

Detecting missing beats in the Mediterranean climate rhythm from magnetic identification of oxidized sapropels (Ocean Drilling Program Leg 160)

Juan C. Larrasoaña^{a,*}, Andrew P. Roberts^a, Angela Hayes^c,
Rolf Wehausen^b, Eelco J. Rohling^a

^a School of Ocean and Earth Science, National Oceanography Centre, Southampton, University of Southampton,
European Way, Southampton SO14 3ZH, UK

^b Institut für Chemie und Biologies des Meeres (ICBM), Carl von Ossietzky-Universität, Oldenburg D-26111, Germany

^c Department of Geography, Mary Immaculate College, South Circular Road, Limerick, Ireland

Received 15 June 2004; received in revised form 31 March 2005; accepted 23 April 2005

Abstract

Eastern Mediterranean sapropels are organic-rich sediments whose formation is related to variations in the Earth's orbit. They are therefore important for reconstructing past climatic variations and for producing astronomically tuned geological timescales. Previous studies have suggested that the distinctive magnetic properties of sapropels, which result from non-steady-state diagenetic reactions related to degradation of organic matter, might be used for identifying sapropels that have escaped visual identification after being completely erased during post-depositional oxidation. We present a high-resolution multi-proxy magnetic, geochemical and paleontological data set from selected intervals of Ocean Drilling Program Sites 966 and 967. Our results demonstrate that magnetic properties can be unambiguously used for identifying oxidized sapropels, and also for determining whether suspected intervals actually correspond to oxidized sapropels, because they enable detection of the former presence of organic matter and of climatic and oceanographic conditions suitable for sapropel formation. Systematic application of high-resolution magnetic analyses to future coring efforts in the eastern Mediterranean should allow determination of the original distribution of sapropels through long sedimentary sequences, which will improve our knowledge of paleoceanographic and paleoclimatic conditions that led to their formation.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Environmental magnetism; Sapropels; African monsoon; Saharan dust; bottom-water ventilation; Productivity; Ocean Drilling Program; Eastern Mediterranean

1. Introduction

In the eastern Mediterranean, distinctive organic-rich sediments called sapropels are cyclically intercalated with organic-poor sediments. Sapropels are dark-

coloured layers that usually vary from 1 to 60 cm in thickness, contain up to 25% organic carbon (by weight), are usually enriched in pyrite, and often display clear colour and textural laminations. Sapropels are important because they mark the pace of an orbitally driven climatic system that was exceptionally amplified due to the semi-enclosed nature of the Mediterranean basin. Formation of sapropels was controlled by ca. 22 kyr periodic changes in the amount of solar energy received

* Corresponding author at: Departamento de Ciencias de la Tierra, Universidad de Zaragoza, Zaragoza 50009, Spain.

E-mail address: jclarra@unizar.es (J.C. Larrasoaña).

in the northern low- and mid-latitudes during summer insolation maxima (precession minima) (Hilgen, 1991; Lourens et al., 1996; Emeis et al., 2000). At these times, intensification (Rossignol-Strick, 1983; Lourens et al., 2001) and enhanced northward penetration (Rohling et al., 2002; Larrasoña et al., 2003a) of the African monsoon led to an increase in the freshwater discharge into the eastern Mediterranean, not only via the Nile but also via the north African margin. This resulted in decreased dust production in the Sahara, enhanced riverine input and primary productivity in the surface waters and restricted ventilation of the eastern Mediterranean bottom waters, which favoured the production and preservation of organic matter in the deep basins (Rohling, 1994; Cramp and O'Sullivan, 1999). In contrast, drier climates in northern Africa prevailed during intervening insolation minima (precession maxima). This resulted in deposition of nannofossil oozes under (present-day type) conditions of low monsoon water discharge, low surface water productivity, efficient bottom-water ventilation and increased airborne dust delivery from the Sahara.

Since sapropel formation is related to changes in the Earth's orbit, the occurrence of sapropels allows the tuning of the sedimentary record to astronomical target curves (Hilgen, 1991; Lourens et al., 1996). This results in accurate age models of unprecedented resolution that can be used to date a variety of geological processes such as geomagnetic events (Hilgen, 1991; Langereis et al., 1997) and paleoclimatic and paleoceanographic variations (Rossignol-Strick et al., 1998; Emeis et al., 2000; Lourens et al., 2001; Larrasoña et al., 2003a), among others. Typically, correlation is made to curves of summer insolation at 65°N, with sapropels tuned to even-numbered insolation maxima (i-cycles) assuming a 3-kyr lag between the insolation maximum and the sapropel mid-point (Hilgen, 1991; Lourens et al., 1996). Unfortunately, identification of sapropels can be made difficult by their complete removal via post-depositional oxidation (Higgs et al., 1994; Thomson et al., 1995; van Santvoort et al., 1997; Emeis et al., 2000; Calvert and Fontugne, 2001). Their paleoclimatic and geochronological relevance makes it useful to be able to distinguish between situations where sapropels had formed but were subsequently removed by post-depositional oxidation and situations where the prevailing conditions did not promote sapropel formation (Emeis et al., 2000; Calvert and Fontugne, 2001). Visual identification of oxidized sapropels might be possible if they preserve remnants of the original laminated fabric and/or if they develop a distinctive reddish colour resulting from intense post-depositional flushing of the bottom waters (e.g., Emeis et al., 2000). When such characteristic features are not

observed, oxidized sapropels may remain undetected unless analytical techniques are used to infer their presence in the sedimentary record.

One of the techniques used to identify oxidized sapropels is geochemistry. Ti/Al ratios in sapropels show distinctive minima that are related to decreased input of Saharan (Ti-rich) and increased riverine (Al-rich) supply that result from enhanced monsoon intensity (Wehausen and Brumsack, 2000; Lourens et al., 2001; Calvert and Fontugne, 2001). Sapropels are also characterized by high Ba/Al ratios that are related to increased productivity of the surface waters (Thomson et al., 1995; Langereis et al., 1997; van Santvoort et al., 1997; Wehausen and Brumsack, 2000; Calvert and Fontugne, 2001). In addition, sapropels are often enriched in redox-sensitive trace metals (e.g., V, Mo) that provide evidence for low bottom water oxygen concentrations (Pruysers et al., 1993; Thomson et al., 1995; van Santvoort et al., 1997; Warning and Brumsack, 2000; Wehausen and Brumsack, 2000; Calvert and Fontugne, 2001). Moreover, sapropels are enriched in calcophilic elements such as Fe and Ni, which attest to the formation of iron sulphide minerals, mostly pyrite, under sulphate-reducing conditions derived from the accumulation and degradation of organic matter (Pruysers et al., 1993; Thomson et al., 1995; van Santvoort et al., 1997; Warning and Brumsack, 2000; Calvert and Fontugne, 2001). Thus, low Ti/Al and high Ba, V, Mo, Fe, Ni to Al ratios provide evidence for the occurrence of oxidized sapropels.

Paleontological data also enable identification of oxidized sapropels. Due to increased productivity in the surface waters, planktic foraminiferal abundances are usually larger in sapropels than in background sediments (Rohling et al., 1993). If organic matter is transferred to the seafloor, it is available for consumption by benthic foraminifera who might, as a result, increase significantly in abundance. When the amount of organic matter arriving to the seafloor becomes high, available oxygen will be consumed during degradation of organic carbon and populations of benthic foraminifera might decrease significantly, so that they might become extinct (Rohling et al., 1993). Thus, identification of high numbers of planktic foraminifera simultaneously with marked variations in the amount of benthic foraminifera may provide additional evidence for the presence of an oxidized sapropel.

Magnetic measurements also provide useful information about paleoceanographic conditions during sapropel formation because magnetic minerals are highly sensitive to non-steady-state diagenetic reactions related to accumulation and degradation of organic matter (van Hoof et al., 1993; Dekkers et al., 1994; Tarduno and

Wilkinson, 1996; Roberts et al., 1999; Robinson et al., 2000). When sapropels form, accumulation and burial of organic matter leads to sulphate-reducing conditions that cause reductive dissolution of magnetite, which is the main low coercivity magnetic mineral in eastern Mediterranean sediments (Passier et al., 2001; Kruiver and Passier, 2001; Larrasoña et al., 2003b), and formation of iron sulphides, mostly pyrite (Pruysers et al., 1993; Passier et al., 1996; van Santvoort et al., 1997; Roberts et al., 1999). If sulphate-reducing conditions are strong, excess sulphide produced in the sapropel will diffuse downward into previously deposited oxic sediments, causing simultaneous pyritization and dissolution of magnetite (van Hoof et al., 1993; Passier et al., 1996, 2001; van Santvoort et al., 1997; Roberts et al., 1999; Kruiver and Passier, 2001; Larrasoña et al., 2003b). When bottom waters are reoxygenated after sapropel formation, the organic matter within the sapropel oxidizes and promotes diagenetic formation of magnetite at paleo-oxidation fronts that develop on top of the sapropels (van Hoof et al., 1993; Higgs et al., 1994; Thomson et al., 1995; Passier et al., 2001; Kruiver and Passier, 2001; Larrasoña et al., 2003b). Besides the sensitivity of magnetic properties to non-steady-state diagenesis, magnetic properties also provide information about depositional processes. Thus, comparison of magnetic data with Ti/Al results have demonstrated that variations in the amount of hematite, the main high-coercivity magnetic mineral in eastern Mediterranean sediments, reflect variations in the input of aeolian (Saharan) dust. These variations are driven by enhanced intensity and northward penetration of the African monsoon over the northern Sahara (Larrasoña et al., 2003a).

Due to their sensitivity to diagenetic reactions associated with accumulation and degradation of organic matter in sapropels, and also to their usefulness in identifying paleoceanographic and paleoclimatic conditions suit-

able for sapropel formation, magnetic properties have been proposed as a useful tool for identifying oxidized sapropels (van Santvoort et al., 1997; Larrasoña et al., 2003b). However, they have never been studied in combination with both geochemical and paleontological data. Such a combination is appealing because it can provide information about the three main variables that condition sapropel formation, namely primary productivity, bottom water ventilation and intensity/penetration of the African monsoon. In this paper, we adopt such a multi-disciplinary approach to show that the magnetic properties of eastern Mediterranean sediments can be used to distinguish between situations where sapropels formed and were later removed by post-depositional oxidation and situations where prevailing conditions did not promote sapropel formation. Our data set includes high-resolution (1 cm) magnetic measurements obtained from u-channel samples as well as geochemical and paleontological data from selected intervals of Ocean Drilling Program (ODP) Leg 160 sediment cores. These intervals include: (1) a visible, partially oxidized sapropel representative of most sapropels recovered during ODP Leg 160 (see Larrasoña et al., 2003b); (2) an additional interval that has been interpreted as an oxidized sapropel according to its visual appearance (Emeis et al., 2000) and (3) two additional intervals whose visual characteristics do not suggest the possible presence of oxidized sapropels. The multi-proxy data set is shown for all intervals at two sites (Fig. 1). Site 966 was drilled on top of the Eratosthenes Seamount at a water depth of 926 m, whereas Site 967 was located on the northern slope of the Eratosthenes Seamount, 30 km to the north of Site 966 but at a much deeper water depth (2553 m) (Emeis et al., 1996). Use of multi-proxy data for the same intervals at two different paleoceanographic sites allows independent validation of the reliability of magnetic properties for identifying oxidized sapropels. Identification of oxi-

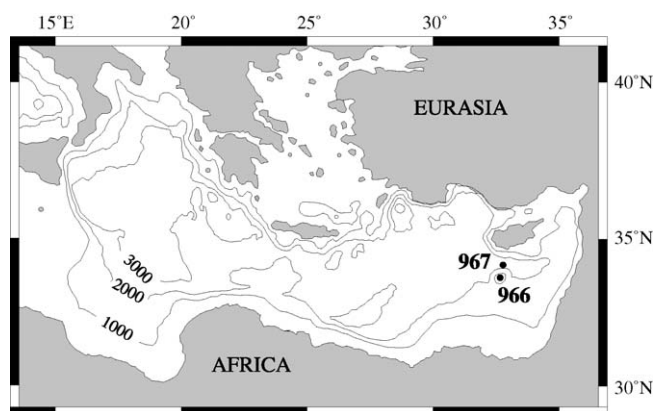


Fig. 1. Location of ODP Leg 160 Sites 966 and 967 from which magnetic, geochemical and paleontological data are shown in this study.

Table 1

Summary of the terminology used to describe different types of oxidized sapropel in previous studies and here

Reference	Term	Significance	Identification
Emeis et al. (2000)	Red interval	Oxidized sapropel	Visual
Emeis et al. (2000)	Ghost sapropel	Oxidized sapropel	Visual
Calvert and Fontugne (2001)	Ghost sapropel	Oxidized sapropel	Analytical
Langereis et al. (1997)	Ghost sapropel	Oxidized sapropel	Analytical
van Santvoort et al. (1997)	Missing sapropel	Oxidized sapropel	Analytical
Calvert and Fontugne (2001)	Missing sapropel	Never-formed sapropel	None
This study	Ghost sapropel	Oxidized sapropel	Visual
This study	Hidden sapropel	Oxidized sapropel	Analytical
This study	Missing sapropel	Never-formed sapropel	None

dized sapropels using magnetic properties is particularly interesting because long-core magnetic measurements allow time-efficient study of long (100's of m) sedimentary sequences from different paleoceanographic sites. Therefore, magnetic properties can be used to determine the original distribution of sapropels on a basin-wide scale, which is essential for a better understanding of the paleoceanographic and paleoclimatic conditions that led to their formation and post-depositional oxidation.

Due to the different approaches and techniques used to identify oxidized sapropels, a number of different (and confusing) terms have been proposed to name them (Table 1). Oxidized sapropels that have been visually identified because they preserve either their original laminated fabric or because they have a reddish colour as a result of intense post-depositional flushing have been termed “ghost sapropels” and “red intervals”, respectively (see Emeis et al., 2000). On the other hand, oxidized sapropels whose occurrence has been determined using analytical (e.g., geochemical) techniques have been considered either as “ghost sapropels” (see Langereis et al., 1997; Calvert and Fontugne, 2001) or as “missing sapropels” (see van Santvoort et al., 1997). The later term has been, however, used by other authors (e.g., Calvert and Fontugne, 2001) for describing a different situation in which sapropels did not form because paleoclimatic and paleoceanographic conditions did not change sufficiently. To avoid confusion, in this paper we use “ghost sapropels” to refer to oxidized sapropels whose identification relies upon visual recognition, and we use the term “hidden sapropel” for describing oxidized sapropels whose identification is based on analytical techniques. Though the paleoclimatic and paleoceanographic significance of ghost and hidden sapropels might be comparable, the later deserve special attention because failure to recognize them implies the loss of detected beats in the Mediterranean climate rhythm and of tie points for astronomical tuning. Finally, we use the term “missing sapropels” for

describing cases where the prevailing climatic conditions at a given insolation maximum did not promote sapropel formation.

2. Methods

Rock magnetic properties were measured at 1 cm intervals from u-channel samples using a shielded narrow-access 2G Enterprises cryogenic magnetometer (Weeks et al., 1993) at the National Oceanography Centre, Southampton (noise level of about 4×10^{-12} Am²). U-Channel samples were collected by pushing rigid, u-shaped plastic liners (2 cm × 2 cm cross section, up to 1.5 m in length) into the archive halves of the cores. The samples were freed from the cores by guiding a nylon fishing line under the plastic liners. To minimize sediment dehydration, u-channels were sealed using tightly fitting caps. Magnetic properties measured include: (1) an anhysteretic remanent magnetization (ARM), applied in a dc bias field of 0.05 mT parallel to an axially oriented peak AF of 100 mT while the u-channel was passed through the demagnetizer at 1 cm/s and (2) an isothermal remanent magnetization applied at 0.9 T and later AF demagnetized at 120 mT (IRM@AF). ARM values have been used as a proxy for the concentration of magnetite, whereas IRM@AF values have been used as a proxy for the concentration of hematite (see Larrasoña et al., 2003a,b for a detailed explanation). To avoid edge effects at the ends of the u-channels, which result from the Gaussian shape of the magnetometer response function (Weeks et al., 1993), data from the uppermost and lowermost 4 cm of each u-channel sample were removed from the data set.

Geochemical data shown in this paper include the ratios of abundances of different elements (Ba, V, Mo, Ti, Fe and Ni) to Al, and have been partially published in previous papers (Wehausen and Brumsack, 1998, 2000; Lourens et al., 2001; Larrasoña et al., 2003a,b). Paleontological data include abundances of planktic and benthic

foraminifera. Samples were dried at 40 °C and weighed to obtain a total sample dry weight. Samples were then disaggregated in demineralized water and wet sieved through a 63 μm mesh before drying. Finally, each sample was dry sieved through a 150 μm mesh. Using a random splitter, planktonic and benthic foraminifera from the >150 μm size-fraction were counted from aliquots of approximately 250 foraminifera. Faunal counts are expressed in absolute abundances per gram of dry sediment.

3. Results and discussion

3.1. Representative sapropels

Magnetic, geochemical and paleontological data for sapropel i-272 (~2.83 Ma), recovered at Sites 966 and 967, are shown in Fig. 2. Sapropel i-272 is characterized by a six- to 10-fold increase in Ba/Al ratios compared to background sediments located away from the sapropel, which indicates that primary productivity was significantly enhanced during its formation (Thomson et al., 1995; Langereis et al., 1997; van Santvoort et al., 1997; Wehausen and Brumsack, 2000; Calvert and Fontugne, 2001). High Ba/Al ratios also appear up to ~15 cm above the visible part of the sapropel, which indicates that sapropel deposition under high productivity conditions also occurred above the current visible upper boundary of the sapropel. Planktic foraminifera in the sapropel

undergo a four-fold increase compared to background sediments, concomitant with a decrease in the number of benthic foraminifera. This indicates that the increased number of planktic foraminifera is not an artefact conditioned by decreased sedimentation rates at the time of sapropel formation, but rather that it reflects enhanced primary productivity, as suggested by the Ba/Al ratios.

Sapropel i-272 is characterized by enrichments in trace metals such as V and Mo, which indicates that bottom water oxygen was depleted as a result of restricted ventilation conditions (Pruysers et al., 1993; Thomson et al., 1995; van Santvoort et al., 1997; Warning and Brumsack, 2000; Wehausen and Brumsack, 2000; Calvert and Fontugne, 2001). In addition, Ti/Al ratios reach a minimum within sapropel i-272 compared to background sediments. This indicates a simultaneous increase of riverine input and a decreased supply of Saharan dust at the time of sapropel deposition as a result of enhanced intensity (Lourens et al., 2001) of the African monsoon.

As a result of the paleoceanographic and paleoclimatic conditions prevailing at the time of sapropel i-272 formation, oxygen in the bottom waters was rapidly consumed by microbes as they degraded the enhanced concentrations of organic matter that arrived at the seafloor. These anoxic conditions enabled preservation and burial of organic matter in the sediments. Geochemical and paleontological data attest to this depletion of oxygen in the bottom waters. Enrichment of Fe and Ni in

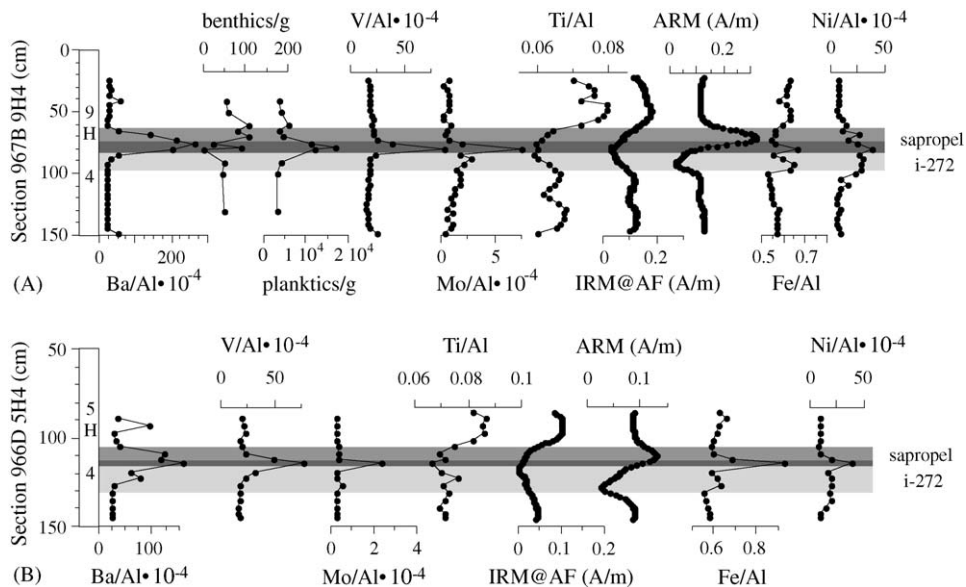


Fig. 2. Magnetic, geochemical and paleontological data from a representative sapropel (i-cycle 272; ~2.83 Ma) recovered at sites (A) 967 and (B) 966. Dark grey shading indicates the position of the sapropel. Light grey shading below the sapropel marks the position of a dissolution front whereas dark grey shading above the sapropel indicates the position of an oxidation front. Sapropel stratigraphy is after Emeis et al. (2000).

the sapropel indicates that formation of iron sulphides, mostly pyrite, occurred under sulphate-reducing diagenetic conditions. Oxygen depletion is also reflected by the decrease, and even disappearance in some levels, of benthic foraminifera in the sapropel.

Distinctively low ARM intensities (<0.05 A/m) below sapropel i-272 indicate low concentrations of magnetite at a dissolution front that extended 15 cm below the sapropel. Dissolution fronts formed when excess sulphide was produced in the sapropels, which happens under strongly anoxic conditions at the time of sapropel formation (Passier et al., 1996, 2001). In contrast, high ARM intensities are found up to 15 cm above the sapropel. This indicates that magnetite concentrations are highest at these positions as a result of magnetite formation at a paleo-oxidation front that developed above the sapropel as a result of post-depositional reoxygenation of the bottom waters (Kruiver and Passier, 2001; Passier et al., 2001; Larrasoña et al., 2003b). Notably, sediments from the oxidized part of the sapropel are characterized by high Ba/Al ratios, and ARM and Ba/Al ratios reach background values at the same position above the sapropel. This indicates that both parameters give consistent results in delineating the original, upper boundary of the sapropel prior to post-depositional oxidation. Due to the expense of producing high-resolution records of Ba/Al for long sedimentary sequences, high-resolution ARM data might provide a useful constraint on the original thickness of sapropels, which would reduce errors introduced by tuning the mid-point of the (visible parts of the) sapropels to astronomical target curves. While this might only result in adjustment of age models by less than a few (<1 – 2) thousand years, it is important to keep in mind when studying high-resolution (millennial and sub-millennial scale) records and when performing between-site correlations.

ARM values within sapropel i-272 decrease from the high values at the oxidation front to the low values at the dissolution front. This steady decline observed between horizons with contrasting magnetizations is due to the smoothing of the magnetic signal inherent to u -channel measurements, and cannot be considered as a real indication of variations in the concentration of magnetic minerals within the sapropel. Low ARM values measured for discrete samples of many other sapropels indicate that the concentration of magnetite is low as a result of reductive dissolution that occurred under sulphate-reducing conditions at the time of sapropel formation (Langereis et al., 1997; van Santvoort et al., 1997; Roberts et al., 1999; Passier et al., 2001; Kruiver and Passier, 2001; Larrasoña et al., 2003b). The ubiquitous presence of pyrite in most eastern Mediterranean sapropels recov-

ered during ODP Leg 160 (Emeis et al., 1996, 2000) is consistent with this interpretation. Geochemical data indicate that, in the case of sapropel i-272, both restricted bottom water ventilation and enhanced productivity were responsible for the burial of organic matter in the sapropel and for the resulting anoxic diagenetic conditions.

Variations in IRM@AF mimic the decrease in Ti/Al ratios observed across sapropel i-272. Decreased Ti/Al ratios at the time of sapropel formation reflect an increase in the riverine input and a decrease in the amount of Saharan dust supply, which would be related to an enhanced intensity of the African monsoon (Lourens et al., 2001). Hematite in eastern Mediterranean sediments is sourced in the eastern Saharan regions north of the central Saharan watershed. Thus, variations in the supply of hematite into the eastern Mediterranean indicate that not only an enhanced intensity (Rossignol-Strick, 1983; Lourens et al., 2001), but also enhanced northward penetration of the African monsoon (Rohling et al., 2002; Larrasoña et al., 2003a), conditioned climatic conditions in northern Africa during formation of sapropels.

Available magnetic and geochemical data for sapropel i-272 are similar at both Sites 966 and 967, which indicates that paleoceanographic and paleoclimatic conditions during its formation were similar at both paleoceanographic settings.

3.2. *Ghost sapropels*

The magnetic signature described above in relation to accumulation and degradation of organic matter in sapropel i-272 is representative of most sapropels recovered during ODP Leg 160, regardless of age (see Larrasoña et al., 2003b). Since this is the case, magnetic properties should be useful for determining whether layers that have been interpreted as ghost sapropels actually represent oxidized sapropels. One of these layers is a red interval found at 77.94 rmcd (revised metre composite depth, see Sakamoto et al., 1998) at Site 967 (Emeis et al., 2000) (Fig. 3A). This red interval can be correlated to insolation cycle 246 based on the age and position of the characteristic underlying Gauss/Matuyama (i-250 to i-260; ~ 2.6 – 2.7 Ma) sapropel cluster (see Emeis et al., 2000). Ba/Al ratios and planktic foraminiferal abundances indicate that enhanced primary productivity, as expected at times of sapropel formation, prevailed during deposition of the red interval. It is also characterized by low Ti/Al ratios and IRM@AF values similar to those found for sapropel i-272, which indicates that the enhanced intensity and northward penetration of the African monsoon during its deposition were comparable to those prevailing at the time of sapropel i-272 formation. The absence

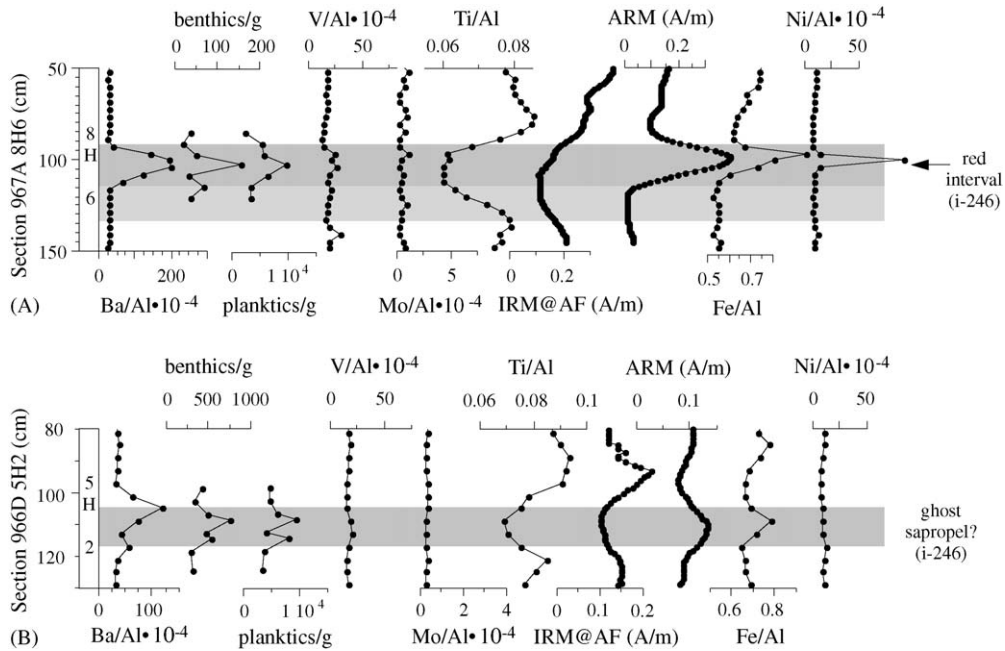


Fig. 3. Magnetic, geochemical and paleontological data for insolation cycle 246 (~2.54 Ma) recovered both at sites (A) 967 and (B) 966. Dark grey shading indicates the position of the oxidised sapropel. Light grey shading at Site 967 indicates the position of a dissolution front. Sapropel stratigraphy is after Emeis et al. (2000).

of V and Mo enrichments within the red interval indicates that oxygen concentrations in the bottom water were not severely depleted. ARM values in the red interval are comparable to those that characterize the oxidized part of sapropel i-272 at the same site. This indicates that accumulation of organic matter must have occurred since high ARM values are related to high concentrations of magnetite formed during post-depositional oxidation, which requires the presence of pyrite and/or dissolved Fe^{2+} that must have been formed under previous sulphate-reducing conditions. Enrichments of Fe and Ni in the same interval are consistent with the former presence of pyrite. Low ARM values underneath the red interval indicate that sulphate-reducing conditions at the time of deposition were severe enough to allow production, and subsequent downward migration, of excess sulphide (Fig. 3A). Benthic foraminiferal abundances are relatively low in the lower and upper part of the red interval and increase significantly in its middle part. This suggests that higher availability of organic matter in the middle part of the red interval compensated for the relatively low oxygen concentrations at the onset and end of deposition of the red interval, which favoured the flourishing of benthic populations. Variations in benthic foraminifera abundances are significantly different from the changes in the numbers of planktic foraminifera, suggesting that this is a genuine signal rather than an

artefact related to variations in sediment accumulation rates. Overall, magnetic, geochemical and paleontological data indicate that the red interval shown in Fig. 3A corresponds to a former sapropel (i-246), which has been removed by post-depositional processes and has been correctly identified as a ghost sapropel after visual inspection of the core.

At Site 966, sedimentary cycle i-246 is represented by a possible ghost sapropel (Emeis et al., 2000) (Fig. 3B). Magnetic, geochemical and paleontological data from this possible ghost sapropel are comparable to those of the red interval at Site 967. High Ba/Al ratios, low Ti/Al values and lack of significant Mo and V enrichments within the possible ghost sapropel indicate that its deposition occurred under conditions of high productivity, with relatively suppressed bottom water ventilation and enhanced intensity/penetration of the African monsoon. Relatively high ARM values indicate that magnetite formed as a result of post-depositional oxidation. This process requires pyrite and/or dissolved Fe^{2+} that derive from sulphate-reducing conditions, and therefore indicates that some burial of organic matter must have occurred. However, lack of a dissolution front suggests that organic matter was buried in lower amounts than at the same interval at Site 967, which has a dissolution front associated with it. This agrees with an enrichment in Fe in i-cycle 246 at Site 966, which is not as marked

as that found in the same interval at Site 967 and which therefore attests to weaker sulphate-reducing conditions. Available data indicate that the possible ghost sapropel found at i-cycle 246 at Site 966 also represents a former sapropel that has been post-depositionally oxidized and correctly identified as a ghost sapropel.

It is likely that weaker sulphate-reducing conditions during deposition of i-cycle 246 at Site 966 might have occurred in response to alternating (e.g., seasonal) anoxic and oxic conditions rather than to continuous moderate sulphate-reducing conditions prevailing throughout sapropel formation. This idea is in line with the dynamic concept for sapropel formation envisaged by Casford et al. (2003). In this dynamic concept, it is argued that intermittent ventilation of the bottom waters at the time of sapropel formation is one of the main factors conditioning development of anoxia (e.g., sulphate-reducing conditions), because it controls the amount of oxygen at the seafloor and hence the amount of organic matter that can be degraded before it is buried. It also accounts for the short timescales at which the processes that drive bottom water ventilation operate. Following this argument, different intensities of sulphate reduction will develop at different locations depending on the

intensity of bottom water ventilation. This dynamic concept provides a reasonable mechanism for explaining the differences found for deposition of i-246 cycle at Sites 966 and 967. Site 967 is located at 2553 m water depth, whereas Site 966 is located at shallower depths (926 m). Productivity of surface waters and export production to deeper water masses may be considered similar since both sites are close to each other. Thus, the most reasonable explanation for interpreting the overall stronger sulphate-reducing conditions at Site 967 is that ventilation of the deep waters potentially decreases with depth. This circumstance is supported by TOC values of the youngest sapropel (sapropel i-2; ~8 ka), whose TOC content increases progressively with depth probably in response to lower bottom water oxygen concentrations (Murat and Got, 2000).

3.3. Hidden sapropels

Magnetic, geochemical and paleontological data similar to those characterising i-cycle 246 at Site 966 are also found for two other intervals at Sites 966 (40.70 and 41.20 rmcd) and 967 (83.04 and 84 rmcd) (Fig. 4). Astronomical tuning of Ti/Al curves (Lourens et al., 2001)

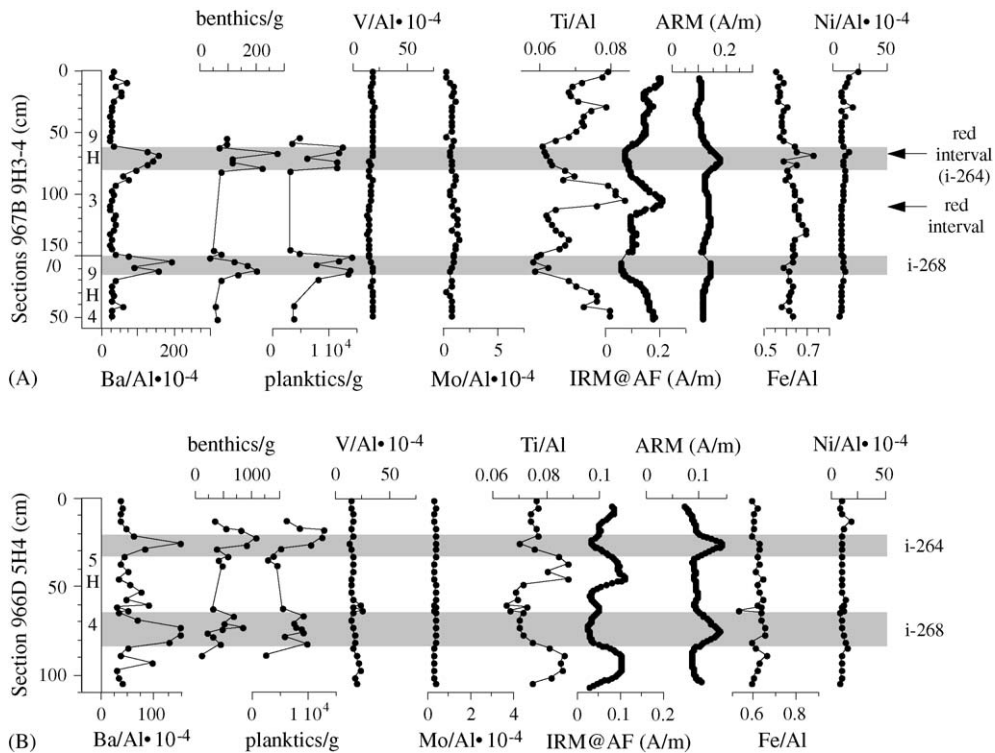


Fig. 4. Magnetic, geochemical and paleontological data for insolation cycles 264 (~2.75 Ma) and 268 (~2.79 Ma) recovered both at sites (A) 967 and (B) 966. Dark grey shading indicates the position of oxidized sapropels. The position of the red intervals is after Emeis et al. (2000) and the correlation of sedimentary cycles to i-cycles is after Lourens et al. (2001).

enables correlation of the two intervals at Site 967, and hence of those at Site 966, with *i*-cycles 264 (~2.75 Ma) and 268 (~2.79 Ma). Overall, magnetic, geochemical and paleontological data indicate that these two intervals at both sites correspond to former sapropels that have been post-depositionally oxidized. Of these two intervals, only the uppermost one at Site 967 has been previously identified as a red interval (Emeis et al., 2000). Our data agree with visual inspections of the core in determining the presence of a ghost sapropel at that position. On the contrary, the lowermost interval at Site 967 and the two intervals at Site 966 have not been previously recognized as oxidized sapropels (see Emeis et al., 2000). Our multi-proxy data set indicates that these intervals can thus be considered as hidden sapropels whose occurrence might have remained ignored unless analytical techniques were used in their detection after having escaped visual inspection.

These hidden sapropels have similar properties to those of the ghost sapropels shown above. They were formed under conditions of high surface water productivity, as indicated by high Ba/Al ratios and high planktic foraminiferal abundances, and of enhanced intensity and penetration of the African monsoon, as indicated by low Ti/Al ratios and IRM@AF values. The only paleoceanographic scenario that distinguishes the formation of these ghost and hidden sapropels from sapropel *i*-272 and other visible sapropels (see Larrasoña et al., 2003b) is the lack of severe oxygen depletion in the bottom waters, which is indicated by the absence of V and Mo enrichments. As a result of relatively efficient bottom water ventilation, diagenetic conditions within most ghost and hidden sapropels seem to have been only moderately anoxic, as indicated by relatively low Fe and Ni to Al ratios and the general lack of dissolution fronts. This is consistent with the continued presence of benthic foraminifera across ghost and hidden sapropels, which do not undergo extinction but instead show an overall increase in their abundance. Benthic foraminiferal abundances decreased significantly in intervals where significant depletion of oxygen in the bottom waters likely occurred (e.g., the lower part of sapropel *i*-268 at Site 966 and the middle part of sapropel *i*-264 at Site 967). We stress, however, that some burial of organic matter in the ghost and hidden sapropels must have occurred, albeit probably restricted to intermittent episodes (e.g., the dynamic concept of Casford et al., 2003), in order to explain sulphate-reducing conditions and subsequent oxidation of pyrite and/or dissolved Fe²⁺. Based on the above, we consider that ghost and hidden sapropels represent former sapropels that were deposited under climatic and oceanographic conditions less favourable than those

governing deposition of typical (e.g., visible) sapropels. Given the sensitivity of magnetic data for detecting oxidized sapropels and conditions suitable for their formation, we consider that magnetic analyses could also be used for the identification of insolation cycles where climatic and oceanographic conditions were insufficient to promote sapropel formation (e.g., missing sapropels).

To conclude, we notice that, in the same stratigraphic section of Site 967 shown in Fig. 4, another red interval located at 83.60 rncd has been reported (Emeis et al., 2000). This red interval does not have any properties typical of sapropels. Instead, it coincides with a prominent peak in the Ti/Al and IRM@AF curves. This indicates that the colour of this red interval does not derive from intense post-depositional oxidation of an insolation maximum-related sapropel, but instead from the occurrence of high concentrations of aeolian, northern Saharan hematite that probably accumulated during an insolation minimum. This circumstance implies that: (1) the red interval at 83.60 rncd at Site 967 seems to be mistuned by half an insolation cycle because it is likely related to an insolation minimum instead of to an insolation maximum; (2) visual identification of red intervals, and probably of ghost sapropels, is not straightforward and should be validated by analytical techniques; and (3) reddish colouring of eastern Mediterranean sediments (determined by the a^* parameter) is controlled by two different processes, so that colour should not be used alone to make inferences about bottom water ventilation or Saharan dust supply.

4. Conclusions

A combination of magnetic, geochemical and paleontological data for selected intervals of ODP Leg 160 Sites 966 and 967 demonstrates that magnetic methods provide a sensitive tool for identifying oxidized (ghost and hidden) sapropels and for determining whether interpreted ghost sapropels correspond to former sapropels that were erased by post-depositional oxidation. This is due to the sensitivity of magnetic minerals to non-steady-state diagenetic reactions related to the former presence of organic matter and also to paleoceanographic and paleoclimatic conditions that led to sapropel formation (e.g., the interplay between productivity/ventilation and the intensity/northward penetration of the African monsoon). In particular, ARM data indicate variations in magnetite content that result from non-steady-state diagenetic processes associated with degradation of organic matter, whereas AF demagnetization (at 120 mT) of an IRM indicates variations in hematite content related to climatically modulated supply of Saharan dust. ARM

values can also be used to determine the original thicknesses of partially oxidized sapropels, which represent the majority of sapropels recovered during ODP Leg 160 (Larrasoña et al., 2003b). Magnetic measurements performed with u-channels are much faster, yet they are still as sensitive, as geochemical and paleontological methods. Thus, systematic high-resolution magnetic analyses of eastern Mediterranean sediment cores should enable documentation of complete records of sapropel deposition, which can be cross-checked where necessary with geochemical and paleontological data. Determination of the original distribution and thickness of sapropels throughout long sedimentary sequences in different paleoceanographic settings will improve age models based on astronomical tuning and also our knowledge of the spatial and temporal characteristics of paleoceanographic and paleoclimatic conditions that led to sapropel formation and oxidation.

Acknowledgements

We thank C.G. Langereis and S.K. Banerjee for their constructive reviews, and M. Fuller for editorial handling. This work was supported by European Community TMR Network Contract MAG-NET (ERBFMR-XCT98-0247) and the U.K. NERC (project NER/B/S/2002/00268). J.C. Larrasoña benefits from a MEC “Ramón y Cajal” contract. Samples were provided by the ODP, which is sponsored by the U.S. National Science Foundation and participating countries (including the U.K.) under management of Joint Oceanographic Institutions, Inc. We thank the staff from the ODP Core Repository in Bremen for technical assistance and hospitality during sampling.

References

- Calvert, S.E., Fontugne, M.R., 2001. On the late Pleistocene-Holocene sapropel record of climatic and oceanographic variability in the eastern Mediterranean. *Paleoceanography* 16, 78–94.
- Casford, J.S.L., Rohling, E.J., Abu-Zied, R.H., Fontanier, C., Jorissen, F.J., Leng, M.J., Schmiedl, G., Thomson, J., 2003. A dynamic concept for eastern Mediterranean circulation and oxygenation during sapropel formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 190, 103–119.
- Cramp, A., O’Sullivan, G.O., 1999. Neogene sapropels in the Mediterranean: a review. *Mar. Geol.* 153, 11–28.
- Dekkers, M.J., Langereis, C.G., Vriend, S.P., van Santvoort, P.J.M., de Lange, G.J., 1994. Fuzzy c-means cluster analyses 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.
- Emeis, K.-C., Robertson, A.H.F., Richter, C., Camerlenghi, A. (Eds.), 1996. Proceedings of the ODP Init. Repts. 160. Ocean Drilling Program, College Station, TX, 972 pp.
- Emeis, K.-C., Sakamoto, T., Wehausen, R., Brumsack, H.-J., 2000. The sapropel record of the eastern Mediterranean Sea—results of Ocean Drilling Program Leg 160. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 371–395.
- Higgs, N.C., Thomson, J., Wilson, T.R.S., Croudace, I.W., 1994. Modification and complete removal of eastern Mediterranean sapropels by postdepositional oxidation. *Geology* 22, 423–426.
- Hilgen, F.J., 1991. Astronomical calibration of Gauss to Matuyama sapropels in the Mediterranean and implications for the geomagnetic polarity timescale. *Earth Planet. Sci. Lett.* 104, 226–244.
- Kruiver, P.P., Passier, H.F., 2001. Coercivity analysis of magnetic phases in sapropel S1 related to variations in redox conditions, including an investigation of the S-ratio. *Geochem. Geophys. Geosys.* 2 (Paper # 2001GC000181).
- 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.
- Larrasoña, J.C., Roberts, A.P., Rohling, E.J., Winkhofer, M., Wehausen, R., 2003a. Three million years of monsoon variability over the northern Sahara. *Clim. Dyn.* 21, 689–698.
- Larrasoña, J.C., Roberts, A.P., Stoner, J.S., Richter, C., Wehausen, R., 2003b. A new proxy for bottom-water ventilation in the eastern Mediterranean based on diagenetically controlled magnetic properties of sapropel-bearing sediments. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 190, 221–242.
- Lourens, L.J., Antonarakou, A., Hilgen, F.J., van Hoof, A.A.M., Vergnaud-Grazzini, C., Zachariasse, W.J., 1996. Evaluation of the Plio-Pleistocene astronomical timescale. *Paleoceanography* 11, 391–413.
- Lourens, L.J., Wehausen, R., Brumsack, H.J., 2001. Geological constraints on tidal dissipation and dynamical ellipticity of the Earth over the past three million years. *Nature* 409, 1029–1033.
- Murat, A., Got, H., 2000. Organic carbon variations of the eastern Mediterranean Holocene sapropel: a key for understanding formation processes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 241–257.
- 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 sulfide diffusion. *Geochim. Cosmochim. Acta* 60, 751–763.
- Passier, H.F., de Lange, G.J., Dekkers, M.J., 2001. Magnetic properties and geochemistry of the active oxidation front at the youngest sapropel in the eastern Mediterranean Sea. *Geophys. J. Int.* 145, 604–614.
- Pruyvers, 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.
- Roberts, A.P., Stoner, J.S., Richter, C., 1999. Diagenetic magnetic enhancement of sapropels from the eastern Mediterranean Sea. *Mar. Geol.* 153, 103–116.
- Robinson, S.G., Sahota, J.T.S., Oldfield, F., 2000. Early diagenesis in North Atlantic abyssal plain sediments characterised by rock-magnetic and geochemical indices. *Mar. Geol.* 163, 77–107.
- Rohling, E.J., 1994. Review and new aspects concerning the formation of eastern Mediterranean sapropels. *Mar. Geol.* 122, 1–28.
- Rohling, E.J., de Stigter, H.C., Vergnaud-Grazzini, C., Zaalberg, R., 1993. Temporary repopulation by low-oxygen tolerant benthic foraminifera within an upper Pliocene sapropel: evidence for the

- role of oxygen depletion in the formation of sapropels. *Mar. Micropaleontol.* 22, 207–219.
- Rohling, E.J., Cane, T.R., Cooke, S., Sprovieri, M., Bouloubassi, I., Emeis, K.-C., Schiebel, R., Kroon, D., Jorissen, F.J., Lorre, A., Kemp, A.E.S., 2002. African monsoon variability during the previous interglacial maximum. *Earth Planet. Sci. Lett.* 202, 61–75.
- Rossignol-Strick, M., 1983. African monsoons, an immediate climatic response to orbital insolation. *Nature* 303, 46–49.
- Rossignol-Strick, M., Paterne, M., Bassinot, F.C., Emeis, K.-C., de Lange, G.J., 1998. An unusual mid-Pleistocene monsoon period over Africa and Asia. *Nature* 392, 269–272.
- Sakamoto, T., Janecek, T., Emeis, K.-C., 1998. Continuous sedimentary sequences from the eastern Mediterranean Sea: composite depth sections. *Proc. ODP Sci. Res.* 160, 37–59.
- Tarduno, J.A., Wilkinson, S.L., 1996. Non-steady state magnetic mineral reduction, chemical lock-in, and delayed remanence acquisition in pelagic sediments. *Earth Planet. Sci. Lett.* 144, 315–326.
- 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.
- 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., Paterne, M., 1997. Geochemical and paleomagnetic evidence for the occurrence of “missing” sapropels in eastern Mediterranean sediments. *Paleoceanography* 12, 773–786.
- Warning, B., Brumsack, H.-J., 2000. Trace metal signatures of eastern Mediterranean sapropels. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 293–309.
- Weeks, R., Laj, C., Endignoux, L., Fuller, M., Roberts, A., Manganne, R., Blanchard, E., Goree, W., 1993. Improvements in long-core measurement techniques: applications in palaeomagnetism and palaeoceanography. *Geophys. J. Int.* 114, 651–662.
- Wehausen, R., Brumsack, H.-J., 1998. The formation of Pliocene Mediterranean sapropels: constraints from high-resolution major and minor element studies. *Proc. ODP Sci. Res.* 160, 207–218.
- Wehausen, R., Brumsack, H.-J., 2000. Chemical cycles in Pliocene sapropel-bearing and sapropel-barren eastern Mediterranean sediments. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 325–352.