus, a characterization of the magnetic properties as a function of diagenetic conditions is possible over the complete redox interval from (sub)oxic to post-oxic.

2 MATERIALS AND METHODS

2.1 Eastern Mediterranean sediments

The most recent organic-rich sediment layer in the eastern Mediterranean Sea (sapropel S1) was deposited between 9 and 6 ka BP. This period was characterized by a relatively wet climate during a precession-induced insolation maximum. The wet climate is thought to have caused enhanced productivity and increased preservation of organic matter (e.g. Rossignol-Strick *et al.* 1982; Calvert *et al.* 1992; Rohling 1994; Rossignol-Strick 1999). S1 is usually a few centimetres thick and is situated a few decimetres below the sediment–water interface. Anoxic sulphidic conditions during deposition of the sapropel from 9 to 6 ka BP caused reductive dissolution of iron oxides and pyritization in the sapropel and sediments directly below S1. This pyritized zone below the sapropel can be up to a few decimetres thick (Passier *et al.* 1997). From 6 ka BP until present, an oxidation front has been situated at the top of the organic-rich layer of S1, dividing oxic surface sediments and underlying sediments that are currently suboxic. As a result of oxidation of organic carbon and pyrite at the oxidation front, the sapropel has become progressively thinner and the sediments immediately above the sapropel have become enriched in Fe oxides (Higgs *et al.* 1994; van Santvoort *et al.* 1996). The centimetre-wide zone of active oxidation, where dissolved Fe^{2+} is transformed into Fe oxides, is situated in the top of the organic-rich layer. The upper boundary of this zone is the Mn-redox boundary (MnRB), and the lower boundary is the Fe-redox boundary (FeRB). Above its redox boundary, the metal is oxidized and immobilized as an oxide, while below its redox boundary a metal is reduced into a dissolved mobile form.

2.2 Samples

Box-core BC19 (35 cm long) was recovered in the Herodotus Abyssal Plain (33°47.8′N, 28°36.4′E, water depth 2750 m) in the eastern Mediterranean Sea during the 1991 MD69-Marflux expedition with R/V Marion Dufresne. In BC19, S1 contains at maximum 3.9 wt per cent C_{org} (Passier *et al.* 2001); the organic-rich layer is preceded by grey oozes and is followed by cream to brown Pteropod-rich ooze. Furthermore, the ash layer of the Minoan Eruption of Santorini (3.6 ka BP) is present in BC19. A subcore that had been sealed air-tight and stored vertically at 4 °C, was subsampled in 1998 at a resolution of 5 mm. The sediment was freeze-dried and pulverized in an agate mortar.

2.3 Earlier rock-magnetic measurements at and above room temperature

Earlier magnetic measurements (Passier *et al.* 2001) from box-core BC19 (see also Fig. 2) suggested a number of transformations in the magnetic fraction of the sediments. Below, we summarize the main findings of this research. The dominant magnetic mineral throughout the core is (maghemitized) magnetite. The sediments received variable amounts of single-domain (SD) to pseudo-single-domain (PSD) magnetite grains from aeolian dust. The reductive dissolution of Fe oxides and pyritization that took place predominantly during sapropel formation, resulted in lower magnetic intensities, a coarser magnetic grain size and slightly higher magnetic coercivities (possibly caused by maghemitization). These manifestations of magnetic dissolution are clear in the pyritized zone below S1. The sapropel itself, in which reductive dissolution was also important, seems to contain another magnetic phase, perhaps a ferrimagnetic

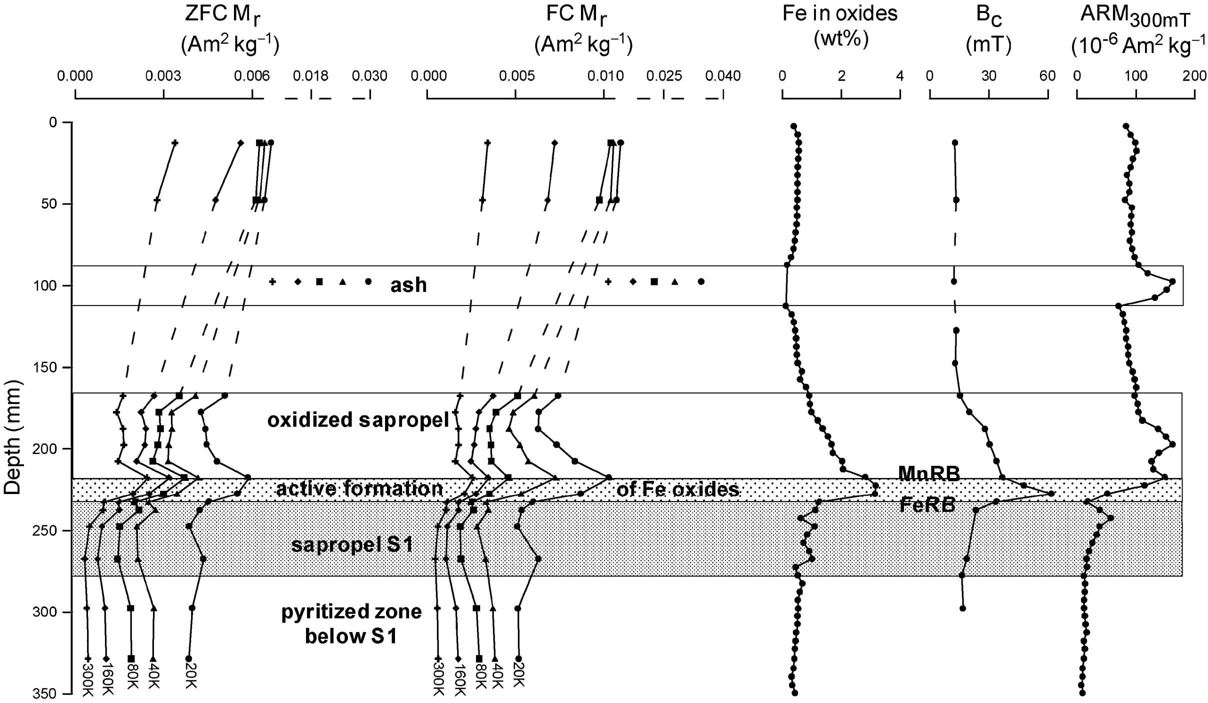


Figure 2. Zero-field-cooled M_r and field-cooled M_r at 20, 40, 80, 160 and 300 K versus depth, and Fe in oxides, B_c (room temperature), and ARM$_{300\,\mathrm{mT}}$ (room temperature) versus depth in box-core BC19. Fe in oxides was calculated from total Fe minus pyritic Fe, and was corrected for an estimated background value of Fe depending on Al, which presumably resides in aluminosilicates. Fe in oxides was not calculated in the ash layer, because background Fe is unknown here (see Passier *et al.* 2001, for details on the latter three parameters). Note the different scale of the dashed part of the x-axis. MnRB: manganese redox boundary; FeRB–Fe redox boundary.

Fe sulphide, that masks the magnetic expressions of reductive dissolution. Ongoing oxidation after sapropel deposition has produced Fe oxides with relatively high coercivity that carry a relatively high ARM in a ~10 cm thick interval on top of the organic-rich layer.

Changes in magnetic properties of these sediments suggest that there is a sequence of processes and products leading to the formation of Fe oxides at the oxidation front. The first sign (i.e. that occurs deepest in the cores) of oxidation is a lower ARM in the upper part of the organic-rich interval, possibly caused by oxidation of the magnetic Fe sulphide phase in the sapropel and formation of SP or amorphous Fe oxides. A second population of extremely high-coercivity grains is present at the site of active oxidation at the top of the sapropel, as evident from wasp-waisted hysteresis loops. These high-coercivity grains may be fossil magnetosomes, which are high-coercivity SD magnetite grains. They occur in the oxidized sapropel, in the setting where, for example, Karlin *et al.* (1987), Tarduno & Wilkison (1996), Robinson & Sahota (2000), Robinson *et al.* (2000) and Kruiver & Passier (2001) argue for biological mediation of chemical precipitation of iron oxides, sometimes referred to as bioauthigenesis. Higher in the oxidized sapropel (i.e. in older precipitates) the distinction between these two coercivities disappears and the freshly precipitated Fe oxides age to slightly lower-coercivity SD grains.

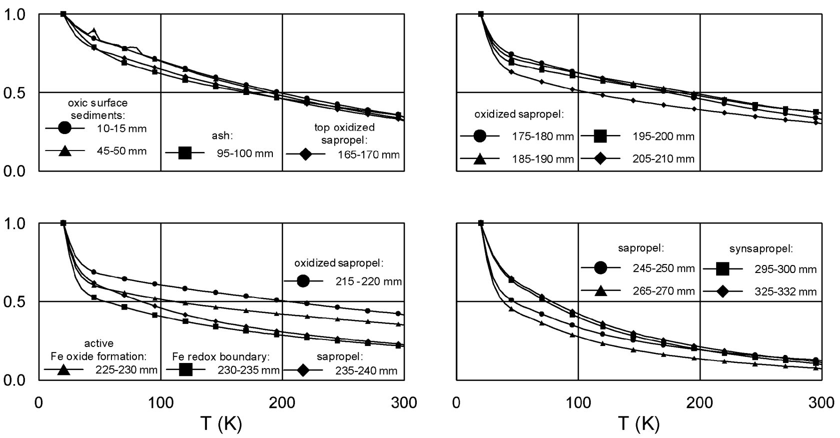
2.4 Low-temperature magnetic measurements

Low-temperature magnetic measurements were performed with a superconducting, Quantum Design MPMS 5S susceptometer at the Institute for Rock Magnetism in Minneapolis, USA. The sensitivity of this device is 1×10^{-11} A m^2, and our measurements are all three to six orders of magnitude higher. The instrument was used with a sweep rate of 5 K min^{-1} and a maximum field of 2.5 T. Of 16 samples from BC19, 100–200 mg of sediment was weighed into a gelatin capsule. The capsule was placed in a plastic drinking straw that served as a sample holder. Results of three types of low-temperature measurements are discussed here. These measurements were performed on the subset of 16 samples in the following order: (1) zero-field-cooled (ZFC) measurements, whereby a sample was cooled from room temperature to 20 K in a zero field, subsequently, a field of 2.5 T was applied at 20 K, switched off and the saturation remanent magnetization (M_r) was measured during continuous warming to 300 K at 5 K intervals. (2) Field-cooled (FC) measurements, whereby a sample was cooled to 20 K in a field of 2.5 T, at 20 K the field was switched off and subsequently M_r was measured during continuous warming to 300 K at 5 K intervals. (3) Room-temperature saturation isothermal remanent magnetization (RTSIRM) measurements on four of the 16 samples, whereby a 2.5 T field was applied to a sample at 300 K, and M_r was measured at 5 K intervals upon continuous cooling to 20 K and subsequent continuous warming back to 300 K.

3 RESULTS

The remanence curves show distinct variations with depth, associated with different diagenetic zones. Variations in magnitude of the remanence with depth can largely be attributed to the Fe-oxide content (Fig. 2). The characteristic features of the remanence curves are expressed in a plot where the magnetization is normalized, so that the content of magnetic Fe oxides does not affect the curves (Fig. 3). In addition, the first derivative of the remanence curves (Fig. 4) indicates that the extent of the decrease in magnetization up to 100 K is the most prominent difference between the curves. In the top of

(a) Zero Field Cooled, normalized M_r



(b) Field Cooled, normalized M_r

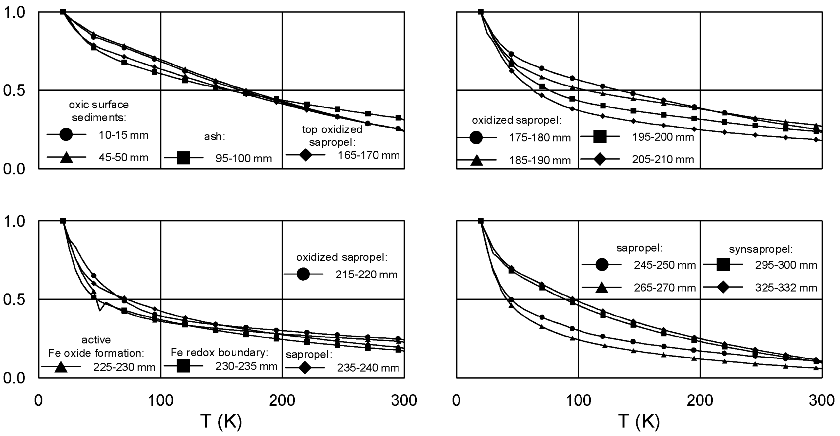
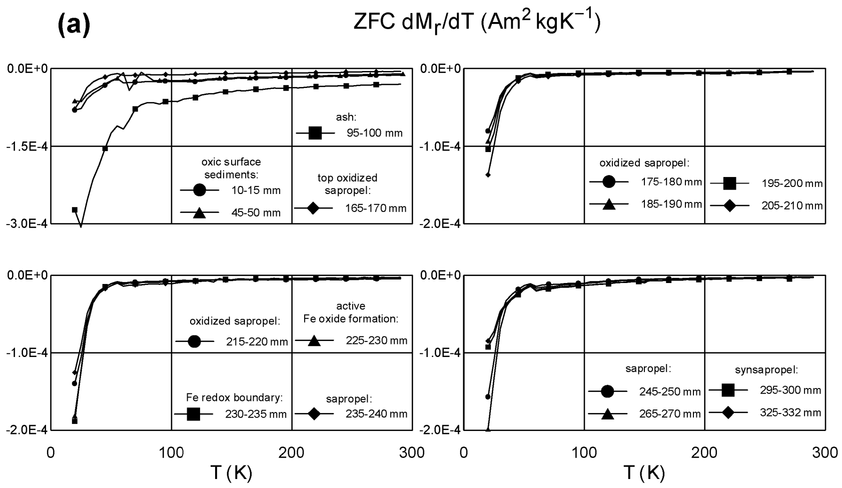


Figure 3. Normalized M_r versus T in samples from different sedimentary zones (oxic surface sediments, ash layer, oxidized sapropel, zone of active Fe oxide formation, Fe redox boundary, sapropel and pyritized zone below S1) in BC19. Symbols are plotted every fifth data point. (a) Zero-field-cooled data; (b) field-cooled data.

the sediment (above the Mn-layer that marks the top of the original sapropel), where no diagenetic Fe oxide formation and/or no reductive dissolution of Fe oxides has yet taken place, the decrease with increasing temperature at low temperatures is least steep (Fig. 4). The magnetization reaches half of its initial value at 20 K above 150 K (Fig. 3). In the oxidized sapropel and in the actively oxidizing part of the sapropel, the initial slope of the curves is steeper (Fig. 4) and the original magnetization decreases to half its value at a wide range of temperatures (50–200 K), on average below 150 K (Fig. 3). The initial decrease is steepest within the sapropel (Fig. 4), where the magnetization reaches half its original value below 50 K (Fig. 3). In the pyritized zone below S1, the decrease is less steep again, with half the magnetization reached just below 100 K. Variations of the slope at 20 K, the absolute initial slope, are plotted against depth in Fig. 5(a). The relative initial slope, i.e. the slope of the remanence-vs-T curve at 20 K divided by M_r at 20 K, is shown in Fig. 5(b). The relative initial slopes have a local minimum at the site of active oxidation of the sapropel, i.e. at the Fe-redox boundary.

Evidently, the ZFC and FC remanences are highest at 20 K and gradually decrease with increasing temperature (Figs 2 and 3). No distinct drops in remanence occur that may indicate the presence of magnetite, pyrrhotite, haematite, siderite or rhodochrosite. Pyrrhotite cannot occur in oxic sediments and was never reported in and below sapropels. The 'undefined magnetic sulphide' in organic-rich sapropels reported on by Roberts *et al.* (1999) shows more similarities to greigite than to pyrrhotite. Comparatively well-crystalline (six-line) ferrihydrite that is reported to possess a Néel temperature of *c.* 120 K (Zergenyi *et al.* 2000) was not reported in sapropels either. In mixed magnetite–ferrihydrite assemblages detection of ferrihydrite with magnetic means would be complicated by the Verwey transition. Although it cannot be ruled out completely, the presence of poorer crystalline ferrihydrite (two- or four-line) with presumably a lower Néel temperature is unlikely here. It would have been transformed into poorly crystalline haematite during storage as dry powder in air. The shape of the FC and ZFC curves does not hint at the occurrence of siderite, the curves measured here do not show sharp Néel points at *c.* 35 K like those of Housen *et al.* (1996). The same applies to rhodochrosite with a similar Néel point. LT warming curves of some titanomagnetites bear a resemblance to our curves (Moskowitz *et al.* 1998). However, the coercive forces reported by Moskowitz *et al.* (1998) are distinctly lower than the present B_c values (~3.5–7 mT versus ~13 mT). The ash layer has a coercivity very similar to the other surficial sediments, so the occurrence of titanomagnetites in the present samples is unlikely.

There are pronounced differences between the FC and ZFC remanent magnetization curves. These differences are normalized to


(a) ZFC dM_r/dT ($Am^2\,kgK^{-1}$)

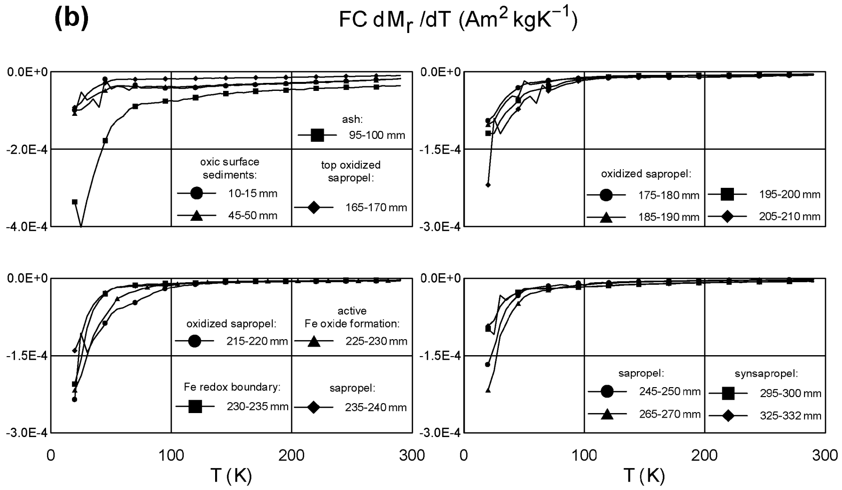

(b) FC dM_r /dT ($Am^2\,kgK^{-1}$)

Figure 4. dM_r/dT versus T in samples from different sedimentary zones (oxic surface sediments, ash layer, oxidized sapropel, zone of active Fe oxide formation, Fe redox boundary, sapropel, and pyritized sone below S1) in BC19. Symbols are plotted every fifth data point. (a) Zero-field-cooled data; (b) field-cooled data.

FC M_r at 20 K in Fig. 6. The largest differences between FC and ZFC curves are found below ~100 K. The curves converge towards 300 K. The differences are especially pronounced within the oxidized part of the sapropel.

The only significant feature in the curves produced by cooling and subsequent warming of an RTSIRM (Fig. 7) is the Verwey transition at ~120 K. This transition is only present in a sample from the top of the core, and is not present in samples from within the oxidized zone of the sapropel. Its expression in the warming curves of the 20 K remanence of the sample is very subdued, if present at all, in contrast with observations by Vigliotti *et al.* (1999) in C_{org}-enriched layers in the Western Mediterranean. Cycling of an RT-induced IRM seems to be more suited to tracing subtle expressions of the Verwey transition than warming of a LT remanence.

4 DISCUSSION

The behaviour of LT warming curves is an interplay between unblocking of very fine iron oxide particles (e.g. Banerjee *et al.* 1993; Smirnov & Tarduno 2000, 2001), possible compositional gradients between cores and rims of particles causing non-stoichiometric structures, which may lead to prominent surface effects, particularly in fine grains (Tronc *et al.* 2000), and magnetic interaction (Pike *et al.* 2000). Magnetosome magnetite plays a role as well (Karlin *et al.* 1987; Moskowitz *et al.* 1993; Passier *et al.* 2001; Kruiver & Passier 2001). These aspects will be addressed in the following.

4.1 SP grains

Changes in the initial slopes of the FC and ZFC curves versus depth (Fig. 5) are affected mostly by the distribution of very small grains that carry a remanence at low temperatures and that unblock and lose their remanence (becoming SP grains) with increasing temperature (Banerjee *et al.* 1993). The most important SP unblocking occurs below 50 K (Fig. 4), which corresponds to an equivalent particle size (in the case of discrete particles) of ~10 nm by inserting realistic values for M_s and B_c of magnetite at 50 K, and a relaxation time of ~60 s, assuming uniaxial anisotropy and no particle interaction (Dunlop & Özdemir 1997). The steep initial slopes in the zone of active oxidation of the sapropel (Fig. 5), indicate a relatively high content of SP grains in this zone where fresh diagenetic Fe oxides precipitate. This interpretation is in accordance with earlier magnetic hysteresis and ARM observations at room temperature (Passier *et al.* 2001). In the upper part of the oxidized sapropel, the

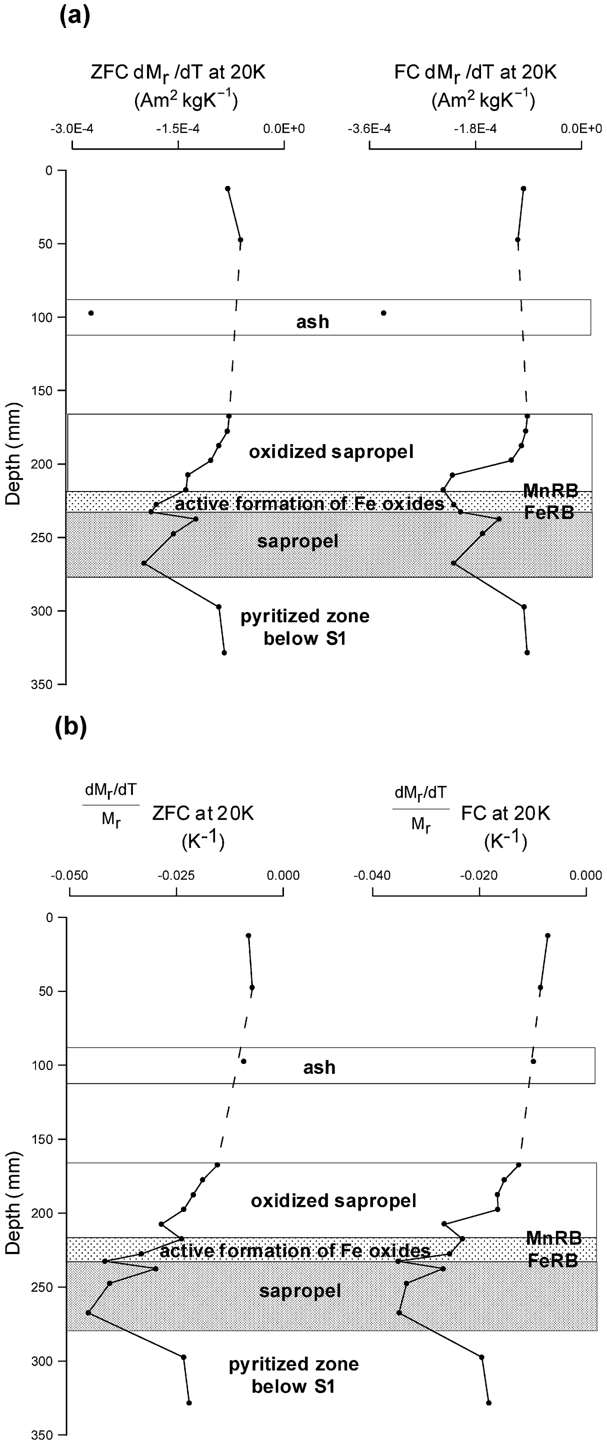


Figure 5. (a) Zero-field-cooled and FC dM_r/dT at 20 K versus depth in BC19 (absolute initial slope). (b) Zero-field-cooled and FC $(dM_r/dT)/Mr$ at 20 K versus depth in BC19 (relative initial slope). MnRB, manganese redox boundary; FeRB, Fe redox boundary. The parameters plotted here indicate the importance of SP grains (see text).

absolute initial slope (Fig. 5a) is less steep, which suggests that there is a lower content of SP grains, which can partly be explained by the lower Fe oxide content (Fig. 2). However, the relative initial slope becomes less steep upward in the oxidized sapropel as well (Fig. 5b). This indicates that SP grains become relatively less important upward in the oxidized sapropel. Thus, the SP grains probably age into larger grains, because the Fe oxides in the oxidized sapropel grow older with distance upwards from the site of active oxidation. The relatively high contribution from SP grains within the sapropel may be caused by the presence of magnetic iron sulphides (Roberts *et al.* 1999; Passier *et al.* 2001).

Although superparamagnetism is an attractive scenario for explaining the observed behaviour, alternative explanations must be assessed as well. These include magnetic interaction, surface effects that may be prominent in very fine particles, and the presence of surface layers around magnetic particles with a composition differing from the particle cores. Pike *et al.* (2000) modelled fine particle magnetic moments with a mean interaction field that is directed oppositely to the M_{rs} direction because interaction tends to demagnetize a magnetic particle ensemble. Their calculations showed that with increasing interaction M_{rs} curves have an increasingly steeper slope at low temperatures. Although magnetic interaction is in itself a relevant aspect, particles have to be spaced very closely to each other for interaction to become truly meaningful (particle spacing must be closer than the diameters of the particles themselves). In dilute magnetic systems such as the present sediments this is unlikely to occur unless newly formed magnetic particles are all intimately associated with existing ones. More plausible aspects that warrant consideration are surface effects in very fine particles and the effects of a coated surface layer around the magnetic particles. For very fine-grained maghemite (3–10 nm) Tronc *et al.* (2000) showed that below *c.* 85 K the surface spin structure is canted. Also 'M_s' (a underestimation of the true M_s as realized by Tronc *et al.* 2000) was shown to increase distinctly with decreasing temperature, in particular, in very fine particles in dilute suspension below 25 K (Tronc *et al.* 2000). This is interpreted as being a result of a surface effect with the surface/volume ratio becoming increasingly important with decreasing particle size. The surface spins are strongly coupled to the core spins. The additional decrease in FC and ZFC remanence warming curves of the oxidized sapropel may be interpreted along similar lines. Tronc *et al.* (2000) also studied phosphate-coated maghemite spinel particles and concluded that the phosphate was adsorbed to the spinel particles and did not form a separate iron phase. The phosphate forms a shell of ~0.3 nm thickness around spinel cores. Mössbauer results indicate that the shell is paramagnetic down to 20 K and magnetically disordered at lower temperatures. For our experiment the magnetic behaviour of a possible coating is therefore not so important. If there is any effect for a (phosphate) coating above 20 K, it would make the particles behave more like bulk particles because the presence of the phosphate coating was also shown to reduce the canting of the surface spin structure, and the increasing high-field susceptibility was notably less.

4.2 Fossil magnetosomes

The difference between the FC and ZFC remanent magnetization curves can also be used to study the presence of fossil magnetosomes (SD magnetite produced intracellularly by magnetotactic bacteria). Moskowitz *et al.* (1993) showed that an FC M_r curve of intact magnetosome chains underwent a marked decrease at the Verwey transition, whereas the ZFC M_r curve underwent a minor decay only. They proposed a ratio, δ_{FC}/δ_{ZFC}, to diagnose the presence of magnetosome chains, where δ is a measure of the amount of remanence lost by warming through the Verwey transition ($\delta = (M_r^{80\,K} - M_r^{150\,K})/M_r^{80\,K}$). Intact chains of unoxidized magnetite magnetosomes have $\delta_{FC}/\delta_{ZFC} > 2$, whereas disruption of the chain structure or conversion to maghemite reduces

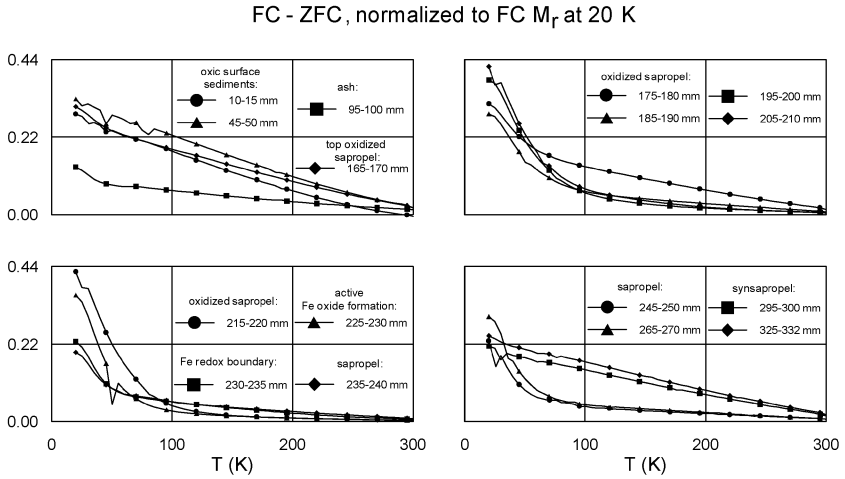


Figure 6. Field-cooled minus zero-field-cooled M_r (FC–ZFC) normalized to field-cooled M_r at 20 K versus T in samples from different sedimentary zones (oxic surface sediments, ash layer, oxidized sapropel, zone of active Fe oxide formation, Fe redox boundary, sapropel, and pyritized zone below S1) in BC19. Symbols are plotted every fifth data point.

$\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ to $\sim$1, which is similar to the value for inorganic magnetite, maghemite, greigite and some extracellularly produced bacterial magnetite. The ZFC and FC curves measured in this study do not show clear evidence of the Verwey transition (Figs 3 and 4), but the parameter $\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ does vary significantly with depth (Fig. 8), suggesting that (fossil) magnetite magnetosome chains are enriched within the oxidized sapropel. Whereas earlier measurements of coercivity suggested that magnetosomes are particularly enriched in the small zone of active oxidation at the boundary between oxic and suboxic sediments (Passier *et al.* 2001; Kruiver & Passier 2001), the present LT results indicate the presence of magnetosomes predominantly in the central part of the oxidized sapropel. Two cautionary aspects should be mentioned here. (1) Surface effects are manifest dominantly below 50 K but may also be present at higher temperatures. (2) The difference between FC and ZFC curves may be underestimated if the magnetosome chains were (partially) disrupted, which could have occurred during sample preparation. These aspects make a quantitative assessment of the amount of magnetosomes difficult. The observed differences between FC and ZFC curves as expressed in $\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ are large though.

The Verwey transition is only present in the uppermost oxic sediment in RTSIRM measurements (Fig. 7). ZFC and FC curves (Fig. 3) do not show the Verwey transition clearly. However, as mentioned before, $\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ (Fig. 8) indicates an increased importance of phenomena within the oxidized sapropel, which may be related to the Verwey transition. These apparent inconsistencies may be explained by the fact that there are different types of grains that show the Verwey transition. The Verwey transition that is observed in the uppermost sediments (Fig. 7) may be caused by stoichiometric

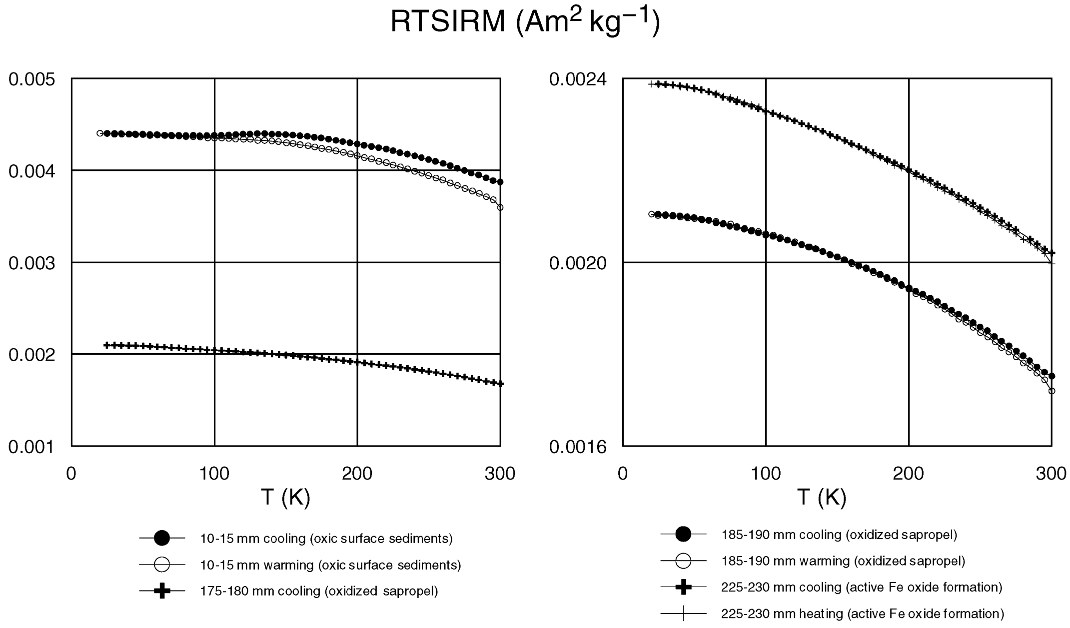


Figure 7. RTSIRM during cooling and subsequent warming versus T in samples from different sedimentary zones (oxic surface sediments, oxidized sapropel, zone of active Fe oxide formation) in BC19.

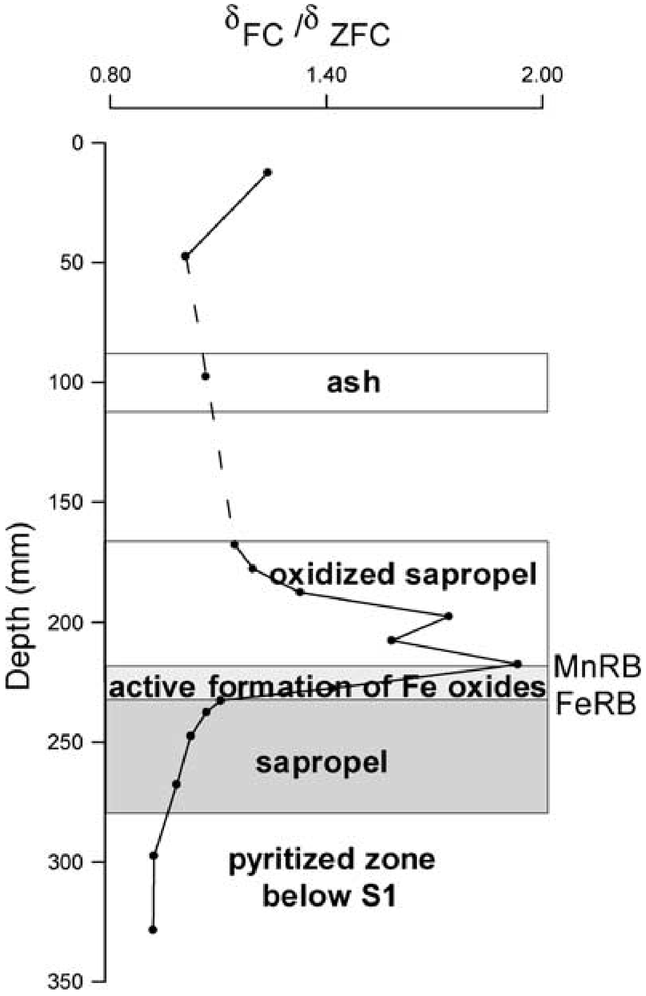


Figure 8. $\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ ($\delta = (M_{\mathrm{r}}^{80\,\mathrm{K}} - M_{\mathrm{r}}^{150\,\mathrm{K}})/M_{\mathrm{r}}^{80\,\mathrm{K}}$) versus depth in BC19. This parameter indicates the relative importance of fossil magnetosomes (see text; Moskowitz *et al.* 1993). MnRB, manganese redox boundary; FeRB, Fe redox boundary.

magnetite, whereas maghemitization suppresses the expression of the Verwey transition (Dunlop & Özdemir 1997). In the (oxidized) sapropel and in the pyritized zone below S1, the original stoichiometric magnetite has been largely reductively dissolved and the remaining magnetite has been partially maghemitized. Keep in mind that anoxic conditions in and below the sapropel ceased to exist upon reoxigenation of the bottom waters when 'normal' sedimentation resumed. However, in the oxidized sapropel, magnetite magnetosomes seem to have formed. Moskowitz *et al.* (1993) pointed out that the Verwey transition is only observable when magnetite magnetosomes are present in chains. Loose magnetosomes from disrupted chains may lack expression of the Verwey transition because the magnetosomes are elongated and elongated grains do not show the Verwey transition (Dunlop & Özdemir 1997). It is envisaged that magnetosome chains, which must be to some extent intact, would cause the elevated $\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ (Fig. 8) in the oxidized sapropel. It remains unclear, however, why similar effects are not visible in the RTSITM curves (Fig. 7). It may be that surficial oxidation is a more important phenomenon than the occurrence of 'intact' magnetosome chains. It should be mentioned that the Verwey transition is only visible in the derivative curves of Vigliotti *et al.* (1999), so the effects are subtle.

4.3 Defects

The FC and ZFC curves converge only far above the Verwey transition (Fig. 6). Therefore, it is evident that the difference between the curves is not only related to whether or not the Verwey transition occurs. The curves converge only at 300 K. This was also observed in pelagic sediments by Smirnov & Tarduno (2000). They argued that this may be related to the fact that PSD particles stabilize to metastable SD grains during cooling in a strong field. This process will be more important when more defects are present in the crystal lattice. Thus, the effect will be greater in oxidized, substantially non-stoichiometric (partially maghemitized) magnetite that has more defects than stoichiometric magnetite. As a result of this stabilization, the initial FC M_{r} is higher at low temperatures. The metastable SD grains return to their initial PSD state during warming, thereby decreasing the remanence. According to this reasoning (Smirnov & Tarduno 2000), the convergence temperature of FC and ZFC curves is the temperature at which the field was switched on for FC measurements during cooling (300 K in this case).

We introduce the parameter D to estimate the relative importance of the difference between FC and ZFC remanent magnetization that is not influenced by the Verwey transition, i.e. between 150 and 300 K, to obtain information on the extent of maghemitization:

$$D = \frac{\bar{M}_{\mathrm{r\,FC}}^{150-300\,\mathrm{K}} - \bar{M}_{\mathrm{r\,ZFC}}^{150-300\,\mathrm{K}}}{M_{\mathrm{r\,FC}}^{300\,\mathrm{K}}}.$$

D is relatively high in the pyritized zone below S1 (Fig. 9), indicating that partial maghemitization may be more important there. The presence of maghemitized magnetite in the pyritized zone below S1 has been concluded from earlier observations of elevated coercivities in these zones where reductive dissolution and pyritization have been important (Passier *et al.* 2001). This partial maghemitization is possibly the result of the preferential diffusion of Fe(II) out of magnetite grains, as Fe(II) is more loosely bound than Fe(III) (Cornell & Schwertmann 1996). As mentioned previously, anoxic conditions ceased when 'regular' sediment started to be deposited. Both aspects have contributed to the partially maghemitized magnetite. D is lowest within the oxidized sapropel (Fig. 9), with a minimum in the zone of active oxidation, suggesting that freshly precipitated magnetite is least maghemitized. Further up in the oxidized sapropel, D is only slightly higher, indicating only little maghemitization during ageing. Consequently, high coercivities (Passier *et al.* 2001, Fig. 2) that were found in the oxidized sapropel, seem to be mainly caused by the presence of magnetosomes and not so much by partial maghemitization of magnetite.

Surface effects may also have consequences for the very fine-grained particles found in the zone of active oxidation. Upon ageing the particles enlarge, thereby reducing the surface-to-volume ratio and thus the surface effect. The magnetite particles are at least surficially maghemitized, which leads to a surface layer that behaves differently from the cores of the particles. Spin canting of the surface layer has been demonstrated for nanoparticles of maghemite, $NiFe_2O_4$ and $CoFe_2O_4$ (Kodama & Berkowitz 1999 and references therein). For ball-milled $NiFe_2O_4$ Kodama & Berkowitz (1999) argue that the magnetically disordered surface spin structure would freeze at *c.* 50 K and also note that the coercivity markedly increases below this temperature and that shifted hysteresis loops occur. They suggest that coupling of the frozen surface spin structure would pin the magnetic structure of the whole particle and make reversal of the core spins more difficult. It is remarkable that FC and ZFC warming curves show the steepest decrease with increasing

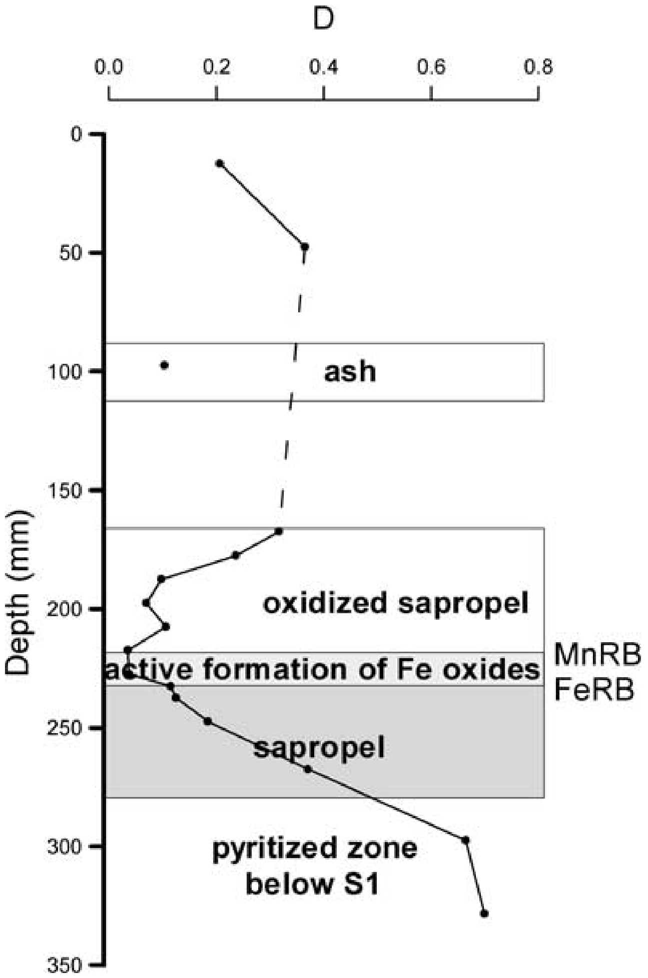


Figure 9. $D = \bar{M}_{\mathrm{r\,FC}}^{150-300\,\mathrm{K}} - \bar{M}_{\mathrm{r\,ZFC}}^{150-300\,\mathrm{K}})/M_{\mathrm{r\,FC}}^{300\,\mathrm{K}}$ versus depth in BC19. This parameter is used to estimate the relative importance of partial maghemitization of magnetite. MnRB, manganese redox boundary; FeRB, Fe redox boundary.

temperature in the oxidized sapropel (Fig. 4) where precipitation of iron oxides has occurred; this decrease levels off at *c.* 50 K as well. Kodama & Berkowitz (1999) also discuss that field cooling may select a surface spin configuration that favours the particles being magnetized in the direction of the applied field. Thus effects of a surface layer that is exchange coupled to the supposedly stoichiometric cores of the particles, could be a cause for the observed differences between FC and ZFC remanences. It could be that in larger particles, which clearly have stable remanences at room temperature, the exchange coupling extends to higher temperatures, even up to room temperature. In the presence of a (large) magnetic field, the surface layer would be magnetically coupled to the cores thereby gaining remanence parallel to the cores when the field is switched off at low temperature, 20 K in the present case. Spin canting in the surface layer that occurs at low temperature, precludes saturation in a 2 T field at 20 K, so the FC and ZFC remanences differ. FC and ZFC differences at these temperatures would then be related to maghemitized surface layers rather than to PSD grains that become metastable SD grains in large fields. To allow discrimination of the effects of a surface layer and effects related to the occurrence of the Verwey transition, the temperature trajectory between 150 and 300 K is selected here.

5 CONCLUSIONS AND IMPLICATIONS

The measurement of low-temperature magnetic properties of sediments provides a valuable tool for investigating the effects of diagenesis on magnetic mineralogy. The shape of ZFC and FC remanent magnetization curves and the divergence between the two curves yield especially useful information. The sediments of this study contain an active oxidation front where Fe oxides form at the present-day oxic–suboxic boundary that is situated in previously (until 6 ka BP) anoxic sapropel sediments. In these sediments there are three main parameters ($(dM_{\mathrm{r}}/dT)/M_{\mathrm{r}}$ at 20 K, $\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ and D) that can be related to the different diagenetic zones. These three parameters each yield different information and are helpful for assessing the magnetic mineralogy. First, the initial decrease with temperature of M_{r} acquired at 20 K indicates that SP grains form at the redox boundary where Fe oxides precipitate. Higher in the oxidized sapropel the relative contribution of SP grains decreases, as they probably age into larger grains. Second, the ratio $\delta_{\mathrm{FC}}/\delta_{\mathrm{ZFC}}$ (Moskowitz *et al.* 1993), which reveals differences between the ZFC and FC remanent magnetization curves around the Verwey transition, suggests the presence of magnetosomes in the oxidized part of the sapropel. Third, the parameter D that we propose, indicates the extent of divergence of the ZFC and FC remanent magnetization curves above the Verwey transition. This divergence could indicate the extent of maghemitization (Smirnov & Tarduno 2000). Following this line of reasoning, the magnetite in the pyritized zone below S1 is relatively maghemitized, and probably resulted from reductive dissolution of Fe oxides and pyritization during deposition of the sapropel or upon re-establishment of suboxic conditions. The freshly precipitated Fe oxides in the zone of active oxidation have the least defects, and thus may be the least maghemitized. Maghemitization increases only slightly upward in the oxidized sapropel, i.e. after ageing of the initial precipitate.

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REFERENCES

Banerjee, S.K., Hunt, C.P. & Liu, X.-M., 1993. Separation of local signals from the regional paleomonsoon record of the Chinese loess plateau: a rock-magnetic approach, *Geophys. Res. Lett.,* **20,** 843–846.

Calvert, S.E., Nielsen, B. & Fontugne, M.R., 1992. Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels, *Nature,* **359,** 223–225.

Cornell, R.M. & Schwertmann, U., 1996. *The Iron Oxides—Structure, Properties, Reactions, Occurrence and Uses,* VCH Verlagsgesellschaft mbH.

Dekkers, M.J., Mattéi, J.-L., Fillion, G. & Rochette, P., 1989. Grain-size dependence of the magnetic behavior of pyrrhotite during its low-temperature transition at 34 K, *Geophys. Res. Lett.,* **16,** 855–858.

Dekkers, M.J., Langereis, C.G., Vriend, S.P., van Santvoort, P.J.M. & de Lange, G.J., 1994. Fuzzy *c*-means cluster analysis of early diagenetic effects on natural remanent magnetisation acquisition in a 1.1 Myr piston core from the Central Mediterranean, *Phys. Earth planet Int.,* **85,** 155–171.

Dunlop, D.J. & Özdemir, Ö., 1997. *Rock Magnetism—Fundamentals and Frontiers,* Cambridge University Press.

Higgs, N.C., Thomson, J., Wilson, T.R.S. & Croudace, I.W., 1994. Modification and complete removal of eastern Mediterranean sapropels by postdepositional oxidation, *Geology,* **22,** 423–426.

Housen, B.A., Banerjee, S.K. & Moskowitz, B.M., 1996. Low-temperature magnetic properties of siderite and magnetite in marine sediments, *Geophys. Res. Lett.,* **23,** 2843–2846.

Karlin, R., Lyle, M. & Heath, G.R., 1987. Authigenic magnetite formation in suboxic marine sediments, *Nature,* **326,** 490–493.

Kodama, R.H. & Berkowitz, A.E., 1999. Atomic-scale magnetic modeling of oxide nanoparticles, *Phys. Rev.,* **59,** 6321–6336.

Kruiver, P.P. & Passier, H.F., 2001. Coercivity analysis of magnetite phases in sapropel S1 related to variations in redox conditions, including an investigation of the *S*-ratio, *Geochem. Geophys. Geosyst.,* paper number 2001GL000181/http://g-cubed.org.

Langereis, C.G. & Dekkers, M.J., 1999. Magnetic cyclostratigraphy: high-resolution dating in and beyond the Quaternary and analysis of periodic changes in diagenesis and sedimentary magnetism, in *Quaternary Climates, Environments and Magnetism,* pp. 352–382, eds Maher, B.A. & Thompson, R., Cambridge University Press.

Langereis, C.G., Dekkers, M.J., de Lange, G.J., Paterne, M. & van Santvoort, P.J.M., 1997. Magnetostratigraphy and astronomical calibration of the last 1.1 Myr from an eastern Mediterranean piston core and dating of short events in the Brunhes, *Geophys. J. Int.,* **129,** 75–94.

Morin, F.J., 1950. Magnetic susceptibility αFe$_2$O$_3$ and αFe$_2$O$_3$ with added titanium, *Phys. Rev.,* **78,** 819–820.

Moskowitz, B.M., Frankel, R.B. & Bazylinski, D.A., 1993. Rock magnetic criteria for the detection of biogenic magnetite, *Earth planet. Sci. Lett.,* **120,** 283–300.

Moskowitz, B.M., Jackson, M. & Kissel, C., 1998. Low-temperature magnetic behavior of titanomagnetites, *Earth planet. Sci. Lett.,* **157,** 141–149.

Passier, H.F., Middelburg, J.J., van Os B.J.H. & de Lange, G.J., 1996. Diagenetic pyritisation under eastern Mediterranean sapropels caused by downward sulphide diffusion, *Geochim. cosmochim. Acta.,* **60,** 751–763.

Passier, H.F., Middelburg, J.J., de Lange, G.J. & Böttcher, M.E., 1997. Pyrite contents, microtextures, and sulfur isotopes in relation to formation of the youngest eastern Mediterranean sapropel, *Geology,* **25,** 519–522.

Passier, H.F., Dekkers, M.J. & de Lange, G.J., 1998. Sediment chemistry and magnetic properties in an anomalously reducing core from the eastern Mediterranean Sea, *Chem. Geol.,* **152,** 287–306.

Passier, H.F., de Lange, G.J. & Dekkers, M.J., 2001. Rock-magnetic properties and geochemistry of the active oxidation front and the youngest sapropel in the eastern Mediterranean, *Geophys. J. Int.,* **145,** 604–614.

Pike, C.R., Roberts, A.P. & Verosub, K.L., 2000. The effect of magnetic interactions on low temperature saturation remanence in fine magnetic particle systems, *J. appl. Phys.,* **88,** 967–974.

Roberts, A.P., Stoner, J.S. & Richter, C., 1999. Diagenetic magnetic enhancement of sapropels from the eastern Mediterranean Sea, *Mar. Geol.,* **153,** 103–116.

Robinson, S.G., 2001. Early diagenesis in an organic-rich turbidite and pelagic clay sequence from the Cape Verd Abyssal Plain, NE Atlantic: magnetic and geochemical signals, *Sediment. Geol.,* **143,** 91–123.

Robinson, S.G. & Sahota, J.T.S., 2000. Rock-magnetic characterization of early, redoxomorphic diagenesis in turbiditic sediments from the Madeira Abyssal Plain, *Sedimentology,* **47,** 367–394.

Robinson, S.G., Sahota, J.T.S. & Oldfield, F., 2000. Early diagenesis in North-Atlantic abyssal plain sediments characterized by rock-magnetic and geochemical indices, *Mar. Geol.,* **163,** 77–107.

Rohling, E.J., 1994. Review and new aspects concerning the formation of eastern Mediterranean sapropels, *Mar. Geol.,* **122,** 1–28.

Rossignol-Strick, M., 1999. The Holocene climatic optimum and pollen records of sapropel 1 in the eastern Mediterranean, *Quatern. Sci. Rev.,* **18,** 515–530.

Rossignol-Strick, M., Nesteroff, W., Olive, P. & Vergnaud-Grazzini, C., 1982. After the deluge: Mediterranean stagnation and sapropel formation, *Nature,* **295,** 105–110.

Sahota, J.T.S., Robinson, S.G. & Oldfield, F., 1995. Magnetic measurements used to identify paleoxidation fronts in deep-sea sediments from the Madeira Abyssal Plain, *Geophys. Res. Lett.,* **22,** 1961–1964.

Schwartz, M., Lund, S.P., Hammond, D.E., Schwartz, R. & Wong, K., 1997. Early sediment diagenesis on the Blake/Bahama Outer Ridge, North Atlantic Ocean, and its effects on sediment magnetism, *J. geophys. Res.,* **102,** 7903–7914.

Smirnov, A.V. & Tarduno, J.A., 2000. Low-temperature magnetic properties of pelagic sediments (Ocean Drilling Program Site 805C): tracers of maghemitization and magnetic mineral reduction, *J. geophys. Res.,* **105,** 16 457–16 471.

Smirnov, A.V. & Tarduno, J.A., 2001. Estimating superparamagnetism in marine sediments with the time dependency of coercivity of remanence, *J. geophys. Res.,* **106,** 16 135–16 143.

Tarduno, J.A., 1995. Superparamagnetism and reduction diagenesis in pelagic sediments: enhancement or depletion?, *Geophys. Res. Lett.,* **22,** 1337–1340.

Tarduno, J.A. & Wilkison, S., 1996. Non-steady state magnetic mineral reduction, chemical lock-in, and delayed remanence acquisition in pelagic sediments, *Earth planet. Sci. Lett.,* **144,** 315–326.

Tarduno, J.A., Tian, W. & Wilkison, S., 1998. Biogeochemical remanent magnetization in pelagic sediments of the Western Pacific Ocean, *Geophys. Res. Lett.,* **25,** 3987–3990.

Thomson, J., Jarvis, I., Green, D.R.H., Green, D.A. & Clayton, T., 1998. Mobility and immobility of redox-sensitive elements in deep-sea turbidites during shallow burial, *Geochim. cosmochim. Acta.,* **62,** 643–656.

Torii, M., 1997. Low-temperature oxidation and subsequent downcore dissolution of magnetite in deep-sea sediments, ODP Leg 161 (Western Mediterranean), *J. Geomag. Geoelectr.,* **49,** 1233–1245.

Tronc, E. *et al.,* 2000. Surface-related properties of γ-Fe$_2$O$_3$ nanoparticles, *J. Magn. Magnetic Mater.,* **221,** 63–79.

Urbat, M. & Dekkers, M.J., 1999. Peru Basin sediments: diagenetic implications of a low coercivity overprint of the NRM, *Geophys. Res. Lett.,* **26,** 545–548.

van Santvoort, P.J.M., de Lange, G.J., Thomson, J., Cussen, H., Wilson, T.R.S., Krom, M.D. & Ströhle, K.D., 1996. Active post-depositional oxidation of the most recent sapropel (S1) in sediments of the eastern Mediterranean Sea, *Geochim. cosmochim. Acta.,* **60,** 4007–4024.

van Santvoort, P.J.M., de Lange, G.J., Langereis, C.G. & Dekkers, M.J., 1997. Geochemical and paleomagnetic evidence for the occurrence of ‘missing’ sapropels in eastern Mediterranean sediments, *Paleoceanography,* **12,** 773–786.

Verwey, E.J., 1939. Electronic conduction of magnetite (Fe$_3$O$_4$) and its transition point at low temperatures, *Nature,* **144,** 327–328.

Vigliotti, L., Capotondi, L. & Torii, M., 1999. Magnetic properties of sediments deposited in suboxic-anoxic environments: relationships with biological and geochemical proxies, in *Palaeomagnetism and Diagenesis in Sediments,* pp. 71–83, eds Tarling, D.H. & Turner, P., *Geol. Soc. Sp. Publ.,* **151**.

Zergenyi, R.S., Hirt, A.M., Zimmerman, S., Dobson, J.P. & Lowrie, W., 2000. Low-temperature magnetic behavior of ferrihydrite, *J. geophys. Res.,* **105,** 8297–8303.