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A new proxy for bottom-water ventilation in the eastern Mediterranean based on diagenetically controlled magnetic properties of sapropel-bearing sediments

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Abstract

Magnetic properties of eastern Mediterranean sediments recovered during Leg 160 of the Ocean Drilling Program (ODP) provide insight into non-steady-state diagenetic reactions associated with accumulation and degradation of organic matter in sapropels. According to their magnetic properties, sapropels can be classified as one of three types that correspond to increasingly anoxic conditions at the time of sapropel formation. A combination of magnetic and geochemical data suggests a causal relationship that enables determination of the relative role of bottom-water ventilation versus productivity in the resulting diagenetic stage reached for the three types of sapropels. It appears that increased productivity is a prerequisite for sapropel formation, but once organic matter is available in sufficient amounts, variable efficiencies in bottom-water ventilation are more important for modulating the diagenetic context in which different types of sapropels formed. Magnetic properties are more sensitive to variations in bottom-water ventilation than to productivity, and can be used to establish relative variations in bottom-water ventilation both at, and after, periods of sapropel formation. Magnetic results and the distribution and type of sapropels at ODP Site 966 (Eratosthenes Seamount) between 2.3 and 4.0 Ma suggest that bottom-water ventilation was modulated by the orbital eccentricity component, with ventilation being restricted during 400-kyr eccentricity maxima and enhanced during eccentricity minima. Enhanced ventilation during eccentricity minima, as indicated by magnetic data, is consistent with the occurrence of red intervals at Site 966 and at other eastern Mediterranean sites drilled during ODP Leg 160, and also with astronomically modulated variations in $CaCO_3$ content found in Mediterranean land-sections. This suggests that variations in bottom-water ventilation modulated by 400-kyr eccentricity cycles operated at a basin-wide scale.

Keywords: magnetic properties; sapropels; early diagenesis; magnetite dissolution; bottom-water ventilation; eastern Mediterranean

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1. Introduction

The role of primary productivity versus bottom-water anoxia has led to a long-lasting debate about the mechanisms leading to sapropel formation (see Cramp and O'Sullivan, 1999). Primary productivity represents the amount of organic matter produced in the water column by marine organisms and is the main factor controlling the flux of organic carbon to the sea floor. The term anoxia is used to indicate oxygen depletion in the bottom waters as a result of restricted bottom-water ventilation, and is related to other concepts such as stagnation, deep-water renewal and enhanced preservation (e.g. Vergnaud-Grazzini et al., 1977; Calvert et al., 1992; Emeis et al., 2000). Different uses of the term anoxia have created confusion between the processes leading to reduced ventilation of bottom waters and the diagenetic stage reached in sapropels, and have contributed to the misleading debate about whether anoxia is a cause or symptom of sapropel formation (see Cramp and O'Sullivan, 1999). In this paper, we use the term bottom-water ventilation instead of anoxia to indicate mechanisms controlling supply of oxygen to the sea floor, and the term anoxia exclusively when dealing with diagenetic processes.

It is now widely accepted that primary productivity and restricted bottom-water ventilation are not mutually exclusive as the mechanisms leading to sapropel formation (Cramp and O'Sullivan, 1999; Sancetta, 1999), because the net burial of organic carbon is controlled by the interplay between these two factors (see Canfield, 1994). In deep-sea sediments with low sedimentation rates (<30 cm/kyr), such as those recovered during Ocean Drilling Program (ODP) Leg 160 in the eastern Mediterranean Sea, microorganisms use dissolved oxygen to degrade organic matter as it arrives at the sea floor. Thus, only minor amounts of organic matter ($<0.5\%$) will accumulate in a sediment if the supply of dissolved oxygen in the pore waters, and the concomitant bacterial and microbial activity, can keep pace with the flux of organic carbon. If the productivity increases and/or the ventilation of the bottom waters diminishes, oxygen will eventually be depleted and organic matter will be preserved, resulting in the formation of a sapropel.

In the Mediterranean Sea, periods of enhanced primary production can be detected by high abundances of marine organisms such as eutrophic planktonic foraminifera (Rohling and Gieskes, 1989) or diatoms (Kemp et al., 1999), as well as by the presence of Ba/Al enrichments (e.g. Thomson et al., 1995; Wehausen and Brumsack, 2000; Calvert and Fontugne, 2001) and light nitrogen isotopic ratios (Calvert et al., 1992). Restricted bottom-water ventilation can be deduced by the lack of benthic fauna and bioturbation and the preservation of laminations (Jorissen, 1999; Kemp et al., 1999). Other evidence includes enrichments in trace metals (Nijenhuis et al., 1998; Warning and Brumsack, 2000), high C_{org}/N ratios (Rullkötter et al., 1998), distinctive isotopic compositions of organic matter, production of iron sulphide in the water column and distinctive sulphur isotopic compositions of pyrite (Passier et al., 1999), the presence of biomarkers derived from green sulphur bacteria (Passier et al., 1999), negative $\delta^{18}O$ values in planktonic foraminifera (Vergnaud-Grazzini et al., 1977) and relatively heavy $\delta^{13}C$ values from benthic foraminifera (Cacho et al., 2000). Despite the number of available proxies used to assess productivity and bottom-water ventilation, high-resolution data sets in the Mediterranean are only available for relatively thin stratigraphic intervals and, therefore, detailed long-term records of variations in their relative contribution to sapropel formation are not yet available. Both primary production and restricted deep-water ventilation have been directly linked to a variety of climatic variables such as land and sea-surface temperatures, precipitation, atmospheric moisture budget, continental run-off and wind strength (e.g. Rossignol-Strick, 1983; Rohling, 1994; Rullkötter et al., 1998; Kemp et al., 1999; Emeis et al., 2000; Cacho et al., 2000; Wehausen and Brumsack, 2000). Thus, studying long-term changes in productivity and bottom-water ventilation is important for understanding climatic variations in the Mediterranean and surrounding landmasses.

Recent studies of eastern Mediterranean sapropel-bearing sediments have shown that early dia-

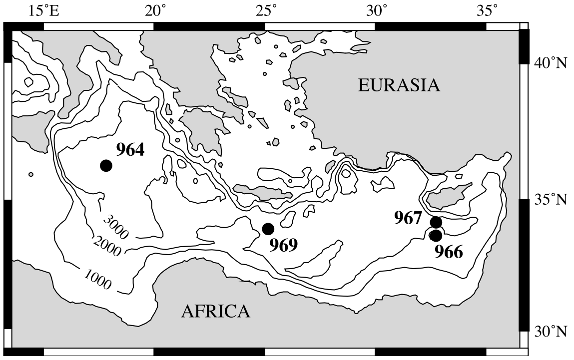


Fig. 1. Location of ODP Leg 160 sites from which sediments were analysed in this study.

genetic processes related to the accumulation and degradation of organic matter strongly affect the magnetic properties of sapropels and surrounding sediments (e.g. Langereis and Dekkers, 1999). Reductive dissolution of magnetic minerals, which leads to weak magnetisations, is usually reported in sapropels (van Santvoort et al., 1997), although in sapropels with high organic carbon concentration, magnetic enhancement can also occur due to authigenic growth of magnetic iron sulphide minerals (Roberts et al., 1999). Weak magnetisations are also observed just beneath many sapropels due to the downward migration of sulphide-rich diagenetic fronts that cause reductive dissolution of magnetic grains (van Santvoort et al., 1997; Passier et al., 2001). In contrast, strong magnetisations are observed on top of many sapropels due to the formation of new magnetic minerals in oxidation fronts that developed during periods after sapropel formation (Passier et al., 2001). From these investigations, it is apparent that the presence of distinctive magnetic properties is related to different, non-steady-state diagenetic stages triggered by accumulation of variable amounts of organic matter in the sapropels. Because this depends in turn on the balance between organic carbon flux (productivity) and available oxygen in the bottom waters (ventilation), magnetic properties might be useful for examining variations in either factor if independent data (i.e. geochemistry) are available to constrain the relative importance of the other. High-resolution studies combining magnetic and geochemical data are available for only a few sapropels (Passier et al., 2001), and the potential use of magnetic properties for unravelling the relationship between sapropel diagenesis and variations in productivity and bottom-water ventilation have therefore not been fully explored.

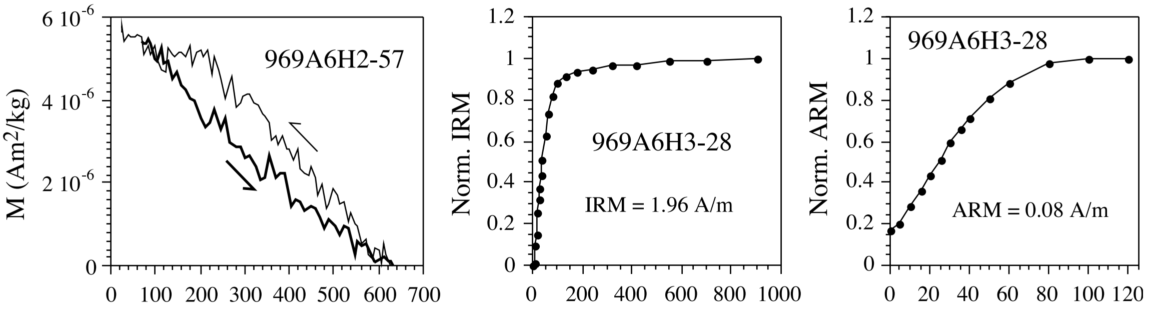
In this paper, we present a rock-magnetic survey of eastern Mediterranean sapropel-bearing sediments recovered during ODP Leg 160 (Fig. 1). The complete catalogue of studied sapropels and surrounding sediments indicates that distinctive magnetic properties, supported by available geochemical data (Wehausen and Brumsack, 1998, 2000), provide evidence for a causal relationship between different diagenetic stages and the relative contribution of productivity and bottom-water ventilation in sapropel formation. This allows development of a palaeo proxy for eastern Mediterranean bottom-water ventilation based on magnetic properties.

2. Materials and methods

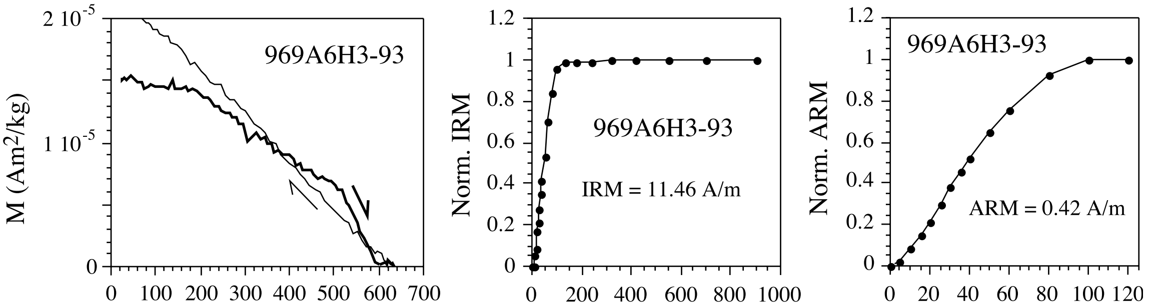
Rock-magnetic properties were measured at 1-cm intervals on u-channel samples using two shielded narrow-access 2-G Enterprises cryogenic magnetometers (e.g. Weeks et al., 1993) at the University of California (Davis) and at the Southampton Oceanography Centre (noise levels of less than 4×10^{-12} A m^2). U-channel samples were collected by pushing rigid, u-shaped plastic liners (2×2 cm cross-section, up to 1.5 m in length) into the archive halves of the cores. Magnetic data obtained from the u-channels are smoothed over a stratigraphic interval of ~4 cm because of the Gaussian shape of the magnetometer response function (Weeks et al., 1993). To avoid edge effects at the ends of the u-channels, data from the uppermost and lowermost 4 cm of each u-channel sample were not used in our analysis.

After measurement and stepwise alternating field (AF) demagnetisation of the natural remanent magnetisation, an anhysteretic remanent magnetisation (ARM) was imparted using a dc bias field of 0.05 mT parallel to a peak AF of 100 mT. An isothermal remanent magnetisation (IRM) was imparted with a field of 1 T using a

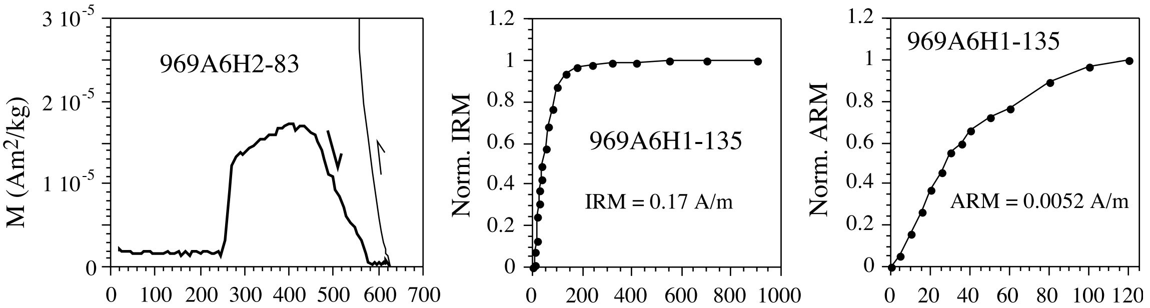
a) Background sediment



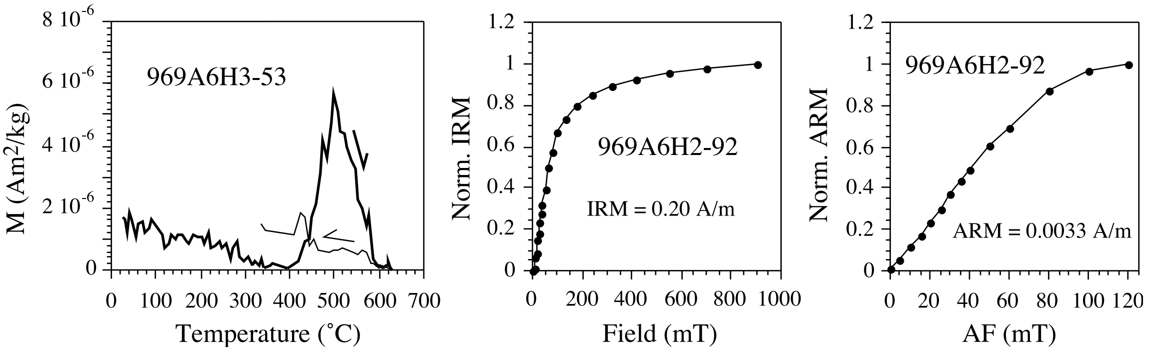
b) Oxidation front



c) Sapropel



d) Dissolution front



pulse magnetizer. We refer to this IRM as IRM@1T. Low-field magnetic susceptibility (χ) was measured on board the *JOIDES Resolution* using a Bartington Instruments MS-2 susceptibility meter with an 8-cm diameter sensing loop that induces a field of 0.1 mT at a frequency of 470 Hz. Susceptibility measurements were made at 3–5-cm intervals on whole-core sections and data were interpolated to the 1-cm u-channel measurement positions to enable direct comparison of results. Discrete samples within and around sapropels were selected for rock-magnetic analyses aimed at identifying the magnetic minerals responsible for the magnetic properties of the studied sediments. ARM acquisition curves were obtained by applying a bias field of 0.05 mT parallel to a peak AF at successive fields of up to 120 mT. IRM acquisition curves were obtained with a pulse magnetizer to a maximum field of 900 mT. Thermomagnetic curves were obtained for bulk samples with a variable field translation balance (VFTB), using a field of 75 mT and a heating rate of 10°C/min in air.

Our rock-magnetic analyses (Fig. 2) are consistent with those of Kruiver and Passier (2001), who demonstrated that the magnetic properties of the most recent Mediterranean sapropel (S1) and its surrounding sediments are mainly controlled by magnetite. Although hematite is also present, it does not substantially affect the bulk magnetic properties because it is weakly magnetic compared to magnetite. Magnetite is sensitive to non-steady-state diagenetic processes in eastern Mediterranean sediments (Kruiver and Passier, 2001), thus ARM, IRM@1T and χ can be used as proxies for the concentration of magnetite in the sediment resulting from early diagenetic processes. Fine ($\sim$0.02–1 μm) single-domain (SD) magnetite grains are more prone to acquire ARM than IRM@1T compared to coarser ($\sim$1–10 μm) pseudosingle-domain (PSD) and multi-domain (MD) grains ($>$10 μm). On the other hand, SD grains have only slightly lower χ values than MD grains. Therefore, interparametric ratios such as ARM/χ and IRM@1T/ARM can be used to examine the relative proportions of fine to coarse magnetite grains: increasing ratios of ARM/χ indicate the predominance of finer grains, whereas increasing values of IRM@1T/ARM indicate relatively higher concentrations of coarser particles. Details on the rock-magnetic parameters used in this study are given by King and Channell (1991), Verosub and Roberts (1995) and Dekkers (1997).

We have studied about 270 m (over 170 u-channels) of Early Pliocene–Holocene eastern Mediterranean sediments recovered at sites 964, 966, 967 and 969 during ODP Leg 160 (Fig. 1). Some of the data presented here were included in a data report by Stoner et al. (1998). The data set includes more than 140 sapropels and 30 oxidised (ghost) sapropels that formed in different palaeoceanographic settings (Emeis et al., 1996). Sapropels and other distinctive layers in the studied cores were identified by Emeis et al. (1996, 2000) and Shipboard Scientific Party (1996a–d). Geochemical data used in this study and details about the analytical techniques employed have been published by Wehausen and Brumsack (1998, 2000). All rock-magnetic and geochemical data shown in this paper are presented using the revised metre composite depth (rmcd) sections established by Sakamoto et al. (1998). The adopted sapropel chronology is that of Emeis et al. (2000), who constructed astronomical age models that provide age control for each analysed stratigraphic interval to better than a few thousand years. The age models are consistent with biostratigraphic, palaeomagnetic and oxygen isotopic data (e.g. Di Stefano, 1998; Howell et al., 1998; Kroon et al., 1998; Richter et al., 1998; Sprovieri et al., 1998; Staerker, 1998). Sapropels are num-

Fig. 2. Thermomagnetic and normalised IRM and ARM acquisition curves for a representative background sediment (a), oxidation front (b), sapropel (c), and dissolution front (d) from ODP Site 969 (see text). The thick and thin lines in the thermomagnetic runs indicate the heating and cooling cycles, respectively. The maximum values of ARM and IRM are given for comparison of intensities among the different types of sediment.

bered after their correlative summer insolation maxima (i-cycles), as proposed by Lourens et al. (1996).

3. Magnetic properties of sapropels and sapropel-bearing sediments

Sediments located away from sapropels, which we refer to as 'background sediments', have typical ARM intensities of ∼0.1 A/m, which is consistent with minor variations in the concentration of magnetic minerals (Figs. 3–5). ARM/χ and IRM@1T/ARM values do not undergo important variations in background sediments, which suggests a relative homogeneity in their magnetic grain size. Although thermomagnetic curves for background sediments are noisy (Fig. 2a), the main loss of magnetisation below 600°C indicates that magnetite is the main magnetic mineral present. The residual magnetisation above 600°C might indicate minor amounts of maghemite or hematite, but their contribution to the magnetisation is small compared to that of magnetite. The presence of a small high-coercivity component is indicated by incomplete saturation above 300 mT in the IRM acquisition data. However, the magnetic assemblage appears to be dominated by the low-coercivity magnetite, as indicated by the IRM and ARM acquisition curves, which reach more than 90% of their maximum value at 100 mT.

In contrast to the background sediments, the magnetic properties around sapropels undergo striking variations. Distinctively low ARM intensities ($\ll$0.1 A/m) are observed just underneath many sapropels, indicating that the concentration of magnetic minerals at these positions is low. This depletion of magnetic minerals has been explained by reductive dissolution of magnetite (Canfield and Berner, 1987) caused by the downward diffusion of excess sulphide from the sapropels into previously deposited oxic sediments (Passier et al., 1996, 2001; van Santvoort et al., 1997). Different terms such as 'proto-sapropel' (Muerdter et al., 1984) and 'syn-sapropel' (Passier et al., 1996) have been used in the literature to refer to these positions underneath sapropels where reductive dissolution has occurred. In this paper, we use the term 'dissolution front' because it better accounts for the magnetic characteristics and it does not have the misleading temporal connotations suggested by the prefixes 'proto' and 'syn'. From our magnetic results, dissolution fronts are commonly about 20 cm in thickness, although they can also extend down to almost 50 cm underneath some sapropels (see i-130 in Fig. 3). The low magnetisation and the formation of new magnetic phases upon heating above 400°C, which is probably due to the thermal breakdown of pyrite (Passier et al., 2001), prevented identification of magnetic minerals in dissolution fronts (Fig. 2d). IRM and ARM acquisition curves are not saturated at 100 mT, although they reach about 70% and 90%, respectively, of their maximum values at that field. The higher coercivity of the magnetic assemblage is consistent with preferential dissolution of low-coercivity magnetite, which is the main magnetic mineral in the sediments before they are affected by downward diffusion of excess sulphide from the sapropels, and the survival of higher-coercivity magnetic grains. Sediments affected by reductive dissolution have distinctive light-grey colours that are clearly reflected in the values of a^*, which gives an indication of the ratio of green versus red colour of the sediment (Emeis et al., 1996). Values of a^* for most intervals affected by dissolution typically range between 0 and -1, indicating a predominance of greenish over reddish colourations (e.g. Figs. 3–6). ARM/χ reaches minimum values within zones of dissolution, which indicates the presence of relatively coarse magnetic grains. It should be noted that paramagnetic and diamagnetic minerals, which do not contribute to ARM, can contribute to χ and, thus, the ARM/χ profile might not be an ideal proxy for grain size. Nevertheless, the presence of relatively coarser-grained magnetic minerals at dissolution fronts is also indicated by an increase in the IRM@1T/ARM ratio, which responds only to minerals that contribute to the remanence. Prominent IRM@1T/ARM peaks usually appear at the position of active dissolution fronts below sapropels (e.g. sapropels i-122, i-126, i-130 and i-140 in Fig. 3), where preferential dissolution of fine magnetite grains occurs (Dekkers et al., 1994; van Santvoort et al., 1997;

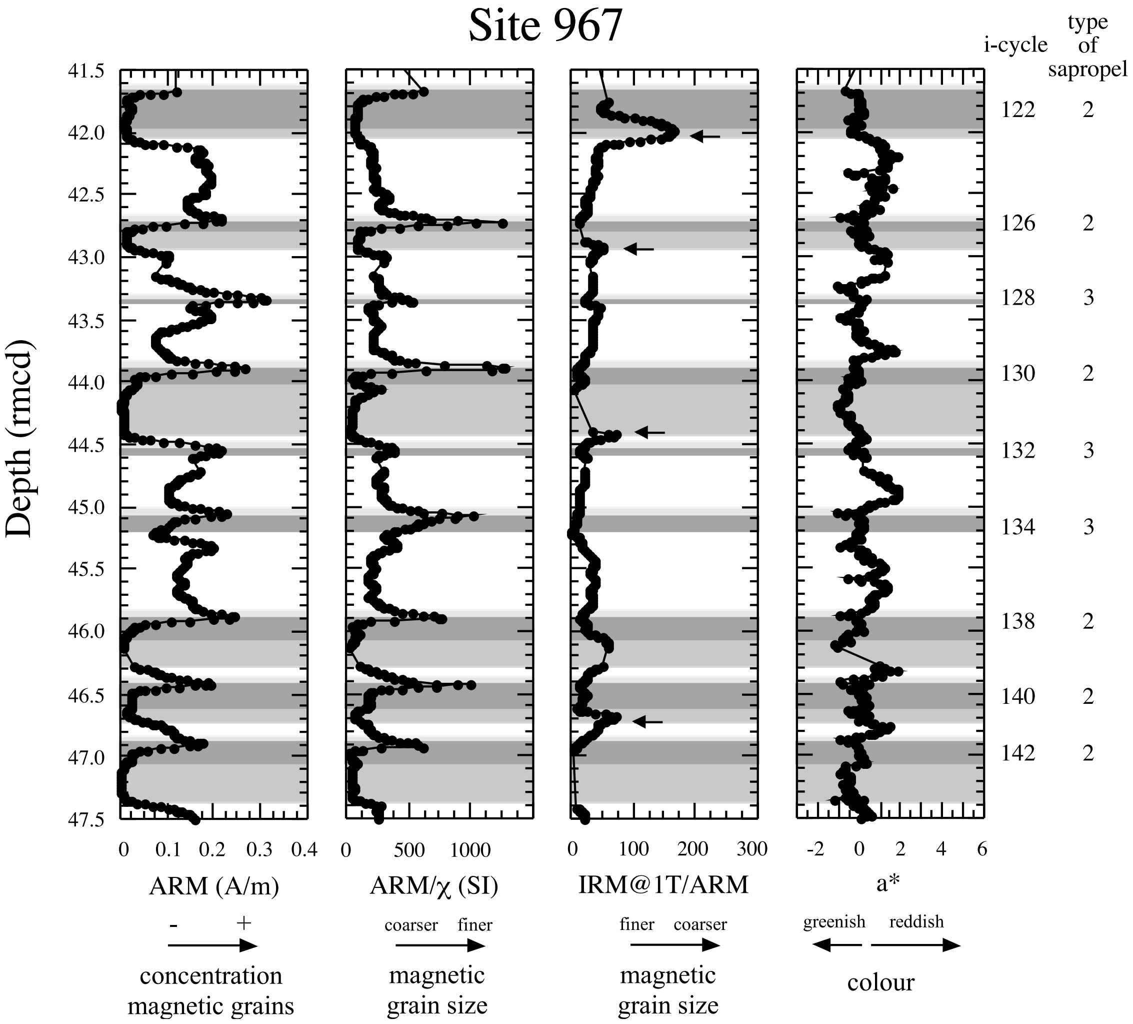


Fig. 3. Magnetic properties and sediment colour variations (red/green) of sapropel-bearing sediments from Site 967 (~1.3–1.5 Ma). The position of sapropels is marked by the dark grey shading. Grey shading underneath indicates areas affected by reductive dissolution of magnetic minerals, whereas the light-grey shading above sapropels indicates oxidation fronts. The arrows indicate the lowermost part of the dissolution fronts. Types of sapropels are listed according to the description given in Section 4.2.

Roberts et al., 1999; Passier et al., 2001). As dissolution fronts progress downward, coarser grains are eventually dissolved, whereas the areas located just above the front start to undergo preferential dissolution of the finer magnetic fraction.

The sediments located immediately above sapropels also have distinctive magnetic properties (Figs. 3–5). ARM intensities are higher than in the background sediments (up to 0.4 A/m), which indicates higher concentrations of magnetic minerals above many sapropels. This is consistent with the formation of new magnetite at oxidation fronts that developed on top of sapropels (Passier et al., 2001) when the sea floor was reoxygenated after sapropel formation (Higgs et al., 1994; Thomson et al., 1995). Oxidation fronts can be up to 20 cm in thickness (e.g. sapropel i-272 in Fig. 4), although they are commonly less than 10–15 cm thick. They usually have *a** values higher than those for dissolution fronts but lower than the background sediments. Rock-magnetic experiments demonstrate that the main magnetic miner-

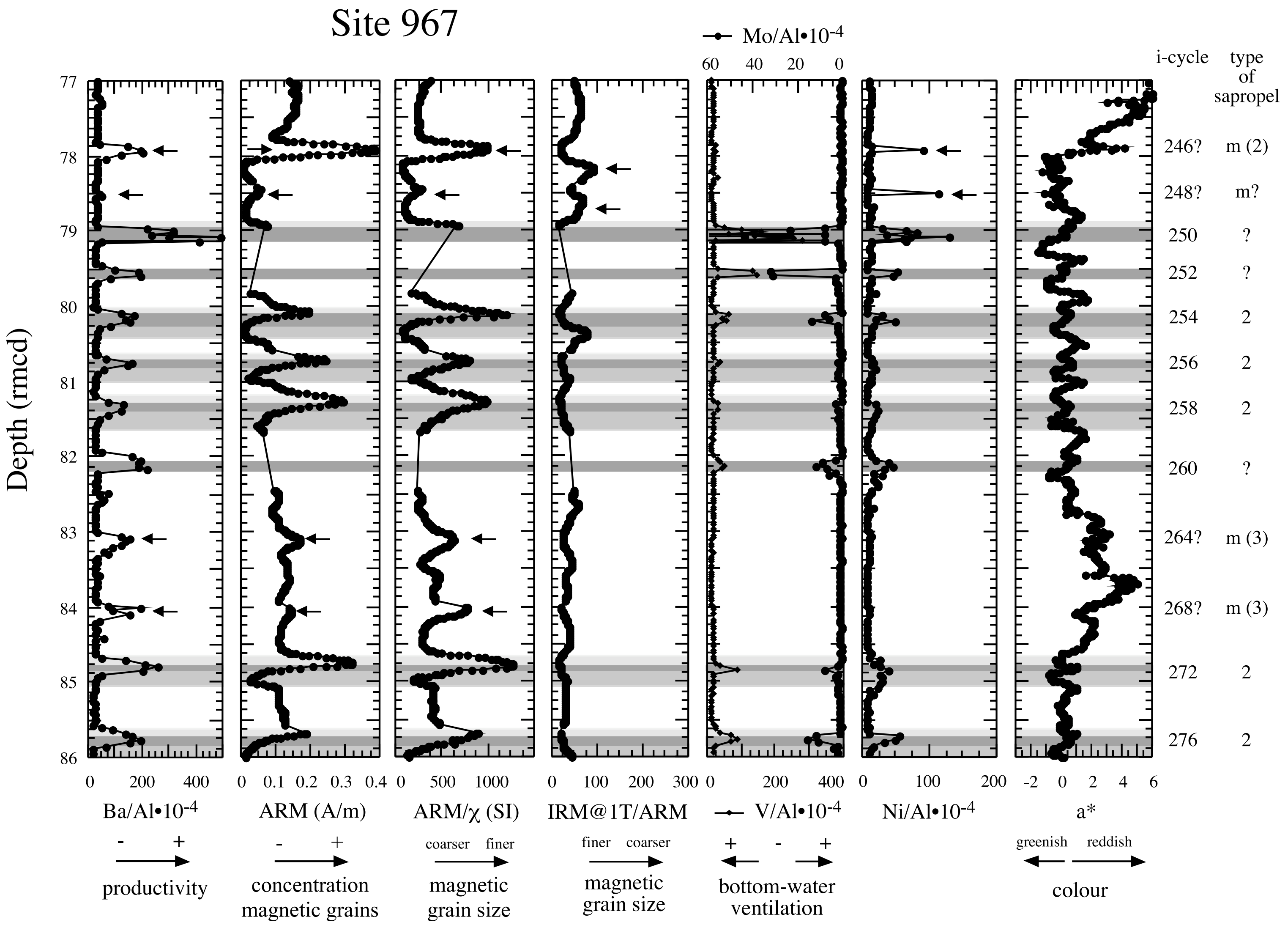


Fig. 4. Comparison of magnetic, geochemical and sediment colour data for sapropel-bearing sediments from ODP Site 967 (∼2.5–2.9 Ma). The position and type of sapropels and the position of dissolution and oxidation fronts is marked as in Fig. 3. The arrows mark the positions where magnetic and geochemical data indicate the presence of missing sapropels. Geochemical data are from Wehausen and Brumsack (2000).

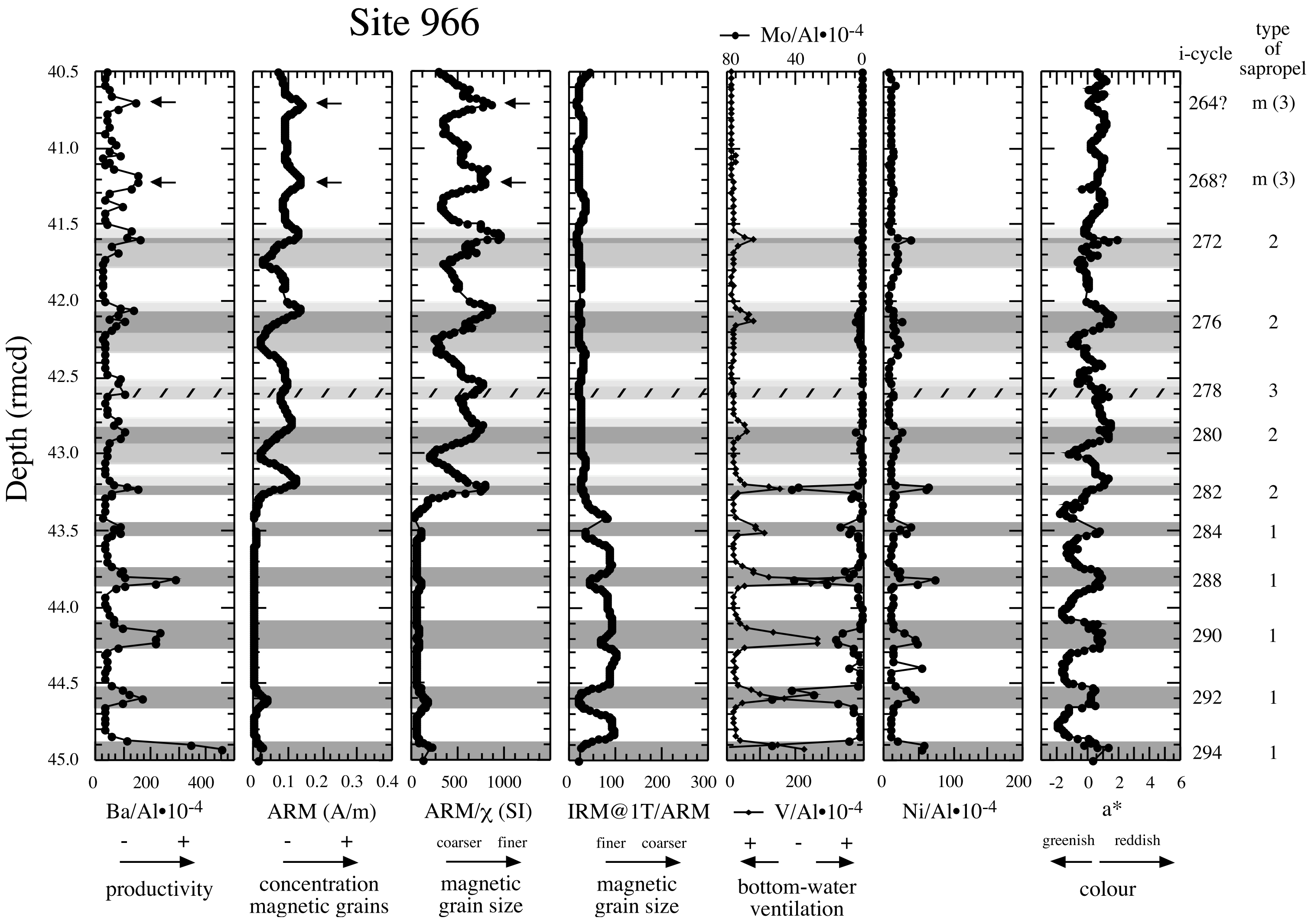


Fig. 5. Comparison of magnetic, geochemical and sediment colour data for sapropel-bearing sediments from ODP Site 966 (∼2.75–3.1 Ma). The positions of sapropels and dissolution and oxidation fronts are marked as in Fig. 3. The light grey, hatched interval at ∼42.6 rmcd represents a ghost (oxidised) sapropel. The arrows indicate positions where magnetic and geochemical data suggest the presence of missing sapropels. For discussion about the position of diagenetic fronts between 43.5 and 45 rmcd, see text (Section 4) and Fig. 9. Geochemical data are from Wehausen and Brumsack (2000).

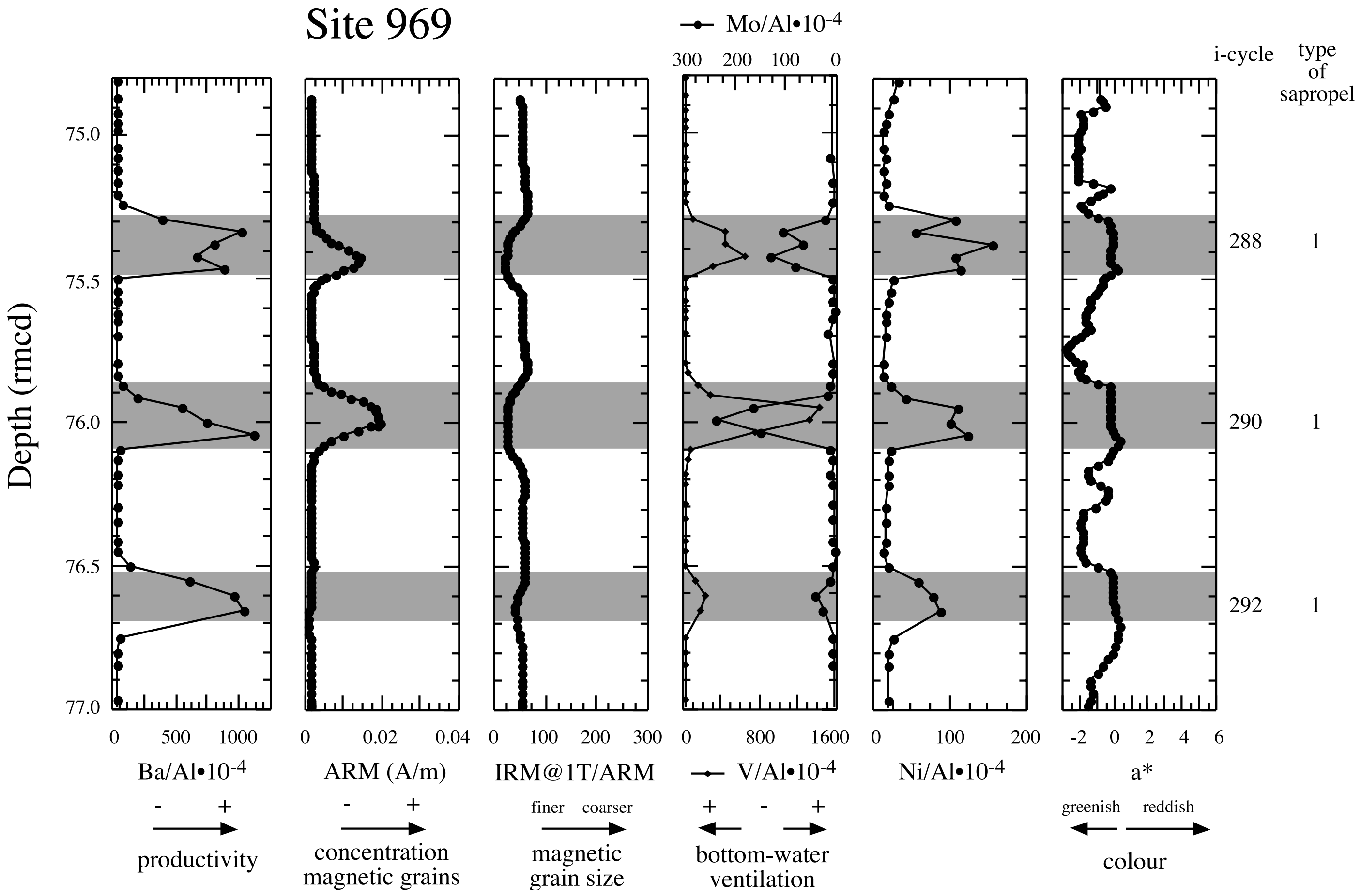


Fig. 6. Comparison of magnetic, geochemical and sediment colour data for sapropel-bearing sediments from ODP Site 969 (∼3.0–3.05 Ma). The positions of sapropels are marked as in Fig. 3. For discussion about the position of diagenetic fronts, see text (Section 4) and Fig. 9. Geochemical data are from Wehausen and Brumsack (2000).

al present at oxidation fronts is low-coercivity ($<$ 100 mT) magnetite (Fig. 2b). Oxidation fronts are characterised by low IRM@1T/ARM and high ARM/χ ratios, which indicates the presence of fine-grained magnetite whose formation is probably bacterially mediated (Passier et al., 2001). Magnetic properties similar to those associated with eastern Mediterranean sapropels have also been reported for dissolution and oxidation fronts outside the Mediterranean (Karlin et al., 1987; Tarduno and Wilkinson, 1996; Tarduno et al., 1998; Vigliotti et al., 1999; Robinson and Sahota, 2000; Robinson et al., 2000).

Interpretation of magnetic properties within sapropels is not straightforward due to the smoothing of the magnetic signal inherent to u-channel measurements. This can be a problem because sapropels are located in positions where the contrast in ARM intensities is largest. ARM values increase progressively between the dissolution fronts below and the oxidation fronts above sapropels, respectively. The smoothing, however, prevents interpretation of this pattern in terms of concentration of magnetic grains. Only when sapropels are thick (e.g. sapropel i-122 in Fig. 3) can reliable interpretations be made. In these cases, low ARM intensities, comparable to those associated with dissolution fronts, are usually observed. Grain-size-dependent parameters are also affected by smoothing, although they seem to show a pattern similar to that observed for dissolution fronts. The low magnetisation and the formation of new magnetic phases upon heating prevented identification of magnetic minerals in sapropels (Fig. 2c). IRM and ARM acquisition curves are almost saturated at 100 mT, which indicates that the magnetic assemblage in sapropels is mainly controlled by low-coercivity minerals. Overall, the data suggest that the magnetic properties of sapropels are mainly controlled by reductive dissolution of magnetite (Passier et al., 2001).

The magnetic signature of dissolution and oxidation fronts described above is representative for most of the sapropels recovered during ODP Leg 160. However, a significant number of sapropels have markedly different magnetic properties. Some sapropels do not have underlying dissolution fronts, as can be deduced by ARM, ARM/χ and IRM@1T/ARM values (e.g. i-128, i-132 and i-134 in Fig. 3). In other cases (see lower part of Fig. 5), there is a striking lack of higher concentrations of fine-grained magnetic minerals typically associated with oxidation fronts. Moreover, some sapropels have ARM intensities that are higher than those of the surrounding sediments (Fig. 6) due to authigenic growth of magnetic iron sulphides (Roberts et al., 1999).

Regardless of their magnetic properties, all of the sapropels for which geochemical data are available are characterised by variable enrichments in Ba/Al and/or trace metals (Figs. 4 to 6), as expected for eastern Mediterranean sapropels (Pruysers et al., 1993; Thomson et al., 1995; van Santvoort et al., 1997; Wehausen and Brumsack, 1998, 2000; Calvert and Fontugne, 2001). Ba/Al ratios are used as a proxy for biogenic barite, which can be related to variations of productivity in the surface waters (e.g. Paytan et al., 1996). On the other hand, enrichments of trace metals such as Mo, V and Ni can be related to restricted bottom-water ventilation because they are incorporated into sapropels either by being bound to organic matter (Mo, V) or by being coprecipitated with iron sulphides (Ni) (Nijenhuis et al., 1998; Warning and Brumsack, 2000). Of particular interest is Mo, because it has a relatively high concentration in seawater compared to other trace metals and is only moderately enriched in organic matter (Schenau et al., 1999). As a result, enhancements in Mo can be related to restricted deep-water ventilation, rather than to increased organic carbon supply.

Distinctive peaks in Ba/Al ratios and trace metals also appear in positions where no sapropels have been reported (Figs. 4 and 5). Such geochemical signatures have been used to detect missing sapropels that escaped visual identification due to their complete removal by post-depositional oxidation (Higgs et al., 1994; Langereis et al., 1997; van Santvoort et al., 1997; Wehausen and Brumsack, 2000; Calvert and Fontugne, 2001). Some of these positions where missing sapropels are detected by their geochemical properties also have conspicuous magnetic properties that are typically related to coupled dissolution/oxidation fronts (e.g. ~78 rmcd in Fig. 4). This indicates that magnetic analyses are a reliable tool for identifying missing sapropels (van Santvoort et al., 1997).

4. Discussion

4.1. Magnetic properties of sapropels and diagenetic scenarios

The set of magnetic properties described above result from the relative strength of diagenetic reactions triggered by degradation of organic matter (e.g. Froelich et al., 1979; Berner, 1980) at the time of, and after, sapropel formation. Reductive dissolution of magnetic minerals is caused when oxygen, nitrate and Mn–Fe oxides, which are used by microorganisms to consume organic matter, are depleted in the sedimentary pore waters. Sulphate ions then provide a new source of electrons for bacterial and microbial metabolism. Reduction of sulphate leads to formation of sulphide, which reacts with Fe^{2+} that is liberated by reductive dissolution of iron-bearing minerals to form pyrite (Passier et al., 1996).

Most of the sapropels recovered during ODP Leg 160 are enriched in pyrite (Emeis et al., 1996), which demonstrates that low ARM intensities found within and below sapropels are caused by reductive dissolution of magnetite. Two different scenarios can be envisaged during anoxic conditions (Berner, 1969; Passier et al., 1999). In the first scenario (high-Fe), sulphide production in the sapropel is smaller than Fe^{2+} liberation within the sapropel and/or in the underlying sediments, which leads to in situ formation of pyrite within the sapropel. In the second scenario (low-Fe), sulphide production occurs at higher rates than Fe^{2+} liberation and, thus, excess sulphide can migrate into sediments below the sapropel. Here, it reacts with magnetic minerals and/or upward-diffusing Fe^{2+} to form pyrite. The diagenetic scenario prevailing at the time of sapropel formation can be determined from magnetic properties, with low- and high-Fe settings corresponding to sapropels with and without dissolution fronts, respectively. Background sediments usually have ARM values of about ~0.1 A/m that are fairly constant and higher than in dissolution fronts, which indicates that reductive dissolution of magnetite did not occur during their deposition. Thus, the main factor controlling formation and development of dissolution fronts is production of excess sulphide in the sapropel as a result of higher availability of organic matter, rather than the supply of Fe^{2+} from underlying sediments. Suboxic dissolution of magnetite in background sediments probably occurred in some intervals (see next section) and, thus, upward-diffusion of Fe^{2+} from underlying sediments may play a role in some cases. Roberts et al. (1999) showed that magnetic enhancement of sapropels is proportional to the organic carbon content. This is supported by the magnetic enhancement reported for sapropels shown in Fig. 6, which have organic carbon contents of up to 30% by weight. These observations suggest that the distinctive but variable magnetic properties associated with sapropels (e.g. the lack or presence of dissolution fronts and diagenetic magnetic enhancement) can be linked to increasingly anoxic conditions at the time of sapropel formation.

Immediately after sapropel formation, diagenetic reactions in sapropels are mainly controlled by downward diffusion of oxygen from overlying sediments (Higgs et al., 1994; Thomson et al., 1995). Oxygen reacts with Fe^{2+} liberated from pyrite and also with upward-diffusing Fe^{2+} coming from the part of the sapropel located underneath the oxidation front (Passier et al., 2001). This oxidation is bacterially mediated and results in the formation of fine-grained magnetite, and probably also amorphous iron oxides (Passier et al., 2001), at the site of active oxidation. Development of oxidation fronts depends on post-depositional supply of oxygen and on the amount of pyrite and Fe^{2+} present in the sapropel, which is conditioned by the strength of anoxic conditions during sapropel formation. If anoxic conditions at the time of sapropel formation were less severe and/or the amount of oxygen in the overlying sediments increased after sapropel deposition, development of oxidation fronts will be favoured until they eventually cause the complete removal of sapropels.

Table 1
Magnetic and geochemical characteristics and environmental significance of different types of sapropels

Sapropel	Magnetic properties				Geochemical properties	Environmental significance
	Sapropel	Overlying sediments	Underlying sediments	Background sediments		
Type 1 (highly anoxic)	Often magnetically enhanced (ARM > 0.01 A/m)	No oxidation front ARM ≪ 0.01 A/m	ARM ≪ 0.01 A/m	ARM ≪ 0.01 A/m	Major Ba and trace metal enhancements	Very high productivity; very low ventilation
Type 2 (anoxic)	ARM < 0.1 A/m	Oxidation front ARM > 0.1 A/m	Dissolution front ARM ≪ 0.01 A/m	ARM ~ 0.1 A/m	Ba and trace metal enhancements	High productivity; low ventilation
Type 3 (less anoxic)	ARM ≤ 0.1 A/m (often completely oxidised)	Oxidation front ARM > 0.1 A/m	No dissolution front ARM ~ 0.1 A/m	ARM ~ 0.1 A/m	Ba enhancements and minor (if any) trace metal enrichment	High productivity; high ventilation

4.2. Types of sapropels and their diagenetic significance

Sapropels recovered during ODP Leg 160 can be grouped into three main categories which represent decreasing anoxic conditions at the time of sapropel formation. They can be described by the distinctive magnetic signatures described above, i.e. dissolution and oxidation fronts and magnetic enhancement (Table 1).

4.2.1. Type 1 – sapropels without oxidation fronts

Type 1 sapropels are shown in Figs. 5 and 6. They occur in long intervals with extremely low ARM intensities and are often related to diagenetic magnetic enhancement (Roberts et al., 1999). The low concentrations of magnetic minerals found between sapropels of this type can be interpreted to reflect a lack of oxidation fronts developed after sapropel formation, or, alternatively, as due to the development of extremely thick dissolution fronts that affected previously formed oxidation fronts. In the first case, anoxic conditions at the time of sapropel formation would have been followed by suboxic conditions between sapropels. In the second case, the effect of oxic conditions between sapropels would have been removed by the ensuing extremely anoxic conditions at the time of formation of the next sapropel. The overall magnetic properties associated with this type of sapropel and their high organic carbon contents (between 10 and 30% by weight) indicate that they were deposited under severely anoxic conditions. We refer to these sapropels as ‘highly anoxic’. Highly anoxic sapropels always have large enrichments in Ba/Al, Mo, V and Ni, which indicates that productivity was high and that bottom-water ventilation was low during their formation.

4.2.2. Type 2 – sapropels with both dissolution and oxidation fronts

Type 2 sapropels are characterised by the presence of both well-developed dissolution and oxidation fronts (Figs. 3–5), and represent the most abundant type of sapropel recovered during ODP Leg 160. The presence of dissolution fronts indicates sufficient accumulation of organic matter to produce excess sulphide, which migrated downward resulting in magnetite dissolution. Diagenetic conditions must have become oxic between periods of sapropel formation in order to promote development of oxidation fronts. No clear ARM peaks are observed within this type of sapropel, which suggests that diagenetic magnetic enhancement was rare if not absent. This is difficult to prove on the basis of magnetic data alone due to the smoothing of the signal just above oxidation fronts, but it is consistent with the lower organic carbon contents of these sapropels ($< 10\%$ by weight) compared with type 1 sapropels. We refer to type 2 sapropels as ‘anoxic’. They are characterised by relatively high concentrations of Ba/Al, and, in most cases, by enrichments in Mo, V and Ni.

4.2.3. Type 3 – sapropels without dissolution fronts

This type of sapropel is characterised by the absence of dissolution fronts and the presence of well-developed oxidation fronts (Fig. 3). The presence of oxidation fronts indicates that anoxic, sulphate-reducing conditions prevailed at the time of sapropel formation because formation of oxidation fronts requires the presence of pyrite and/or Fe^{2+} in the sapropel. The lack of dissolution fronts indicates, however, that no excess sulphide was produced in these sapropels and therefore that anoxic conditions were less severe compared with sapropels of type 2. We refer to type 3 sapropels as ‘less anoxic’. Although less anoxic sapropels are not visible in the intervals where geochemical data are available, closer examination of Figs. 4 and 5 reveals that sapropels of this kind are often present, but that they escaped visual identification due to their complete oxidation by post-depositional processes. Elevated Ba/Al ratios are found in intervals that do not correspond to previously identified sapropels (at 78, 83 and 84 rmcd in Fig. 4 and 40.7 and 41.2 rmcd in Fig. 5). High ARM and ARM/χ values at the same positions indicate increased concentrations of fine-grained magnetite and therefore indicates the former occurrence of a sapropel because both pyrite and/or dissolved Fe^{2+}, which result from anoxic conditions, are required to form magnetite at oxidation fronts (see also Langereis et al., 1997; van Santvoort et al., 1997).

4.3. Environmental significance of different types of sapropels

The interval from Site 966 shown in Fig. 5 provides a good opportunity for comparing Ba/Al ratios and trace metal concentrations to address the relative role played by productivity and bottom-water ventilation, because it contains sapropels of the three types described above and changes in sedimentation rate and carbonate contents are minimised. The highest Ba/Al ratios and concentrations of trace metals appear to be associated with highly anoxic sapropels (type 1), which indicates that they formed under conditions where productivity was highest and where bottom-water ventilation was lowest. The four anoxic (type 2) sapropels shown in the figure have smaller Ba/Al enrichments, which reflect lower primary productivity. V and Ni concentrations are smaller but still important, and Mo is usually almost completely absent. This suggests that bottom-water ventilation was less restricted during formation of such sapropels. It appears that relatively decreased productivity and increased ventilation account for formation of anoxic sapropels, although the latter factor seems to play a major role, as suggested by the marked decrease (or even disappearance) of trace metals compared with relatively smaller changes in Ba/Al ratios. Less anoxic sapropels (type 3) have Ba/Al ratios comparable to those of type 2 sapropels, which indicates that productivity was as high as during the formation of anoxic (type 2) sapropels. Thus, the better explanation to account for the less severely anoxic conditions reached during formation of type 3 sapropels is an increase in bottom-water ventilation, which would allow oxic degradation of organic matter before it is deeply buried in the sediment. This interpretation is supported by the virtual absence of trace metal enrichments associated with such sapropels.

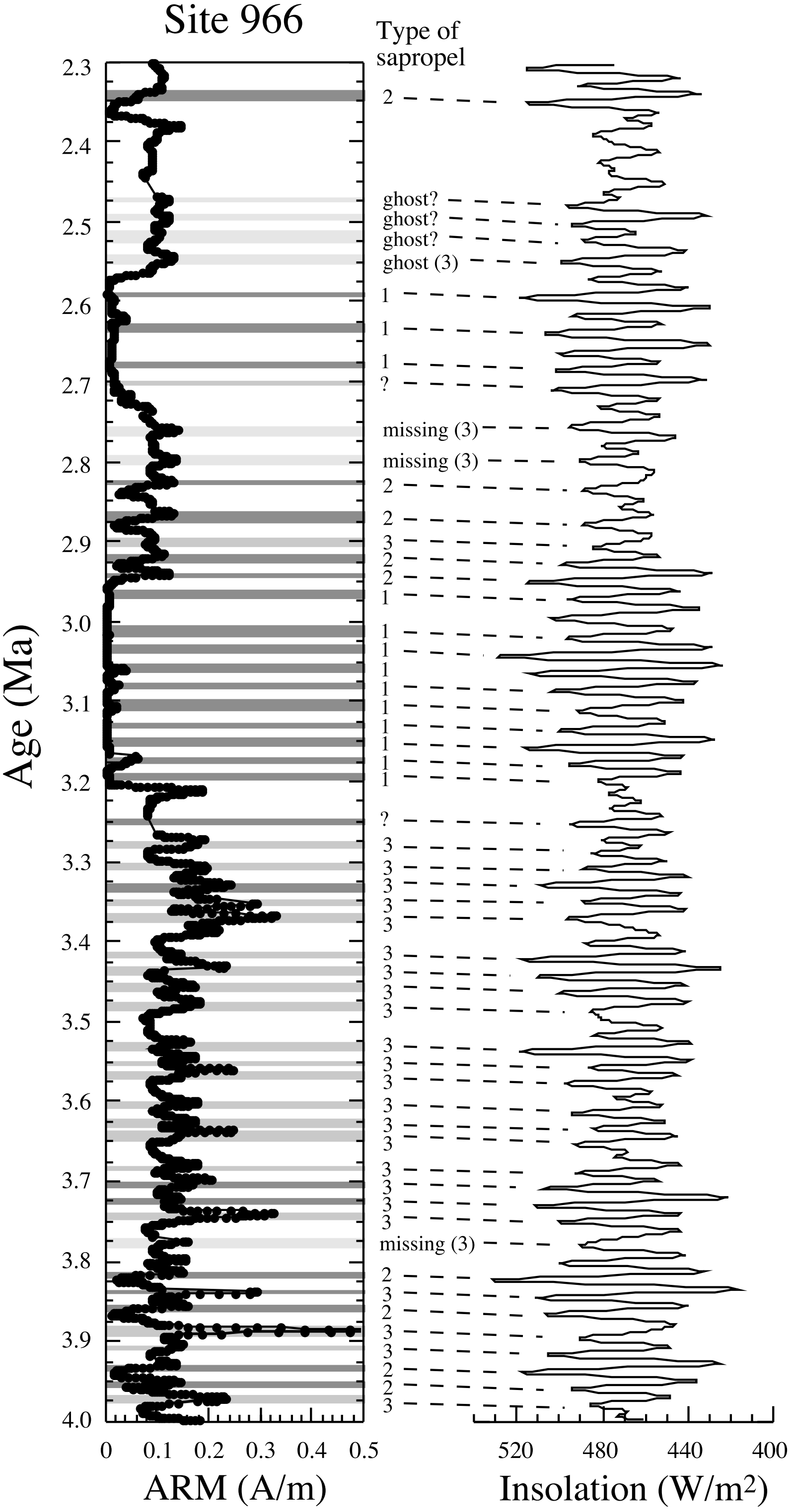
Magnetic and geochemical data from other intervals are consistent with the environmental scenarios proposed for the three types of sapropels at the time of their formation. Highly anoxic sapropels from Fig. 6 have Ba/Al, Mo, V and Ni enrichments not found in any anoxic or less anoxic sapropel, which indicates high productivity and restricted bottom-water ventilation. Anoxic and less anoxic sapropels seem to have formed under similar productivity scenarios (comparably high Ba/Al ratios). However, the diagenetic context in which they formed is different as a result of variable efficiencies in bottom-water circulation, which is evident in the differences observed between anoxic (moderate enrichments in trace metals) and less anoxic (lack of trace metal enrichment) sapropels. Based on their geochemical and magnetic properties, we can assign a relative value of productivity and bottom-water ventilation for three types of sapropels. Productivity at the time of sapropel formation can be described as high for type 1 sapropels and moderate for types 2 and 3 sapropels. Bottom-water ventilation was lower during formation of type 1 sapropels and increased progressively during formation of sapropels of types 2 and 3. Productivity appears to have been less variable compared to bottom-water ventilation. Also, regardless of the presence of trace metal enhancements, none of the sapropels for which geochemical data are available is lacking Ba/Al enrichments. These observations indicate that increased productivity is a prerequisite for sapropel formation and that, once organic matter is available in sufficient amounts, variable efficiencies in bottom-water ventilation are more important for modulating the diagenetic context in which different types of sapropels formed.

The main magnetic and geochemical characteristics of the three different types of sapropels are summarised in Table 1. We note that this scheme applies to sapropels formed in basinal areas under low (<5 cm/kyr) accumulation rates, and that further studies in other settings are required to produce a complete rock-magnetic catalogue of eastern Mediterranean sapropels.

4.4. *Long-term variations in bottom-water ventilation*

A continuous ARM record from Site 966 (Eratosthenes Seamount) between 2.3 and 4.0 Ma (Fig. 7) includes 27 sapropels and 21 ghost sapropels (Emeis et al., 2000). Most of the background sediments have ARM intensities of $\sim$0.1 A/m. Intervals with ARM values below those of normal background sediments are found at around 2.6–2.7 Ma and 3.0–3.2 Ma. Comparably low values are absent between 2.4 and 2.6 Ma, 2.7 and 2.8 Ma, and 3.2 and 3.8 Ma, where distinctive ARM peaks are found. Intervals between 2.8 and 3.0 Ma and between 3.8 and 4.0 Ma are characterised by both ARM peaks and minima associated with sapropels. The three types of sapropels are not randomly distributed. These observations indicate that periods of pronounced and less pronounced anoxic conditions at the sea floor alternated throughout time. Highly anoxic sapropels (type 1) predominate between 2.6 and 2.7 and between 3.0 and 3.2 Ma, whereas anoxic sapropels (type 2) cluster at around 2.9 Ma and at 3.8–4.0 Ma and less anoxic sapropels (type 3) are the only ones found between 3.3 and 3.8 Ma.

We can produce a proxy record of bottom-water ventilation at the time of sapropel formation on the basis of sapropel type (Fig. 8d). Magnetic data might also provide additional information about the relative efficiency of bottom-water ventilation at periods between sapropels (Fig. 8e). Development of oxidation fronts requires a supply of oxygen from the sediments above sapropels, which suggests that bottom waters often reventilated to normal values after periods of sapropel formation, as indicated by the presence of oxidation fronts above most sapropels. Complete oxidation of sapropels might only be accomplished if reventilation of bottom waters was enhanced beyond values operating prior to sapropel deposition, as proposed by Wehausen and Brumsack (2000) to explain the differences in preservation observed for sapropels formed under similar organic carbon fluxes (sapropels i-256 and i-258 and missing sapropel i-264 from Fig. 4). It is possible, however, that oxidation of organic matter occurred before it was buried in the sediment, which raises the question about whether the proposed missing sapropels formed but were subsequently erased by post-depositional processes or whether they did not form at all due to the lack of favourable climatic conditions (Calvert and Fontugne, 2001). Magnetic data favour the first inter-


Site 966
Type of sapropel
2
ghost?
ghost?
ghost?
ghost (3)
1
1
1
?
missing (3)
missing (3)
2
2
3
2
2
1
1
1
1
1
1
1
1
1
1
?
3
3
3
3
3
3
3
3
3
3
3
3
3
3
3
3
3
3
3
missing (3)
2
3
2
3
3
2
2
3
Age (Ma)
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
0
0.1
0.2
0.3
0.4
0.5
ARM (A/m)
520
480
440
400
Insolation ($\mathrm{W/m^2}$)

pretation because the proposed missing sapropels have high concentrations of fine-grained magnetite typical of, although slightly lower than, oxidation fronts. Also, development of oxidation fronts requires Fe^{2+} and pyrite which are produced, in turn, when sulphate-reducing conditions occur in the sediment due to the availability of organic matter (Passier et al., 1999). Clusters of completely oxidised (ghost or missing) sapropels might therefore indicate prolonged periods of enhanced ventilation between sapropels.

Restricted bottom-water ventilation between sapropels is also suggested by magnetic properties. In the intervals characterised by low ARM intensities (lower part of Figs. 5 and 6), S/Al and Fe/Al ratios are enhanced in sapropels due to diagenetic formation of pyrite (Fig. 9). S/Al and Fe/Al peaks are also observed down to 40 cm beneath sapropels and indicate the position of active pyritisation fronts where sulphide migrating downward from a sapropel encountered Fe^{2+} diffusing upward from underlying sediments (Passier et al., 1999). Low ARM values in background sediments below active pyritisation fronts are therefore unrelated to downward sulphide diffusion and must result from in situ dissolution of magnetite before the downward-moving sulphide fronts developed. This solves the question (Section 4.2.1) concerning the lack of oxidation fronts developed above type 1 sapropels, because it indicates that oxygen was depleted in background sediments when bottom-water ventilation did not return to normal conditions after sapropel formation, thereby preventing development of oxidation fronts. Long intervals with low ARM intensities therefore indicate periods with low ventilation between sapropels.

If all the magnetic data are integrated, a general view of the evolution of bottom-water ventilation can be produced for Site 966 (Fig. 8). Periods between 2.6 and 2.7 Ma and between 2.95 and 3.2 Ma are characterised by type 1 sapropels and low ARM values, which indicates that bottom-water ventilation was restricted both at, and after, periods of sapropel formation. The intervals at 2.3–2.4 Ma, 2.85–2.95 Ma and 3.8–4.0 Ma are characterised by type 2, and, to a lesser extent, by type 3 sapropels, which suggests that bottom-water ventilation was relatively higher at these times. In the intervals at 2.4–2.6 Ma, 2.7–2.8 Ma and 3.3–3.8 Ma, ARM minima are almost absent. Most of the sapropels are of type 3 and are, with few exceptions, completely oxidised (e.g. ghosts). This indicates that ventilation during these intervals was the highest, both at the time of sapropel formation and afterward.

The red intervals in ODP Leg 160 sites, which are indicated by distinctively high *a** values, have been suggested to reflect periods of increased flushing at the sea floor (Emeis et al., 2000). This is supported by the geochemical data of Wehausen and Brumsack (2000), who showed that deposition of red sediments at Site 969 was influenced by current-induced transport of Ti-rich minerals from the southeast Aegean onto the Mediterranean Ridge. Values of *a** at Site 966 correspond closely with our proxy for bottom-water ventilation, which validates the use of both data sets to monitor variations in eastern Mediterranean bottom-water ventilation. Red intervals are isochronous at all locations studied in the eastern Mediterranean (Emeis et al., 2000), which indicates that enhanced sea-floor flushing operated on a basin-wide scale. Both magnetic and sediment colour data appear to be modulated by eccentricity (Fig. 8), with redder colours and higher ARM intensities corresponding to 400-kyr eccentricity minima and greener colours and lower ARM intensities correlating with eccentricity maxima. This relationship is clear between 2.3 and 3.3 Ma, when the 400-kyr eccentricity cycles are well marked. It is less clear between 3.3 and

Fig. 7. Sapropel distribution and ARM data for ODP Site 966 between 2.3 and 4.0 Ma plotted against summer insolation at 65°N, which was calculated using the astronomical solution of Laskar (1990) and the Analyseries software package (Paillard et al., 1996). Sapropel types are labelled according to the discussion in Section 4.2. Positions with clear magnetic and/or geochemical evidence for missing sapropels are denoted as 'missing'. Only the lowermost of the four suspected ghost sapropels reported by Emeis et al. (2000) at around 2.5 Ma has magnetic properties entirely consistent with that of sapropels.

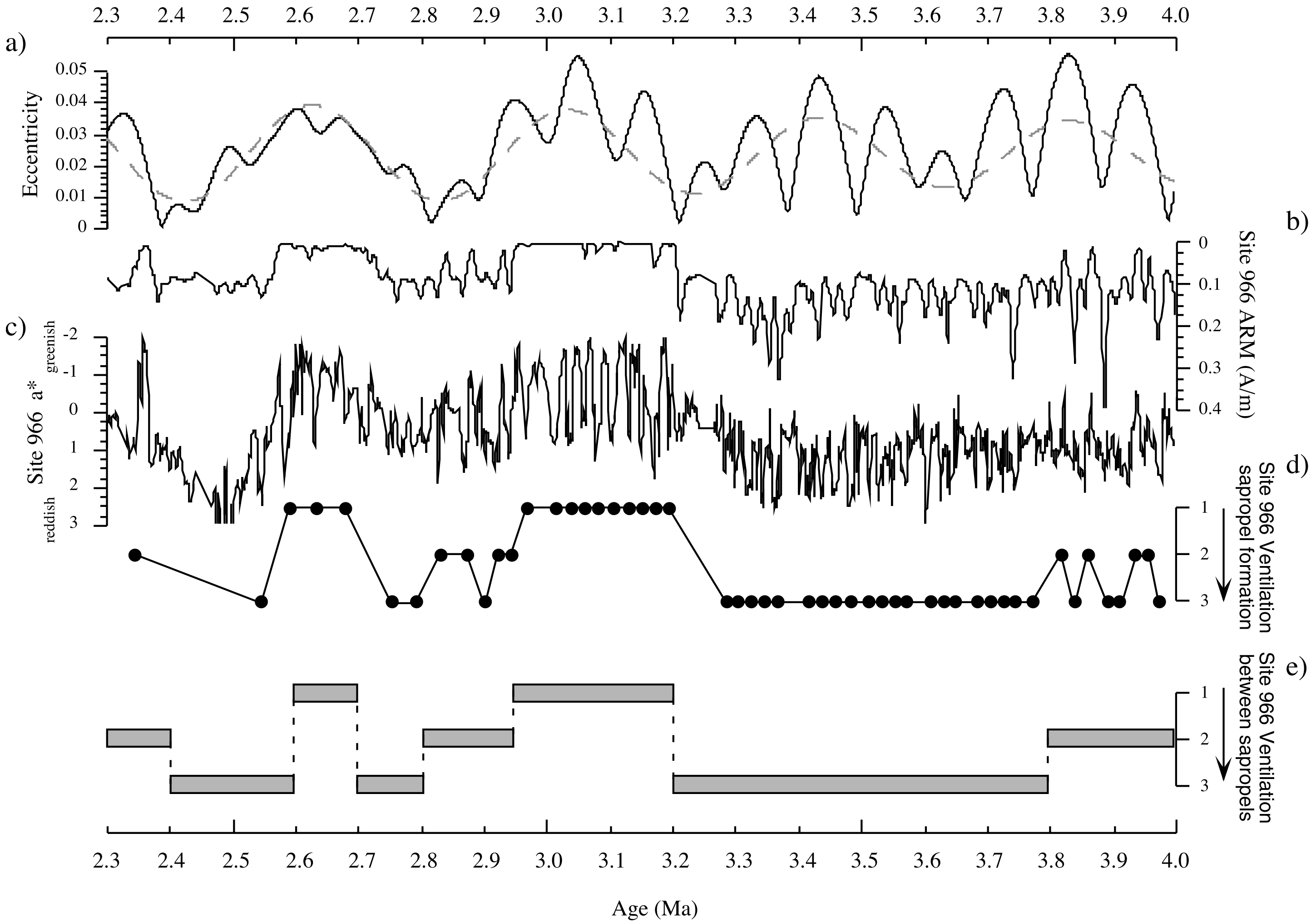


Fig. 8. (a) Variations of eccentricity (solid line) between 2.3 and 4.0 Ma, determined after Laskar (1990) using the Analyseries software package (Paillard et al., 1996). The dashed line shows the 400-kyr component of eccentricity. (b) ARM data for ODP Site 966. (c) Sediment colour data variations at Site 966. (d) Estimations of bottom-water ventilation at the time of sapropel formation, based on magnetic properties (see text). Numbers indicate a relative increase in bottom-water ventilation ranging from (1) low, to (2) intermediate and (3) high. (e) Estimation of bottom-water ventilation between sapropels, based on magnetic properties and the sapropel distribution. Numbers indicate a relative increase in bottom-water ventilation ranging from (1) low, to (2) intermediate and (3) high.

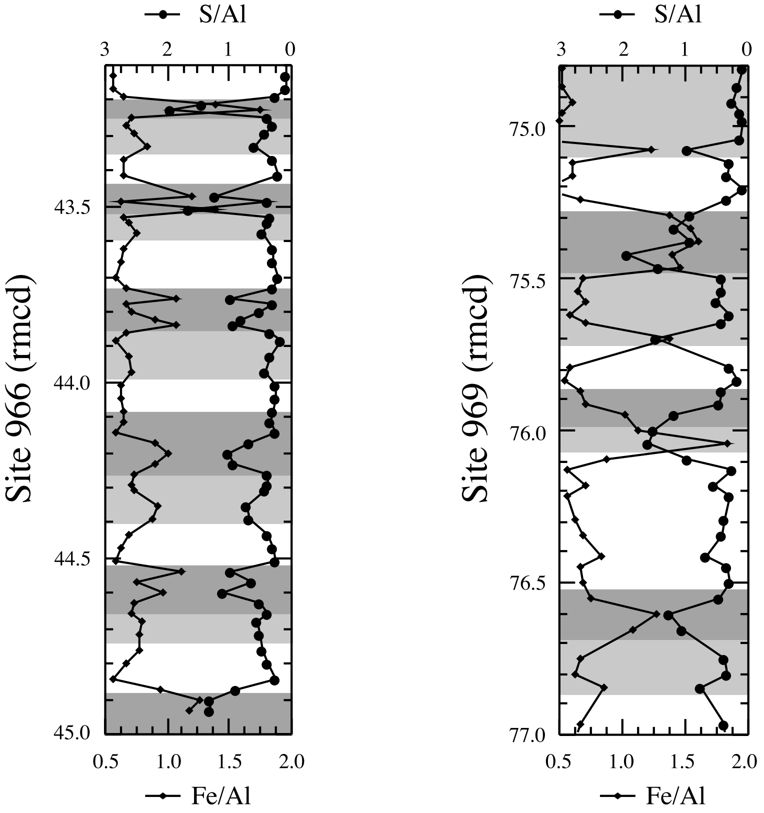


Fig. 9. S/Al and Fe/Al ratios for intervals with type 1 sapropels (dark grey layers) and low ARM values in background sediments. Light grey shading indicates the areas below sapropels that are affected by diagenetic pyritisation. Background sediments that are apparently unaffected by downward migration of sulphide are marked in white. Geochemical data are from Wehausen and Brumsack (2000).

4.4 Ma, where the 100-kyr eccentricity cycles dominate the eccentricity signal (Fig. 8a). The influence of 400-kyr eccentricity variations on eastern Mediterranean climate is also clear in $CaCO_3$ variations in the Trubi formation (Sicily), where higher $CaCO_3$ contents coincide with eccentricity minima (e.g. Hilgen, 1991). We note that dilution by $CaCO_3$ cannot explain the variations in ARM described above, because ARM intensities, and therefore the concentration of magnetic minerals, are higher when the carbonate content is higher. The concentration of $CaCO_3$ at the precessional time scale is driven by changes in the seasonal contrast between summer and winter insolation (van Os et al., 1994). Enhanced seasonal contrast during precession minima (e.g. northern summer insolation maxima) resulted in the collapse of $CaCO_3$ production and in the reduction of bottom-water circulation due to shoaling of the pycnocline into or within the eutrophic layer. It is thus expected that eccentricity minima should lead to higher $CaCO_3$ production and enhanced bottom-water ventilation because at those times the Earth is in perihelion during northern hemisphere winter and therefore the seasonal contrast is strongly reduced. The 400-kyr cyclicity observed in the $CaCO_3$ content therefore provides a link between $CaCO_3$ production, deposition of red intervals and enhanced ventilation at the time of 400-kyr eccentricity minima, because deposition of red intervals during periods with enhanced bottom-water ventilation is also related to weak northern hemisphere insolation maxima (Wehausen and Brumsack, 2000).

5. Conclusions

Magnetic properties of eastern Mediterranean sapropels and surrounding sediments are dominated by diagenetic processes that are controlled by variable accumulations of organic matter and subsequent decomposition of the organic carbon. According to their magnetic and geochemical properties, sapropels can be divided into three groups that correspond to increasingly anoxic conditions at the time of sapropel formation. A combination of magnetic and geochemical data suggest a causal relationship that enables discrimination between the relative role of bottom-water ventilation versus productivity for the three types of sapropels. Magnetic properties are more sensitive to variations in bottom-water ventilation than to productivity, which enables monitoring of changes in bottom-water ventilation both at, and after, periods of sapropel formation. Based on magnetic properties, we suggest a general picture of the evolution of bottom-water ventilation at ODP Site 966 (Eratosthenes Seamount) between 2.3 and 4.0 Ma. Bottom-water ventilation appears to be modulated by eccentricity, with restricted ventilation during 400-kyr eccentricity maxima and enhanced ventilation coinciding with 400-kyr eccentricity minima. Variations in ventilation derived from magnetic data are consistent with the occurrence of red intervals at Site 966 and at other ODP Leg 160 sites, and also with the astronomically modulated variations in $CaCO_3$ content found in eastern Mediterranean land-sections, which can also be related to enhanced ventilation during weak summer insolation maxima at the time of 400-kyr eccentricity minima.

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