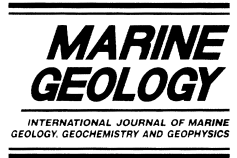




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## Diagenetic magnetic enhancement of sapropels from the eastern Mediterranean Sea

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### Abstract

Diagenetic dissolution of magnetic minerals has been widely observed in organic-rich sediments from many environments. Organic-rich sediments from the eastern Mediterranean Sea (sapropels), recovered during Leg 160 of the Ocean Drilling Program, reveal a surprising catalogue of magnetic properties. Sapropels, from all sites studied across the eastern Mediterranean Sea, are strongly magnetic and the magnetization is directly proportional to the organic carbon content. The magnetization of the sapropels is dominated by a low-coercivity, probably single domain magnetic mineral (with an inverse magnetic fabric) that exhibits a clear decay in magnetic properties when exposed to air. During heating, the magnetic particles irreversibly break down between 360 and 400°C. The contrast between the magnetic properties of sapropels and surrounding sediments is marked, with remanence intensities of sapropels often being more than three orders of magnitude higher than those of underlying sediments. The contrast between the magnetic properties of sapropels and the surrounding sediments is apparently controlled by non-steady-state diagenesis: sulphate-reducing conditions dominated during sapropel deposition, while overlying sediments were deposited under oxic conditions. The mineral responsible for the magnetic properties of sapropels is most likely to have formed under sulphate-reducing conditions that existed during times of sapropel formation. Attempts to identify this mineral have been unsuccessful, but several lines of evidence point toward an unknown ferrimagnetic iron sulphide phase. The influence of diagenesis on the magnetic properties of cyclically-deposited eastern Mediterranean sedimentary sequences suggests that magnetic parameters may be a useful proxy for diagenesis in these sediments. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* iron sulphide; sapropels; diagenesis; environmental magnetism; eastern Mediterranean Sea

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## 1. Introduction

Oxidative decomposition of organic matter is a fundamental diagenetic process in sedimentary environments. Decomposition proceeds according to a well-defined sequence from oxidation by O<sub>2</sub>, and then, in the absence of dissolved oxygen, to microbially-mediated metabolic reactions of manganese, nitrate, iron and sulphate reduction, followed by fermentation and methanogenesis (Froelich et al., 1979). In the eastern Mediterranean Sea, dozens of dark, sharply-defined, organic carbon-enriched sediment layers, termed sapropels, are intercalated with lower Pliocene to Holocene marine sediments. The distribution of redox-sensitive elements in, and around, sapropels demonstrates that even the youngest sapropel (which formed 7–9 <sup>14</sup>C ky BP; Vergnaud Grazzini et al., 1986) has undergone severe diagenetic alteration (e.g., Pruyssers et al., 1993; Thomson et al., 1995). In particular, the enrichment of pyrite in sapropels (Pruyssers et al., 1991, 1993; Thomson et al., 1995; Passier et al., 1996, 1997) demonstrates that these sediments have been subjected to intense sulphate reduction (cf. Berner, 1970, 1984).

Magnetic minerals are highly sensitive to changing redox conditions. In rapidly-deposited sediments with relatively high organic carbon contents, biogenic magnetite can form just above the iron reduction zone (Karlin et al., 1987; Petermann and Bleil, 1993; Van Hoof et al., 1993; Tarduno, 1994). In the iron reduction zone, dissolution removes

many of these fine biogenic magnetite grains and detrital magnetic phases. In sulphate-reducing environments, dissolution of detrital magnetic minerals is widespread (Canfield and Berner, 1987), as has been extensively documented in marine sediments (e.g., Karlin and Levi, 1983, 1985; Channell and Hawthorne, 1990; Karlin, 1990a,b; Leslie et al., 1990a,b; Tarduno, 1992, 1994; Roberts and Pillans, 1993; Roberts and Turner, 1993; Dekkers et al., 1994). The iron that is reduced from detrital iron-bearing minerals as Fe<sup>2+</sup> reacts with dissolved sulphate to form iron sulphide minerals, particularly pyrite (Berner, 1970, 1984).

Because environmental magnetic parameters can be used to detect changes in minute quantities of magnetic particles, they can be sensitive indicators of paleoenvironmental processes. This makes possible the use of magnetic techniques to trace cycles of magnetic mineral dissolution (e.g., Tarduno, 1992, 1994) or cycles of authigenic growth of secondary magnetic phases that may result from fluctuating redox conditions that reflect paleoproductivity changes through time.

The magnetic properties of sapropels have been largely ignored relative to the surrounding sediments, presumably because of the expectation that detrital magnetic phases would occur in dilute concentrations relative to organic matter and that dissolution would accompany organic matter degradation, thereby further reducing the concentration of such grains. Magnetic analyses of fresh sapropel material from the eastern Mediterranean Sea during Leg 160

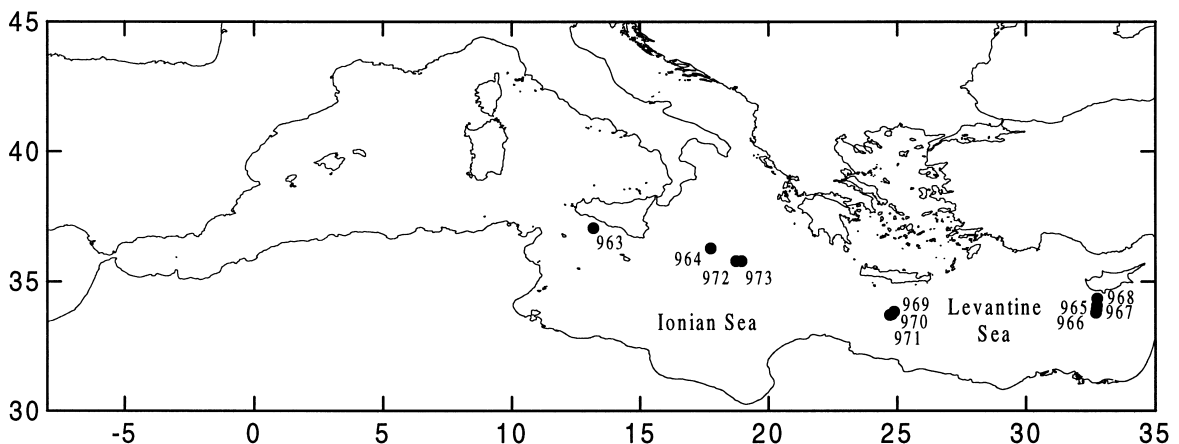


Fig. 1. Location map of the sites occupied during ODP Leg 160.

of the Ocean Drilling Program (ODP) enabled documentation of a surprising enrichment in the magnetic properties of sapropels, as briefly noted by Roberts et al. (1996). Here, we present the first detailed documentation of the magnetic properties of sapropels.

## 2. Magnetic properties of sapropels

Sapropel-bearing sequences were recovered from most of the eastern Mediterranean sites occupied during ODP Leg 160 (Fig. 1), including: Sites 964, 972 and 973 (Ionian Sea); Sites 965–968 (Eratosthenes Seamount); and Sites 969–971 (Mediterranean Ridge). Low-resolution shipboard paleomagnetic analysis on a pass-through 2G Enterprises cryogenic magnetometer (10-cm measurement intervals with a smoothing window of about 15 cm) indicated that the intensity of natural remanent magnetization (NRM) varies cyclically between successive sapropels and that NRM intensity is generally anomalously high within the sapropels. This result has been confirmed (Fig. 2) by high-resolution post-cruise studies of u-channel samples (Richter et al., 1998; Stoner et al., 1998). Replicate measurements from multiple sapropels indicate that the interpretations presented below are applicable to sapropels in general. In the following discussion, results are presented from numerous sapropels to illustrate the magnetic properties rather than reporting extensive results from a single set of samples.

Detailed measurements of discrete samples (7.9 cm<sup>3</sup> volume) from across several sapropels confirms and adds detail to the pattern obtained from long-core results (Fig. 3). Shipboard remanence measurements of discrete samples were conducted with a Minispin spinner magnetometer and low-field magnetic susceptibility ( $k$ ) was measured with a Bartington Instruments MS-2 magnetic susceptibility meter. Samples from a representative 75-cm core segment from Hole 967C on the eastern flank of Eratosthenes Seamount (Fig. 1) display a marked peak in NRM intensity toward the base of the sapropel, with a precipitous decrease in intensity of more than three orders of magnitude from the sapropel to the diagenetically-reduced grey sediment below the sapropel (Fig. 3a). The contrast between sapropels and surrounding sediments is more clearly evident in  $k$ , susceptibility of anhysteretic remanent magnetiza-

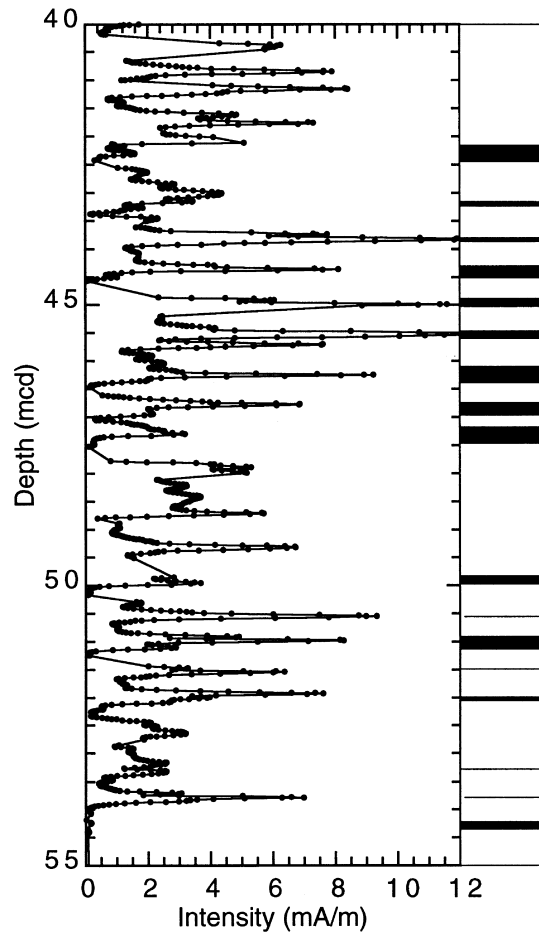
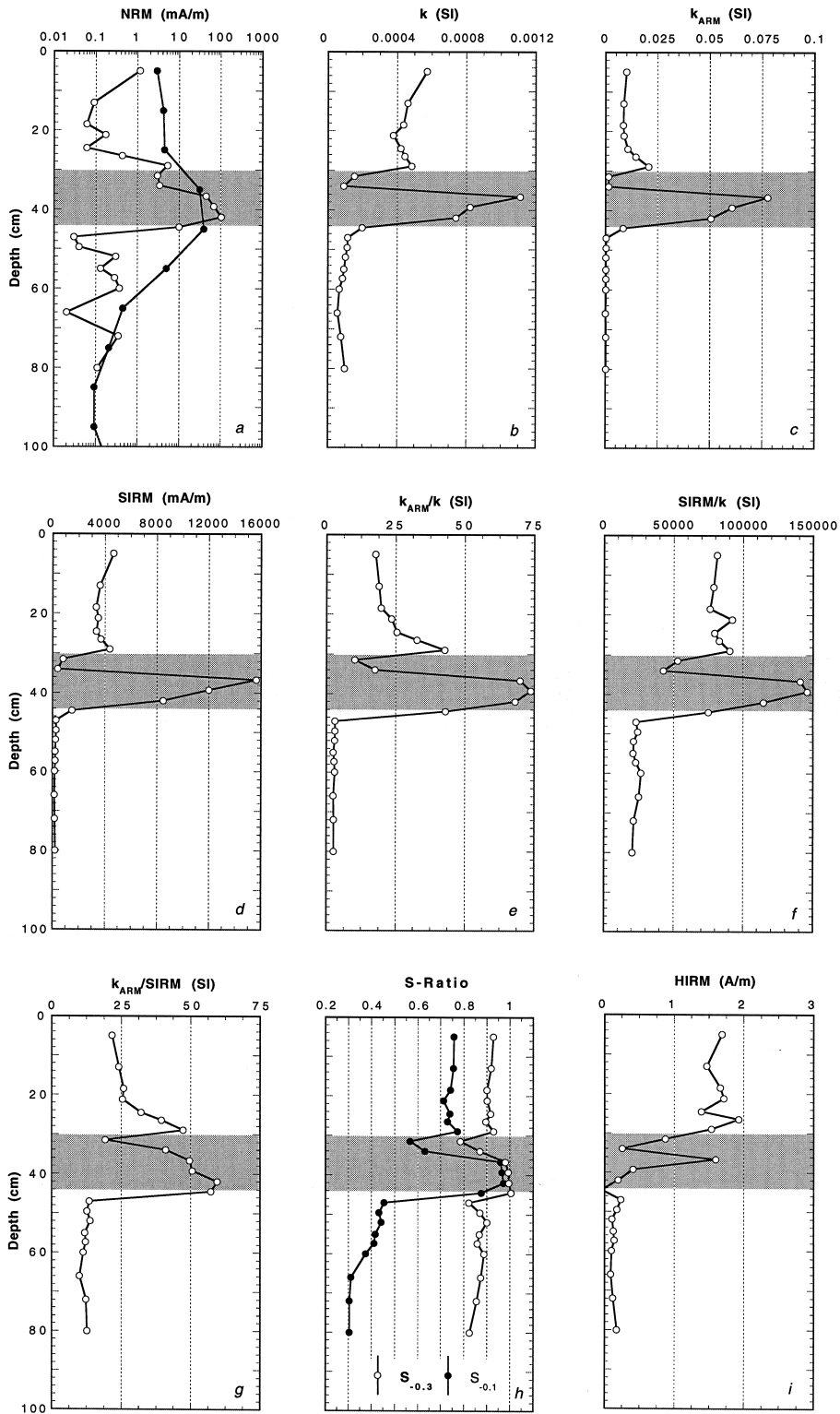


Fig. 2. NRM intensity (after demagnetization at 50 mT) for u-channel samples from 40–55 m composite depth from Site 967 (see Richter et al. (1998) and Stoner et al. (1998) for measurements and composite depth scale details). The stratigraphic position and thickness of sapropels is shown on the right-hand side of the figure. Some intensity peaks are not clearly associated with sapropels, but are usually associated with terrigenous material, associated with mud turbidites which are common in the sequences recovered during Leg 160.

tion ( $k_{\text{ARM}}$ : imparted in an alternating field of 100 mT and a bias field of 0.05 mT), and saturation isothermal remanent magnetization (SIRM: imparted in a pulse magnetizer with an applied field of 1.2 T) (Fig. 3b–d). These parameters indicate that there are relatively high concentrations of magnetic particles within the sapropel.

SIRM/ $k$ ,  $k_{\text{ARM}}/k$  and  $k_{\text{ARM}}/\text{SIRM}$  are useful indicators of magnetic grain size variation (in domi-



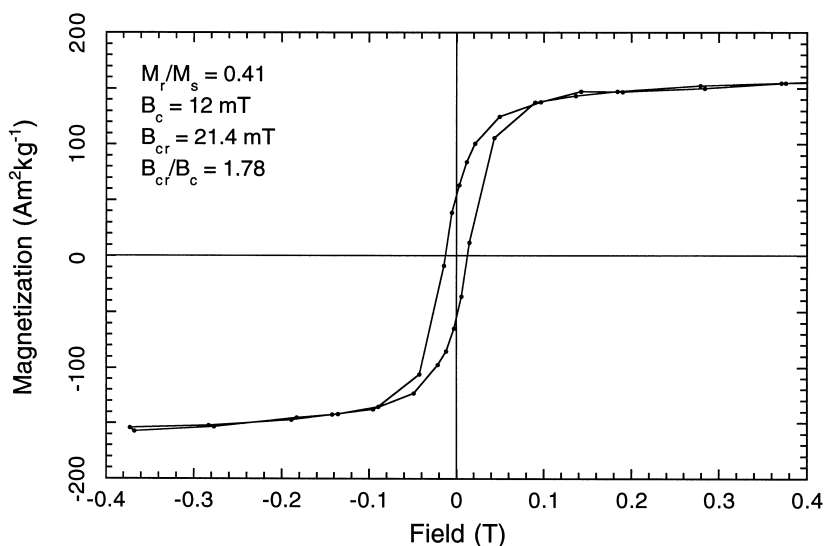


Fig. 4. Representative hysteresis loop for a sapropel sample (from Hole 970B, core 3H-CC; 28.3 mbsf; ca 1.1 Ma). The samples used for Fig. 3 could not be used for post-cruise hysteresis measurements because they were consumed for shipboard geochemical work. Analysis of samples from multiple sapropels indicates that these hysteresis properties are representative of sapropels.

nantly magnetite-bearing sediments), with high values being indicative of fine grains and low values generally being indicative of relatively coarser grains (e.g., Banerjee et al., 1981; King et al., 1982). When a sediment contains more than one magnetic mineral, such simplistic interpretations may not be valid. However, hysteresis measurements confirm that the high values of  $k_{\text{ARM}}/k$ ,  $\text{SIRM}/k$  and  $k_{\text{ARM}}/\text{SIRM}$  within sapropels (Fig. 3e–g) indicate the dominance of fine, nearly single domain (SD) grains: the ratio of saturation remanence to saturation magnetization ( $M_r/M_s$ ) is typically just below 0.5 (Fig. 4), which is the expected value for populations of randomly-oriented SD grains with uniaxial magnetic anisotropy. Comparison of hysteresis results from sediment above and below sapropels also indicates that magnetic grains within sapropels are much finer than in the surrounding sediments.

The S-ratio ( $\text{IRM}_{-0.3\text{T}}/\text{SIRM}_{1.2\text{T}}$ ; see King and Channell, 1991) enables assessment of the relative contributions of low- and high-coercivity magnetic phases because magnetite and other low-coercivity ferrimagnetic minerals reach magnetic saturation in fields of 0.3 T, whereas high-coercivity magnetic minerals such as hematite and goethite do not reach saturation until well above 1 T. S-ratios of 0.95–1.0 (even at backfields as low as  $-0.1$  T) within the lower part of the sapropel indicate the dominance of an extremely low-coercivity magnetic phase in this zone (Fig. 3h). S-ratios remain relatively high in the overlying and underlying sediment and in a thin zone in the uppermost part of the sapropel. The HIRM parameter (or ‘hard’  $\text{IRM} = [\text{IRM}_{-0.3\text{T}} + \text{IRM}_{1.2\text{T}}]/2$ ; see King and Channell, 1991) provides a measure of the abundance of high-coercivity phases. HIRM is highest in the oxic sediments above the

Fig. 3. Summary of mineral magnetic measurements of a transect of continuous discrete samples from above, within, and below a sapropel from Hole 967C, core 6, section 2 (49.5–50.5 m below sea floor (mbsf); ca 1.5 Ma). The sapropel is denoted by the shaded region in each plot. (a) NRM intensity for discrete samples (open circles) compared with continuous long-core measurements at 10-cm intervals (solid circles). Note that the long-core measurements are smoothed due to the broad stratigraphic interval covered by the response function of the magnetometer. Down-core relations are also shown for: (b) low-field susceptibility ( $k$ ); (c) susceptibility of anhysteretic remanent magnetization ( $k_{\text{ARM}}$ ); (d) saturation isothermal remanent magnetization (SIRM); (e)  $k_{\text{ARM}}/k$ ; (f)  $\text{SIRM}/k$ ; (g)  $k_{\text{ARM}}/\text{SIRM}$ ; (h) S-ratio with ratios of back-fields to SIRM for both  $-0.1$  T (solid circle) and  $-0.3$  T (open circle); and (i) HIRM (see text).

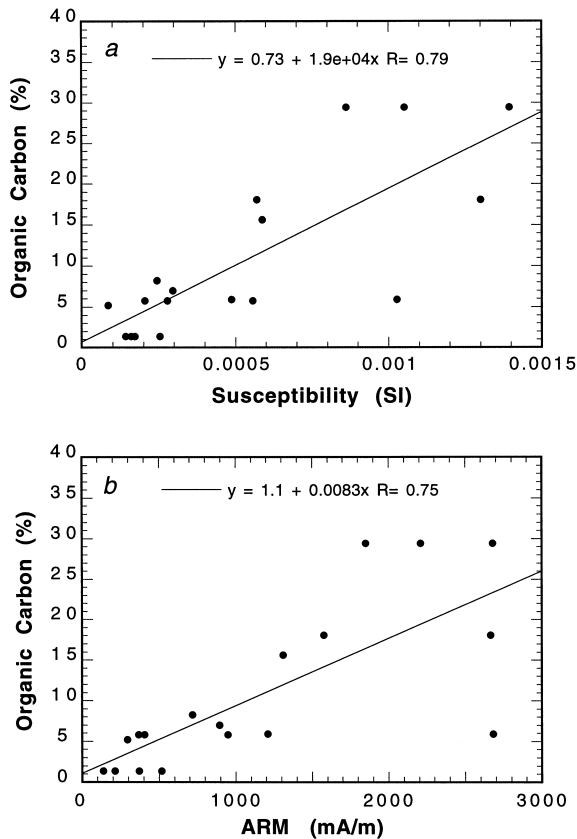


Fig. 5. Relationship of organic carbon to magnetic parameters: (a)  $C_{\text{org}}$  versus low-field susceptibility ( $R = 0.79$ ); (b)  $C_{\text{org}}$  versus anhysteretic remanent magnetization ( $R = 0.75$ ). Note that samples for magnetic measurements are not from identical stratigraphic levels as the  $C_{\text{org}}$  measurements (due to constraints on the availability of sapropel samples for different studies). This may contribute to scatter in the plots because  $C_{\text{org}}$  values are not constant within a given sapropel (e.g., Pruyssers et al., 1993; Thomson et al., 1995; Van Santvoort et al., 1997).  $C_{\text{org}}$  values are from Emeis et al. (1996).

sapropel and at the base of the upper part of the sapropel, but is low in the lowermost part of the sapropel and in the underlying grey sediments.

Several observations can be summarized concerning the magnetic properties of sapropel-bearing sediments. First, contrary to expectation, parts of sapropels contain high concentrations of magnetic particles. Second, diagenetically-reduced grey sediments that underlie sapropels have low concentrations of magnetic particles. Extensive pyritization of the grey sediments (Passier et al., 1996, 1997), will result

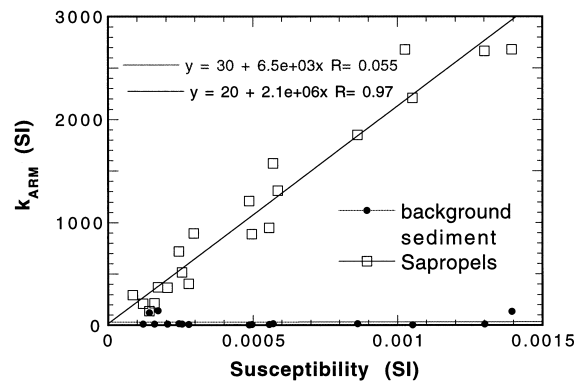


Fig. 6.  $k_{\text{ARM}}$  versus  $k$  for sapropel samples and surrounding 'background' pelagic sediments. Correlation between these parameters for sapropel samples ( $R = 0.97$ ) indicates a uniformly fine magnetic grain size in sapropels (which indicates that similar diagenetic conditions were present in multiple sapropels), while no correlation exists ( $R = 0.055$ ) in the surrounding sediments.

in dissolution of magnetic phases (cf. Canfield and Berner, 1987), which is probably responsible for the low concentration of magnetic particles in these sediments. Third, sediments that overlie sapropels contain relatively large concentrations of high-coercivity particles compared to sapropels or underlying sediments. The presence of high-coercivity particles (such as hematite or goethite) in this zone is consistent with deposition under oxic conditions (e.g., Pruyssers et al., 1993; Thomson et al., 1995; Passier et al., 1996). Fourth, based on documentation of reductive diagenesis in the vicinity of Mediterranean sapropels (e.g., Pruyssers et al., 1993; Dekkers et al., 1994; Thomson et al., 1995; Passier et al., 1996, 1997; Van Santvoort et al., 1997), it is highly probable that magnetic enrichment of sapropels is due to authigenic formation of a new magnetic phase.

Compilation of results from multiple sapropels indicates that the degree of magnetic enhancement of a sapropel is related to the organic carbon content of the sapropel, with, again surprisingly, high organic carbon contents corresponding to high concentrations of magnetic minerals, as indicated by  $k$  and ARM intensity (Fig. 5). The marked divergence of magnetic properties of the sapropels from those of the surrounding sediment is illustrated in Fig. 6. The high degree of correlation between  $k_{\text{ARM}}$  and  $k$  ( $R = 0.97$ ) indicates that the magnetic particles in sapropels are of relatively uniform size. Variation

along this correlation line is indicative of variations in concentration of magnetic minerals, which, as inferred from Fig. 5, is related to the organic carbon content. By comparison, no correlation is observed between  $k_{ARM}$  and  $k$  from the ‘background’ sediment ( $R = 0.055$ ), probably because, in the background sediment,  $k$  is controlled by paramagnetic minerals rather than by ferrimagnetic minerals.

Magnetic particles in nature are usually somewhat ellipsoidal and display different susceptibilities along

their respective maximum, minimum and intermediate axes (Fig. 7a). The respective directions of  $k_{max}$ ,  $k_{min}$  and  $k_{int}$  of sapropel and bulk sediment samples were determined by measuring the magnetic susceptibility in multiple orientations using a Kappabridge KLY-2 magnetic susceptibility meter. In sedimentary environments, the magnetic fabric is usually approximated by an oblate ellipsoid, with  $k_{min}$  perpendicular to the bedding plane (Fig. 7a). Sapropels, however, display an inverse magnetic fabric, with  $k_{max}$  per-

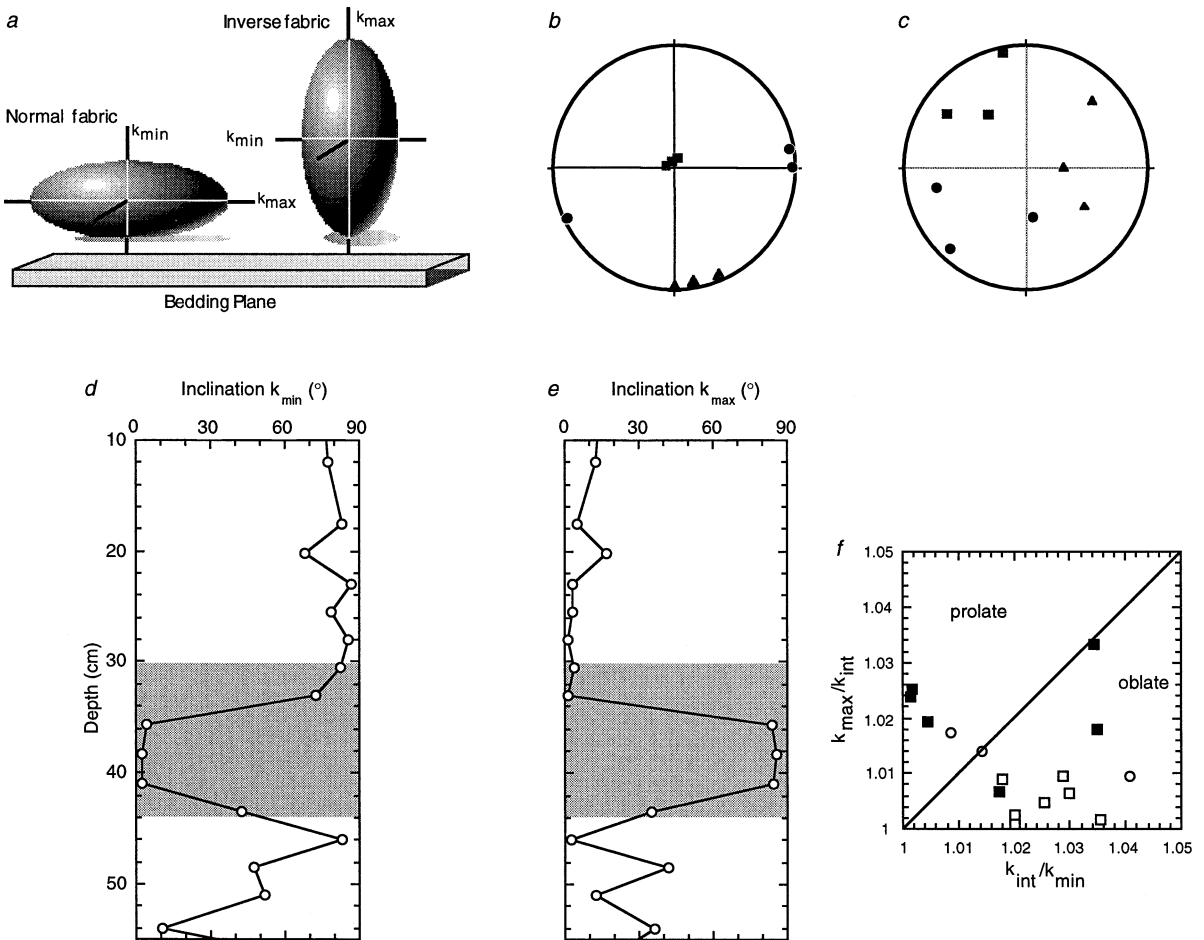


Fig. 7. Magnetic fabric of a sapropel and surrounding sediment from Hole 967C, core 6, section 2 (49.5–50.5 mbsf; ca 1.5 Ma). (a) Schematic diagram of susceptibility ellipsoids for a normal (oblate) and inverse (prolate) magnetic fabric, with respect to the bedding plane. (b, c) Equal area stereographic projections of declination and inclination of  $k_{max}$  (squares),  $k_{min}$  (triangles), and  $k_{int}$  (circles) for three samples from within the sapropel before (b) and after (c) imparting an SIRM of 1.2 T. (d, e) Stratigraphic variations in inclination of  $k_{min}$  and  $k_{max}$  above, within, and below the sapropel (shaded). (f) Variations between prolate and oblate susceptibility ellipsoids ( $k_{max}/k_{int}$  versus  $k_{int}/k_{min}$ ) for samples above (open squares), within (solid squares) and below (open circles) the sapropel. Parts (b), (d–f) indicate that the sapropel has an inverse magnetic fabric (see part a) which suggests that the magnetic mineralogy of the sapropel is different to that of surrounding sediments.

pendicular to bedding (Fig. 7b), as is the case for a prolate ellipsoid (Fig. 7a). The inverse magnetic fabric of sapropels can be easily destroyed by imparting a relatively low-field IRM (about 50 mT). After application of an IRM at 1.2 T in the same direction for all samples, the magnetic fabric changed, with no consistent fabric being evident (Fig. 7c). This change in magnetic fabric probably results from field-impressed anisotropy, which has been reported to result from application of fields as low as 10 mT (e.g., Potter and Stephenson, 1990).

Stratigraphic variations in  $k_{\min}$  and  $k_{\max}$  above, in, and below a sapropel are illustrated in Fig. 7d and e, and the degree of anisotropy and shape of the susceptibility ellipsoid is shown in Fig. 7f. These data demonstrate that the magnetic fabric and magnetic mineralogy of the sapropel are clearly different to that of the surrounding sediments.

Inverse magnetic fabrics are uncommon in nature, and have only been described from iron-bearing calcite (Rochette, 1988), tourmaline, cordierite, goethite (Rochette et al., 1992), siderite (Ellwood et al., 1986; Housen et al., 1996) and possibly from SD magnetite (Rochette, 1988). The mechanism suggested by Rochette (1988) to account for an inverse magnetic fabric in SD magnetite should, in principle, be applicable to other SD ferrimagnetic materials with similar crystallography. Rochette (1988) proposed that SD magnetite has zero magnetic susceptibility along the long axis of the grain (where the spontaneous magnetic moment lies) and that the maximum susceptibility will lie perpendicular to the long axis. Thus, a standard petrofabric with SD magnetite grains will produce an inverse magnetic fabric. Hysteresis data (Fig. 4) are consistent with a dominance of SD grains within sapropels. If the mechanism for susceptibility anisotropy suggested by Rochette (1988) is applicable to assemblages of SD grains other than magnetite, then this mechanism might account for the inverse magnetic fabric of sapropels. The range of options for minerals that may be responsible for the magnetic properties of sapropels is, therefore, probably not as restrictive as would be suggested by the small number of known magnetic phases that display an inverse magnetic fabric.

Low-field magnetic susceptibility and IRM intensity (which was freshly imparted prior to each measurement) were measured repeatedly for two

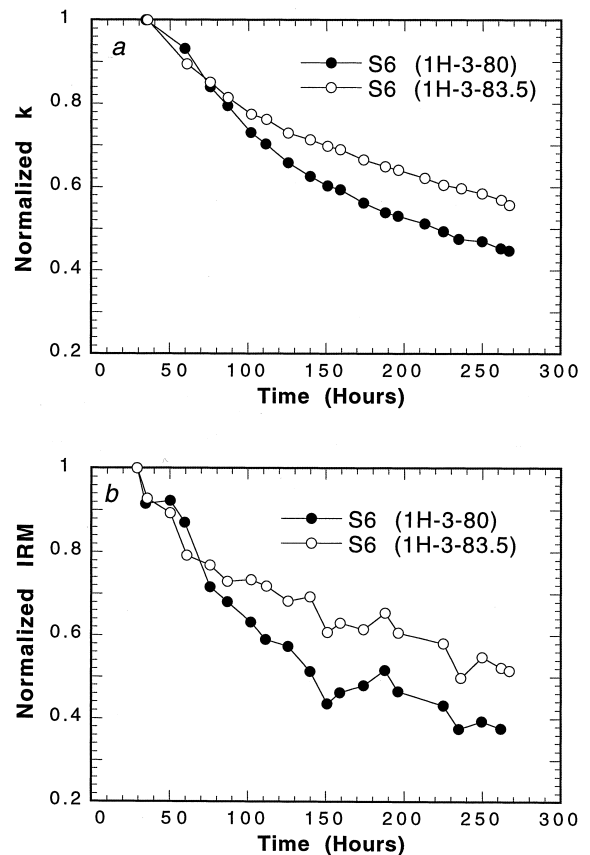


Fig. 8. Time decay (in h) of: (a)  $k$ ; and (b) IRM (imparted at 1 T) for two sapropel samples (from S6) from Hole 969A (core 1, section 3, 80 and 83.5 cm, respectively). The decay of the magnetic parameters is attributable to progressive oxidation of the magnetic particles and surrounding organic matter.

samples from sapropel S6 (Hole 969A) at least twice a day for eleven days (Fig. 8). A 30-h delay from core recovery to initial measurement of these parameters enabled the core to equilibrate at room temperature prior to conducting shipboard multisensor track measurements (which were made prior to splitting the core). Paleomagnetic analysis (including stepwise alternating field demagnetization at 10, 20, 30, 40, 50 and 60 mT) was conducted within a few hours of core splitting and before measurement of time decay of magnetic properties. Over eleven days,  $k$  decreased smoothly between 44 and 56% (Fig. 8a). A corresponding decay was also observed in the ability of samples to acquire an IRM at 1 T (Fig. 8b). The IRM decay is not as smooth as the  $k$  decay



because of electronic difficulties encountered with the shipboard spinner magnetometer (which affected calibration). Oldfield et al. (1992) demonstrated that even magnetite can undergo alteration and substantial susceptibility loss (up to 90%) in organic-rich sediments after exposure to air. Thus, the observed time-dependent decay of magnetic properties might not necessarily indicate inherent metastability of the magnetic mineralogy of sapropels.

### 3. Magnetic mineralogy of sapropels

Post-cruise studies were aimed at attempting to identify the mineral(s) responsible for the magnetic properties of sapropels. Where bulk sapropel samples were available, they were freeze-dried to minimize oxidation (cf. Snowball and Thompson, 1988; Oldfield et al., 1992). Less than 2 cm<sup>3</sup> of freeze-dried sapropel was subjected to temperature-dependent susceptibility measurements using a Kappabridge KLY-2 susceptibility meter with a CS-2 high temperature attachment. Despite the small sample size, the susceptibilities are substantial at room temperature (Fig. 9a, b). Both samples display similar behaviour, with broad susceptibility peaks at 110° and 300°C, and a more sharply-defined peak at 360°C that is succeeded by a precipitous decrease in susceptibility between 360° and 400°C (Fig. 9a, b). Above 400°C, the susceptibility remains low. The behaviour is non-repeatable on cooling, with the only significant feature being a slight increase in susceptibility between 340° and 300°C that is particularly marked for the sapropel from Hole 969A (Fig. 9a). The lack of reproducibility between the heating and cooling curves indicates that the observed susceptibility peaks are probably not true Hopkinson peaks, but, rather, are indicative of thermal breakdown during heating. The major decrease in susceptibility between 360° and 400°C is suggestive of thermal breakdown of an iron sulphide mineral; however, this breakdown temperature is higher than that expected for the known ferromagnetic iron sulphides, including greigite (major decrease in magnetization between 270° and 350°C; Roberts, 1995) and pyrrhotite (maximum unblocking temperature of 325°C; Dekkers, 1989). The increase in susceptibility between 340° and 300°C (during cooling) is probably due to pyrrhotite that formed during heating.

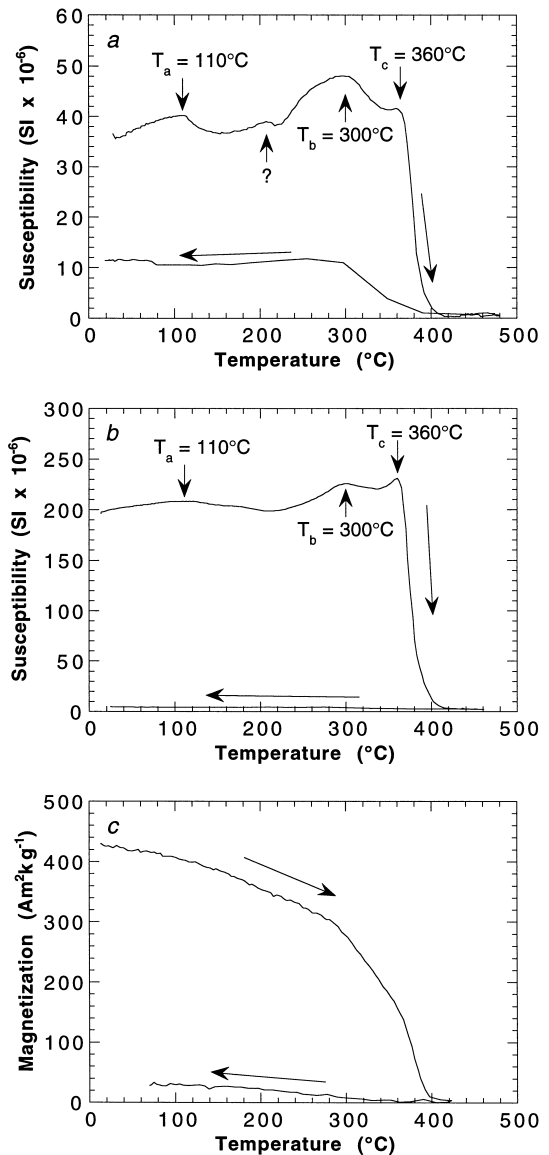


Fig. 9. Temperature-dependence of low-field magnetic susceptibility for freeze-dried sapropel samples from: (a) Hole 969A (core 6H-CC; 55.2 mbsf; ca 2.8 Ma), and (b) Hole 970B (core 3H-CC; 28.3 mbsf; ca 1.1 Ma). (c) Magnetization versus temperature (at an applied field of 46 mT) for the same sample as in (a).

The above results have been confirmed by magnetization versus temperature measurements obtained with a variable field translation balance in an applied field of 46 mT (Fig. 9c). Inflection points are observed at similar temperatures as for the temperature-dependent susceptibility measurements (about

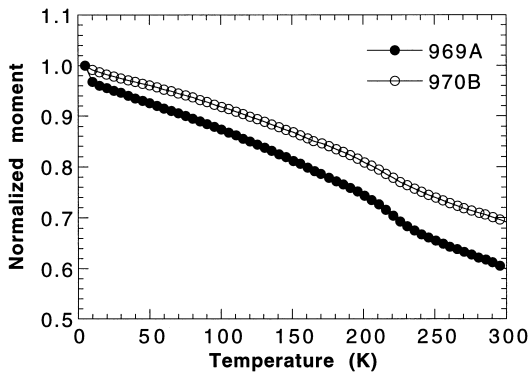


Fig. 10. Zero-field warming of an SIRM (imparted in a field of 2.5 T at 5 K) from 5–300 K for subsamples from the same sapropels analyzed in Fig. 9(a, b). A low-temperature magnetic transition may occur between 210 and 230 K, which has not been previously reported for any known magnetic mineral (see text).

125°, 280° and 360°C), and complete magnetic and thermal breakdown occurs at about 400°C. A small increase in magnetization on cooling through 320°C confirms that pyrrhotite formed during heating. More detailed thermomagnetic analysis, which involved heating/cooling cycles between room temperature and successively higher temperatures (110°, 170°, 220°, 270°, 315°, 360°, 410° and 470°C) indicates that genuine Curie temperatures are not observed during the thermomagnetic cycles. Rather, the inflections observed in Fig. 9c are due to thermal breakdown of the magnetic mineral(s).

Low-temperature magnetic measurements can provide additional constraints on magnetic mineralogy. An SIRM was imparted (in a field of 2.5 T at 5 K) to two sapropel samples from Holes 969A and 970B. The field was nulled and the SIRM was measured as the samples were warmed to room temperature. Both samples display a fairly uniform remanence decay during warming (30–40% SIRM loss from 5 to 300 K; Fig. 10). The distribution of unblocking temperatures between 5 and 300 K is consistent with the presence of a distributed spectrum of grains that are superparamagnetic (SP) at room temperature. SP grains are probably responsible for lowering the room temperature  $M_r/M_s$  values of sapropels below 0.5 (Fig. 4). The only other notable feature of the low temperature curves is the change in slope at 210–230 K, which may indicate the presence of a magnetic transition that

has not been reported elsewhere for any known magnetic mineral. Alternatively, this feature could indicate the presence of a fraction of grains that unblock at this temperature: low-temperature hysteresis measurements are necessary to discriminate between these possibilities. Regardless, the lack of any other low-temperature magnetic transition suggests that pyrrhotite (magnetic transition at 34 K; Dekkers et al., 1989; Rochette et al., 1990), siderite (magnetic unblocking at 30–50 K; Housen et al., 1996), magnetite (Verwey transition at 118 K; Verwey, 1939; Özdemir et al., 1993), or hematite (Morin transition at 250–260 K; Morin, 1950) are not present in significant abundances.

Direct mineralogical identification (e.g., X-ray diffraction) represents the clearest way to identify magnetic minerals that are not identifiable with magnetic techniques. Attempts to obtain magnetic separates from freeze-dried sapropel samples for mineralogical identification, using high-gradient magnetic separation, were unsuccessful. Paramagnetic pyrite ( $\text{FeS}_2$ ) was the only phase identified by X-ray diffraction of a magnetic separate. Identification of the mineral responsible for the observed diagenetic magnetic enhancement of sapropels therefore awaits further work.

#### 4. Magnetic minerals that may be responsible for sapropel magnetism

Sapropels were deposited during periods when eastern Mediterranean bottom waters were more or less anoxic (e.g., Bradley, 1938). Extensive pyritization of sapropels (and underlying sediments) and significant  $\delta^{34}\text{S}$  fractionation in these sediments (Passier et al., 1996, 1997) suggest that intense sulphate reduction occurred during these periods of bottom water anoxia. This observation is supported by correlation of organic carbon content with sulphur content in many sapropels (Pruysers et al., 1993; Passier et al., 1996), which is best explained by bacterial sulphate reduction (cf. Berner, 1984) during sapropel deposition. At the end of periods of sapropel deposition, eastern Mediterranean bottom waters were reventilated and the overlying sediments were deposited under oxic conditions, with variable oxidation of sapropels, including complete oxidative 'burn-down' of some sapropels (e.g., Pruyers et al.,

1993; Thomson et al., 1995; Van Santvoort et al., 1997). Despite uncertainty concerning the mineral responsible for the distinct magnetic signature of eastern Mediterranean sapropels, several constraints are suggested by the above-described magnetic results and the inferred diagenetic conditions that existed during periods of sapropel formation.

Siderite ( $\text{FeCO}_3$ ) commonly forms during diagenesis of carbonate-bearing sediments (Ellwood et al., 1986). Despite the fact that siderite displays an inverse magnetic fabric, it is not responsible for the magnetization of sapropels because it is paramagnetic above 50 K (Housen et al., 1996). Also, siderite is clearly not present in significant concentrations in the studied sapropels because it was not detected in low temperature analyses (Fig. 10) (cf. Housen et al., 1996).

Authigenic magnetite can form under sulphate-reducing conditions (e.g., Sakaguchi et al., 1993); nevertheless, this possibility can be dismissed because high-temperature data from sapropels are not consistent with the presence of magnetite which has a Curie temperature of 580°C (Fig. 9) and low-temperature data do not contain evidence of the Verwey transition at 118 K (Fig. 10). Other magnetic minerals such as maghemite, hematite and goethite would not be expected to form under reducing conditions. Pyrrhotite can also be discounted because the 34 K magnetic transition is absent (Fig. 10) (cf. Dekkers et al., 1989; Rochette et al., 1990).

Other ferrimagnetic iron sulphides should be considered because such minerals are most likely to form under reducing conditions. Paramagnetic pyrite is one of the most common iron sulphide phases to form under sulphate-reducing conditions and its formation has important implications for sediment magnetization because it forms as the final product in a series of reactions in which the ferrimagnetic iron sulphide, greigite ( $\text{Fe}_3\text{S}_4$ ), is an important intermediate product. Because framboidal pyrite formation is favoured by formation of precursor greigite (e.g., Goldhaber and Kaplan, 1974; Wang and Morse, 1996; Wilkin and Barnes, 1996), it is possible that greigite may survive pyritization because pyrite can form as overgrowths on greigite grains (cf. Wang and Morse, 1996), possibly without complete reaction of the precursor greigite. Greigite has also been widely documented in marine environments (e.g., Suttill et al., 1982; Tric et al., 1991; Hornig et al.,

1992; Roberts and Pillans, 1993; Roberts and Turner, 1993; Reynolds et al., 1994; Florindo and Sagnotti, 1995; Lee and Jin, 1995; Housen and Musgrave, 1996). Even though greigite would not be expected to occur, based on the abundance of dissolved sulphate in sedimentary pore waters (cf. Berner, 1970, 1984) in the eastern Mediterranean Sea (Emeis et al., 1996), it should be considered as a candidate for the magnetism of sapropels because it has an affinity for organic-rich environments. For example, greigite has been documented in sapropelitic middle Miocene lacustrine sediments in the Czech Republic (e.g., Krs et al., 1990, 1992; Novák and Jansa, 1992) and in explicit association with organic matter in marine environments (e.g., Jedwab, 1967). In addition, greigite (e.g., Garravelli and Nuovo, 1971; Bracci et al., 1985; Tric et al., 1991; Florindo and Sagnotti, 1995; Mattei et al., 1996) and unidentified magnetic iron–nickel sulphide minerals (Van Velzen et al., 1993) have been widely documented in Plio–Pleistocene marine sediments in the Mediterranean region.

Regardless of the above arguments, the magnetic characteristics of sapropels are only broadly consistent with those of greigite. The magnetic material in sapropels displays SD-like behaviour (Fig. 4), which is consistent with observations of natural greigite (e.g., Snowball, 1991; Roberts, 1995). However, the coercivity of pristine sapropel samples (Fig. 3h) is low (coercivities of remanence,  $B_{\text{cr}}$ , are 18–20 mT), whereas the wide range of greigite samples studied by Roberts (1995) displayed much higher coercivities ( $B_{\text{cr}} = 45\text{--}95$  mT). Furthermore, sapropels undergo thermal breakdown (Fig. 9) at higher temperatures (360°–400°C) than is expected for greigite (270°–350°C; Roberts, 1995) or smythite ( $\text{Fe}_9\text{S}_{11}$ ), which undergoes thermal breakdown at 260°–380°C (Hoffmann et al., 1993).

Despite the lack of convincing evidence for ferrimagnetic iron sulphide minerals such as pyrrhotite, greigite and smythite, the available evidence suggests that an unidentified iron sulphide mineral is most likely to be responsible for the magnetic properties of sapropels. An iron sulphide mineral is also strongly suggested by high-temperature results (Fig. 9) which indicate thermal breakdown in a similar, but not identical, range of temperatures to other magnetic iron sulphide minerals. Given the presence of numerous redox-sensitive metals in the vicinity

of sapropels, such as nickel and chromium (e.g., Pruyssers et al., 1991; Thomson et al., 1995), it may be possible for such cations to substitute into the crystal structure of the hypothesized magnetic iron sulphide during authigenic formation in sapropels. This hypothesis is supported by the presence of magnetic iron–nickel sulphides in uplifted Pleistocene marine sediments from the Vrica section, Italy (Van Velzen et al., 1993). The presence of nickel or other cations may also give rise to the lower coercivities observed in sapropels, relative to those documented for greigite (cf. Roberts, 1995).

## 5. Conclusions

Eastern Mediterranean sapropels are strongly magnetic, probably as a result of authigenic formation of a magnetic iron sulphide phase during diagenetic sulphate reduction. The strong relationship between organic carbon and magnetic mineral concentration is puzzling because organic-rich sediments with high dissolved pore water sulphate contents would not be expected to allow preservation of intermediate magnetic iron sulphide minerals.

The demonstrated dominance of diagenetic effects on the magnetic record of sapropel-bearing sediments (see also Dekkers et al., 1994; Van Santvoort et al., 1997) suggests that high-resolution studies of geomagnetic field behaviour from such sequences (e.g., Tric et al., 1992; Langereis et al., 1997) will be complex. Van Santvoort et al. (1997) also demonstrated that the positions of missing sapropels (which have been completely oxidized from the record) can be identified with joint geochemical and environmental magnetic studies. The use of environmental magnetism in sapropel-bearing sequences, in conjunction with geochemical studies, could prove to be important for studies of paleoclimate and paleoproductivity (cf. Tarduno, 1992, 1994) because the major determinant of magnetic properties of eastern Mediterranean sediments (diagenesis) varies cyclically, as a result of climatic modulation of the depositional environment.

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## References

- Banerjee, S.K., King, J.W., Marvin, J., 1981. A rapid method for magnetic granulometry with applications to environmental studies. *Geophys. Res. Lett.* 8, 333–336.
- Berner, R.A., 1970. Sedimentary pyrite formation. *Am. J. Sci.* 268, 1–23.
- Berner, R.A., 1984. Sedimentary pyrite formation: An update. *Geochim. Cosmochim. Acta* 48, 605–615.
- Bracci, G., Dalena, D., Orlandi, P., 1985. La greigite di Mentana, Lazio. *Rend. Soc. Ital. Mineral. Petrol.* 40, 295–298.
- Bradley, W.H., 1938. Mediterranean sediments and Pleistocene sea levels. *Science* 88, 376–379.
- Canfield, D.E., Berner, R.A., 1987. Dissolution and pyritization of magnetite in anoxic marine environments. *Geochim. Cosmochim. Acta* 51, 645–659.
- Channell, J.E.T., Hawthorne, T., 1990. Progressive dissolution of titanomagnetites at ODP Site 653 (Tyrrhenian Sea). *Earth Planet. Sci. Lett.* 96, 469–480.
- Dekkers, M.J., 1989. Magnetic properties of natural pyrrhotite. II. High- and low-temperature behaviour of  $J_{rs}$  and TRM as function of grain size. *Phys. Earth Planet. Inter.* 57, 266–283.
- Dekkers, M.J., Mattéi, J.-L., Fillion, G., Rochette, P., 1989. Grain-size dependence of the magnetic behaviour 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. Inter.* 85, 155–171.
- Ellwood, B.B., Balsam, W., Burkart, B., Long, G.J., Buhl, M.L., 1986. Anomalous magnetic properties in rocks containing the mineral siderite: Paleomagnetic implications. *J. Geophys. Res.* 91, 12779–12790.
- Emeis, K.-C., Robertson, A.H.F., Richter, C. and Shipboard

- Scientific Party, 1996. Proc. ODP, Init. Rep. 160. College Station, TX.
- Florindo, F., Sagnotti, L., 1995. Palaeomagnetism and rock magnetism at the upper Pliocene Valle Ricca (Rome, Italy) section. *Geophys. J. Int.* 123, 340–354.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochim. Cosmochim. Acta* 43, 1075–1090.
- Garravelli, C.L., Nuovo, G., 1971. La greigite delle argille di Montemesola. *Period. Mineral.* 40, 305–327.
- Goldhaber, M.B., Kaplan, I.R., 1974. The sulfur cycle. In: Goldberg, E.D. (Ed.), *The Sea*, Vol. 5. Wiley, Chichester, pp. 569–655.
- Hoffmann, V., Stanjek, H., Murad, E., 1993. Mineralogical, magnetic and Mössbauer data of smythite (Fe<sub>9</sub>S<sub>11</sub>). *Stud. Geophys. Geod.* 37, 366–381.
- Hornig, C.S., Chen, J.C., Lee, T.Q., 1992. Variations in magnetic minerals from two Plio–Pleistocene marine-deposited sections, southwestern Taiwan. *J. Geol. Soc. China* 35, 323–335.
- Housen, B.A., Musgrave, R.J., 1996. Rock-magnetic signature of gas hydrates in accretionary prism sediments. *Earth Planet. Sci. Lett.* 139, 509–519.
- 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.
- Jedwab, J., 1967. Minéralisation en greigite de débris végétaux d'une vase récente (Grote Geul). *Bull. Soc. Belge Géol.* 76, 27–38.
- Karlin, R., 1990a. Magnetite diagenesis in marine sediments from the Oregon continental margin. *J. Geophys. Res.* 95, 4405–4419.
- Karlin, R., 1990b. Magnetic mineral diagenesis in suboxic sediments at Bettis site W–N, NE Pacific Ocean. *J. Geophys. Res.* 95, 4421–4436.
- Karlin, R., Levi, S., 1983. Diagenesis of magnetic minerals in Recent haemipelagic sediments. *Nature* 303, 327–330.
- Karlin, R., Levi, S., 1985. Geochemical and sedimentological control of the magnetic properties of hemipelagic sediments. *J. Geophys. Res.* 90, 10373–10392.
- Karlin, R., Lyle, M., Heath, G.R., 1987. Authigenic magnetite formation in suboxic marine sediments. *Nature* 326, 490–493.
- King, J.W., Channell, J.E.T., 1991. Sedimentary magnetism, environmental magnetism, and magnetostratigraphy. *U.S. Natl. Rep., Int. Union Geod. Geophys. 1987–1990, Rev. Geophys.* 29, 358–370.
- King, J.W., Banerjee, S.K., Marvin, J., Özdemir, Ö., 1982. Comparison of different magnetic methods for determining the relative grain size of magnetite in natural materials: Some results from lake sediments. *Earth Planet. Sci. Lett.* 59, 404–419.
- Krs, M., Krsová, M., Pruner, P., Zeman, A., Novák, F., Jansa, J., 1990. A petromagnetic study of Miocene rocks bearing micro-organic material and the magnetic mineral greigite (Sokolov and Cheb basins, Czechoslovakia). *Phys. Earth Planet. Inter.* 63, 98–112.
- Krs, M., Novák, F., Pruner, P., Kouklíková, L., Jansa, J., 1992. Magnetic properties of greigite–smythite mineralization in brown-coal basins of the Krušné hory Piedmont, Bohemia. *Phys. Earth Planet. Inter.* 70, 273–287.
- 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.
- Lee, C.H., Jin, J.H., 1995. Authigenic greigite in mud from the continental shelf of the Yellow Sea, off the southwest Korean Peninsula. *Mar. Geol.* 128, 11–15.
- Leslie, B.W., Hammond, D.E., Burleson, W.M., Lund, S.P., 1990a. Diagenesis in anoxic sediments from the California continental borderland and its influence on iron, sulfur, and magnetite behavior. *J. Geophys. Res.* 95, 4453–4470.
- Leslie, B.W., Lund, S.P., Hammond, D.E., 1990b. Rock magnetic evidence for dissolution and authigenic growth of magnetic minerals within anoxic marine sediments of the California continental borderland. *J. Geophys. Res.* 95, 4437–4452.
- Mattei, M., Kissel, C., Funicello, R., 1996. No tectonic rotation of the Tuscan Tyrrhenian margin (Italy) since late Messinian. *J. Geophys. Res.* 101, 2835–2845.
- Morin, F.J., 1950. Magnetic susceptibility of  $\alpha\text{Fe}_2\text{O}_3$  and  $\alpha\text{Fe}_2\text{O}_3$  with added titanium. *Phys. Rev.* 78, 819–820.
- Novák, F., Jansa, J., 1992. Authigenic smythite and pyrrhotite in the upper part of the Sokolov Formation (the Sokolov Basin, Czechoslovakia). *Bull. Geol. Surv. Prague* 67, 235–244.
- Oldfield, F., Darnley, I., Yates, G., France, D.E., Hilton, J., 1992. Storage diagenesis versus sulphide authigenesis: Possible implications in environmental magnetism. *J. Palaeolimnol.* 7, 179–189.
- Özdemir, Ö., Dunlop, D.J., Moskowitz, B.M., 1993. The effect of oxidation on the Verwey transition in magnetite. *Geophys. Res. Lett.* 20, 1671–1674.
- 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.
- Petermann, H., Bleil, U., 1993. Detection of live magnetotactic bacteria in South Atlantic deep-sea sediments. *Earth Planet. Sci. Lett.* 117, 223–228.
- Potter, D.K., Stephenson, A., 1990. Field-impressed anisotropies of magnetic susceptibility and remanence in minerals. *J. Geophys. Res.* 95, 15573–15588.
- Pruysers, P.A., De Lange, G.J., Middelburg, J.J., 1991. Geochemistry of eastern Mediterranean sediments: Primary sediment composition and diagenetic alterations. *Mar. Geol.* 100, 137–154.
- Pruysers, P.A., De Lange, G.J., Middelburg, J.J., Hydes, D.J., 1993. The diagenetic formation of metal-rich layers in sapropel-containing sediments in the eastern Mediterranean. *Geochim. Cosmochim. Acta* 57, 527–536.

- Reynolds, R.L., Tuttle, M.L., Rice, C.A., Fishman, N.S., Karachewski, J.A., Sherman, D.M., 1994. Magnetization and geochemistry of greigite-bearing Cretaceous strata, North Slope basin, Alaska. *Am. J. Sci.* 294, 485–528.
- Richter, C., Roberts, A.P., Stoner, J.S., Benning, L.D., Chi, C.T., 1998. Magnetostratigraphy of Pliocene–Pleistocene sediments from the eastern Mediterranean Sea, In: Emeis, K.-C., Robertson, A.H.F., Richter, C., Camerlenghi, A. (Eds.), *Proc. ODP, Sci. Results* 160, 61–74.
- Roberts, A.P., 1995. Magnetic properties of sedimentary greigite ( $\text{Fe}_3\text{S}_4$ ). *Earth Planet. Sci. Lett.* 134, 227–236.
- Roberts, A.P., Pillans, B.J., 1993. Rock magnetism of Lower/Middle Pleistocene marine sediments, Wanganui Basin, New Zealand. *Geophys. Res. Lett.* 20, 839–842.
- Roberts, A.P., Turner, G.M., 1993. Diagenetic formation of ferromagnetic iron sulphide minerals in rapidly deposited marine sediments, New Zealand. *Earth Planet. Sci. Lett.* 115, 257–273.
- Roberts, A.P., Stoner, J.S., Richter, C., 1996. Coring-induced magnetic overprints and limitations of the long-core paleomagnetic measurement technique: Some observations from Leg 160, eastern Mediterranean Sea, In: Emeis, K.-C., Robertson, A.H.F., Richter, C. et al., (Eds.), *Proc. ODP, Init. Rep.*, 160. College Station, TX, pp. 497–505.
- Rochette, P., 1988. Inverse magnetic fabric in carbonate-bearing rocks. *Earth Planet. Sci. Lett.* 90, 229–237.
- Rochette, P., Fillion, G., Mattéi, J.-L., Dekkers, M.J., 1990. Magnetic transition at 30–34 Kelvin in pyrrhotite: Insight into a widespread occurrence of this mineral in rocks. *Earth Planet. Sci. Lett.* 98, 319–328.
- Rochette, P., Jackson, M., Aubourg, C., 1992. Rock magnetism and the interpretation of anisotropy of magnetic susceptibility. *Rev. Geophys.* 30, 209–226.
- Sakaguchi, T., Burges, J.G., Matsunaga, T., 1993. Magnetite formation by a sulphate-reducing bacterium. *Nature* 365, 47–49.
- Snowball, I.F., 1991. Magnetic hysteresis properties of greigite ( $\text{Fe}_3\text{S}_4$ ) and a new occurrence in Holocene sediments from Swedish Lapland. *Phys. Earth Planet. Inter.* 68, 32–40.
- Snowball, I.F., Thompson, R., 1988. The occurrence of greigite in sediments from Loch Lomond. *J. Quat. Sci.* 3, 121–125.
- Stoner, J.S., Richter, C., Roberts, A.P., 1998. High resolution study of magnetic properties of sapropel-bearing sediments from ODP Sites 966, 967, and 969, eastern Mediterranean Sea. In: Emeis, K.-C., Robertson, A.H.F., Richter, C., Camerlenghi, A. (Eds.), *Proc. ODP, Sci. Results* 160, 75–82.
- Suttill, R.J., Turner, P., Vaughan, D.J., 1982. The geochemistry of iron in recent tidal-flat sediments of the Wash area, England: A mineralogical, Mössbauer, and magnetic study. *Geochim. Cosmochim. Acta* 46, 205–217.
- Tarduno, J.A., 1992. Magnetic susceptibility cyclicity and magnetic dissolution in Cretaceous limestones of the southern Alps (Italy). *Geophys. Res. Lett.* 19, 1515–1518.
- Tarduno, J.A., 1994. Temporal trends of magnetic dissolution in the pelagic realm: Gauging paleoproductivity? *Earth Planet. Sci. Lett.* 123, 39–48.
- Thomson, J., Higgs, N.C., Wilson, T.R.S., Croudace, I.W., De Lange, G.J., Van Santvoort, P.J.M., 1995. Redistribution and geochemical behaviour of redox-sensitive elements around S1, the most recent eastern Mediterranean sapropel. *Geochim. Cosmochim. Acta* 59, 3487–3501.
- Tric, E., Laj, C., Jehanno, C., Valet, J.-P., Kissel, C., Mazaud, A., Iaccarino, S., 1991. High-resolution record of the Upper Olduvai transition from Po Valley (Italy) sediments: Support for dipolar transition geometry? *Phys. Earth Planet. Inter.* 65, 319–336.
- Tric, E., Valet, J.-P., Tucholka, P., Paterne, M., Labeyrie, L., Guichard, F., Tauxe, L., Fontugne, M., 1992. Paleointensity of the geomagnetic field during the last 80,000 years. *J. Geophys. Res.* 97, 9337–9351.
- Van Hoof, A.A.M., Van Os, B.J.H., Rademakers, J.G., Langereis, C.G., De Lange, G.J., 1993. A paleomagnetic and geochemical record of the upper Cochiti reversal and two subsequent precessional cycles from Southern Sicily (Italy). *Earth Planet. Sci. Lett.* 117, 235–250.
- 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.
- Van Velzen, A.J., Dekkers, M.J., Zijdeveld, J.D.A., 1993. Magnetic iron–nickel sulphides in the Pliocene and Pleistocene marine marls from the Vrica section (Calabria, Italy). *Earth Planet. Sci. Lett.* 115, 43–55.
- Vergnaud Grazzini, C., Devaux, M., Znaidi, J., 1986. Stable isotope ‘anomalies’ in Mediterranean Pleistocene records. *Mar. Micropaleontol.* 10, 35–69.
- Verwey, E.J., 1939. Electronic conduction of magnetite ( $\text{Fe}_3\text{O}_4$ ) and its transition point at low temperatures. *Nature* 144, 327–328.
- Wang, Q., Morse, J.W., 1996. Pyrite formation under conditions approximating those in anoxic sediments I. Pathway and morphology. *Mar. Chem.* 52, 99–121.
- Wilkin, R.T., Barnes, H.L., 1996. Pyrite formation by reactions of iron monosulfides with dissolved inorganic and organic sulfur species. *Geochim. Cosmochim. Acta* 60, 4167–4179.