Biogeosciences Discussions

Productivity patterns and N-fixation associated with Pliocene-Holocene sapropels: paleoceanographic and paleoecological significance

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Abstract

Sapropels are organic matter enriched sediments cyclically deposited in the Eastern Mediterranean. We have studied a suite of 35 sapropel sequences from a transect of four ODP sites across the basin to explore for paleoproductivity patterns and their rela-
5 tionship to ecological changes in the region during their deposition. We assessed paleoproductivity variations using TOC and Ba_{bio} mass accumulation rates and $\delta^{15}N_{total}$ and $\delta^{13}C_{org}$ values. Elevated Ba/Al and TOC mass accumulation rates record periods of basin-wide amplified productivity. $\delta^{15}N$ values are dramatically lower in the sapropels than in TOC-poor background sediments indicating a major contribution from
10 nitrogen-fixing bacteria to the higher productivity during sapropel deposition. Different degrees of denitrification occurred as a function of water column oxygen depletion. The evolution of sapropel deposition over the past 3 My is characterized by increased productivity together with enhanced preservation of organic matter during the late Pliocene, peaks in primary and export production and sedimentation rates during
15 the middle Pleistocene, and a relatively weak increase in productivity during formation of the Holocene sapropel accompanied by high sedimentation rates. We conclude that sapropels were formed by cyclic increases in primary production of marine organic matter largely sustained by N-fixing bacteria that led to depletion of deepwater dissolved oxygen and consequently improved organic matter preservation. The increase
20 in primary production was helped by nutrient input from continental sources climatically induced.

1 Introduction

The multiple sapropel layers that were deposited in the Neogene-Quaternary Mediterranean basin are of particular interest to the topic of enhanced organic carbon accu-
25 mulation in marine sediment. Sapropels, as defined by Kidd (1978) are cyclically deposited dark colored sediment layers that are more than 2 cm in thickness and contain

more than 2% total organic carbon (TOC). A debate about whether improved preservation or elevated productivity is the major cause for high concentrations of organic matter in such sediments has persisted in paleoceanographic studies for decades (e.g., Casford et al., 2003; De Lange et al., 2008; Emeis and Weissert, 2009; Jenkyns, 1980;
5 Mangini and Schlosser, 1986). The traditional interpretation of sedimentary layers rich in organic matter as representative of anoxic events has been challenged by Pedersen and Calvert (1990) (see also Calvert et al., 1996; Calvert and Pedersen, 1993), who argued that increased productivity, rather than absence of oxygen, was the primary factor responsible for the enhanced accumulation of organic carbon in sediments. In-
10 deed, sapropel deposition is usually considered to be related to an increase in marine export productivity (e.g., Calvert et al., 1992; Diester-Haass et al., 1998; Lourens et al., 1992; Martínez-Ruiz et al., 2000, 2003; Meyers and Arnaboldi, 2005; Weldeab et al., 2003a, b). However, how marine productivity increased in a presently oligotrophic, nutrient deficient basin like the Mediterranean raises questions regarding the sources of
15 nutrient that have fueled this productivity increase (e.g., Casford et al., 2003; Filippelli et al., 2003; Menzel et al., 2003; Sachs and Repeta, 1999).

Development of a number of geochemical paleoproductivity proxies that are independent of oxygen abundance has allowed reconstruction of productivity and improved interpretation of the causal mechanisms of organic matter accumulation. Among these
20 proxies, barium excess (Ba_{bio}), and biogenic barite accumulation (e.g., Dehairs et al., 1987; Dymond and Collier, 1996; Dymond et al., 1992; McManus et al., 1998; Paytan and Kastner, 1996), and nitrogen content and isotopic composition (e.g., Altabet and Francois, 1994; Arnaboldi and Meyers, 2006; Calvert, 1992; Meyers and Bernasconi, 2005; Peters, 1978) have been found especially useful in a variety of paleoceano-
25 graphic settings. In recent years several papers have employed some of these paleoproductivity proxies to describe spatial and temporal patterns of sapropel deposition, (e.g., Arnaboldi and Meyers, 2006; Meyers and Bernasconi, 2005; Rinna et al., 2002; Struck et al., 2001). However, it is crucial to carry out further comparison of the isotopic and elemental proxies and Ba_{bio}, the most widely used paleoproductivity proxy in

the Mediterranean, and to highlight any differences of these signals during the paleoceanographic evolution of the basin.

In this paper, we describe the results of a suite of 35 sapropels of different ages that span the late Pliocene through the Holocene and that originate from a four-site transect across the Eastern Mediterranean Basin. We first describe the spatial and temporal patterns of export productivity in sapropel deposition in the Eastern Mediterranean and then interpret the patterns in terms of their possible paleoceanographic significance. We correlate both organic C content and isotope signatures (δ^{15}N and δ^{13}C) to reinforce the information given by Ba/Al, and we employ TOC and Ba$_{bio}$ mass accumulation rates (MAR's) to refine paleoproductivity patterns. We also consider the effect of diagenesis on N and C values, inasmuch as organic matter is susceptible to post-depositional oxidation and alteration (e.g., Martínez-Ruiz et al., 2000; Thomson et al., 1995; van Santvoort et al., 1996).

2 Materials and methods

2.1 Sample settings

Sapropel sequences were sampled in cores recovered at four ODP Leg 160 sites (Fig. 1) that represent different oceanographic regimes within the Eastern Mediterranean Sea. To summarize, the sedimentary sequence deposited at Site 964, located in a deep marine setting (3658 m b.s.l.) on the Pisano Plateau (Ionian Basin), is influenced by the Adriatic Sea and the water masses coming from the Western Mediterranean basin through the Strait of Sicily. Site 969, also in a relatively deep, open marine setting (2200 m b.s.l.) on the Mediterranean Ridge, represents the centermost location in the Eastern Mediterranean. Cores recovered at Site 967 in the Levantine Basin, although containing a sequence of deep pelagic sediments (2555 m b.s.l.), are influenced by detrital input from the Nile River, which drains the Central African craton. Finally, Site 966 is situated on a pelagic high, the Eratosthenes Seamount, at a

relatively shallow water depth of 926 m b.s.l. At each site, high resolution sampling was carried out on selected sapropel-containing depth intervals. These sections represent Pleistocene and Holocene periods of sapropel deposition at the four sites, as well as Pliocene layers for sites 964 and 969.

The sediments in these cores are composed mostly of nannofossil clay, clayey nannofossil ooze and nannofossil ooze with some intervals of clay and foraminifera sand, variably bioturbated, (Emeis et al., 1996). Interspersed throughout the pelagic sediments, dark colored to black sapropel layers appear periodically. Some of these TOC-enriched sediments and sections of the overlying and underlying sediment from these cores were sampled at 2 cm intervals. Where lamination allowed, samples were collected at a resolution as fine as 1 mm.

2.2 Analysis

Samples were dried, homogenized in an agate mortar, and then subdivided for different analyses. TOC measurements for some samples were carried out using a Perkin-Elmer Elemental analyzer at the Stable Isotope Laboratory at Stanford University (Mucciarone, 2003). The rest of the samples were analyzed for total carbon (TC) and TOC separately at Bremen University using a TOC/TC analyzer. TOC was measured on the TOC/TC analyzer after acidification of sediment with 1N HCl to remove carbonates followed by heating to dryness. At Stanford University, parallel to TOC measurements, total N (TN), $\delta^{13}C$ and $\delta^{15}N$ isotopic composition were also carried out using a Finnigan MAT isotope ratio mass spectrometer (IRMS) connected to a Carlo Erba (now CE Elantech, Inc.) NA1500 Series II Elemental Analyzer. TOC/TN ratios are expressed on an atom/atom basis. $\delta^{15}N$ and $\delta^{13}C$ values are, respectively expressed relative to atmospheric dinitrogen and Vienna PeeDee Belemnite (VPDB) standards. These samples were repeatedly acidified with HSO_3 to eliminate all inorganic carbon prior to isotope analysis.

Barium content was determined using an ICP-MS Perkin-Elmer Sciex Elan 5000 spectrometer (CIC; Analytical Facilities of the University of Granada), using Re and

Rh as internal standards. Coefficients of variation calculated by dissolution and subsequent analyses of 10 replicates of powdered samples were better than 3% and 8% for analyte concentrations of 50 and 5 ppm, respectively (Bea, 1996). Aluminium content was analyzed by atomic absorption spectrometry at the Analytical Facilities of the University of Granada. These two analyses were carried out after HNO_3 and HF total digestion of the homogenized sample. Biogenic Ba (Ba_{bio}) was calculated following the equation used by Wehausen and Brumsack (1999) in order to separate detrital barite from barium precipitated as biogenic barite.

Ages of individual sapropel layers and site to site age correlations are based on precessional age scales in Emeis et al. (2000a), Lourens (2004), and Sakamoto et al. (1998). Each sampled layer was directly assigned to the corresponding sapropel name and insolation cycle (i-cycle) using Tables 1 to 4 from Emeis et al. (2000a) on the basis of sample to sample correlation (using ODP nomenclature) and/or revised composite core depths, or correlated using core tie points obtained from the ODP online database.

TOC and Ba_{bio} MAR's were calculated based on the sediment dry bulk density (DBD) obtained from the ODP Leg 160 database (available online) and linear sedimentation rates (LSR), calculated from age models from the database. When borehole LSR were not available, they were calculated for our sampling intervals, either using adjacent age intervals (again obtained from the ODP online database) or based on the methodology used by Meyers and Arnaboldi (2005). In brief, the peak TOC MAR calculated in each sapropel layer was assumed to represent the orbitally tuned age of the corresponding i-cycle. For sapropel 1, the age model obtained by De Lange et al. (2008) was applied, whereas for each of the rest of the analyzed sapropels, its corresponding i-cycle was assigned following the nomenclature and ages defined by Emeis et al. (2000a). The difference in core depths between successive sapropel layers was then divided by the ~21 ky of each precessional cycle to arrive at a linear sedimentation rate for this time and place. This method is consistent with the age model published by Lourens (2004) although it may sometimes contradict the assumptions of sapropel synchronicity

considered by other authors (e.g., Cane et al., 2002; Capotondi et al., 2006; De Lange et al., 2008; Emeis et al., 2003). The LSRs used for MAR calculations are summarized in Table 1.

3 Results

3.1 TOC concentrations and MAR's

TOC concentrations in the samples range from less than 0.1% in the background sediment up to 28.4% in one sapropel layer (Figs. 2 to 5), with the highest values detected in Pliocene sapropels at Sites 964 and 969. The general temporal trend is a progressive increase in sapropel TOC concentrations from the Holocene through the Pleistocene (Fig. 2a,b) and into the Pliocene (Fig. 3). For sapropels deposited during the same insolation cycle, those at Site 966 have the lowest TOC concentrations and lowest TOC MARs (see Figs. 2 and 4).

3.2 Organic carbon isotopic compositions

The C_{org}-isotopic compositions of the sapropel sequences differ spatially and temporally (see Figs. 4 and 5). As a whole, $\delta^{13}C$ values range between −19.0‰ and −26.5‰, and both the highest and lowest values are found within the Pleistocene sapropels sampled from Site 967. Although a general trend of increasing $\delta^{13}C$ values appears at Sites 964 and 966, this tendency is not observed for Site 967 nor in the Pliocene sequence at Site 969. An apparent shift towards heavier C-isotopic composition occurs at the base of the Quaternary sapropels or just before the increase in their TOC content. Again, this feature is not so evident in Pliocene sapropels across the basin, where systematic variations of $\delta^{13}C$ are less discernable.

3.3 Nitrogen isotopic compositions

The δ^{15}N values are strikingly similar at all four locations. They are significantly lower in the TOC rich sections compared to the carbonate oozes. The low δ^{15}N values range from ≈ 1.0 to 0.0‰ for the S1 sapropel to between 0‰ to -3.0‰ for Pleistocene sapropels (see Fig. 4) and down to -3.1‰ in the Pliocene sapropels (Fig. 5). A trend towards increasing average δ^{15}N value from i-cycle 10 (102 ky) to i-cycle 2 (8 ky) exists within the successive Pleistocene sapropels. When same i-cycles are compared between sites, δ^{15}N values are very similar; only those at Site 966 values tend to be slightly larger.

3.4 Ba concentrations and MAR's

Barium concentrations vary in parallel with TOC concentrations (Figs. 2 to 5), although elevated Ba concentrations frequently extend above the organic enriched layer in Quaternary sapropels (Fig. 2), a feature especially visible in sapropels from Site 966. These layers show a distinct offset between organic carbon accumulation and the productivity signal as represented by Ba/Al. In contrast to the patterns common to the Quaternary sapropels, Ba/Al values decrease more than TOC MAR near the tops of Pliocene sapropels at sites 964 and 969 (Figs. 3 and 5). Because of the different patterns in the two proxies, we estimated durations of the sapropel formation events by measuring the Ba peak width in the Quaternary sapropels and the TOC MAR peak in the Pliocene sapropels.

Ba$_{bio}$-MARs are larger in Pleistocene sapropels, particularly during i-cycle 12 (see Figs. 2 and 4). This Ba-MAR maximum coincides with maximum sediment LSR's. The highest Ba$_{bio}$-MARs values are found at Site 964, the deepest studied site. For same-age sapropels, the increases in Ba$_{bio}$-MAR are similar for the three sites located in the deeper parts of the basin but they are notably lower at shallower Site 966 (Figs. 2 and 4).

3.5 TOC/TN ratios

The atomic TOC/TN ratio varies similarly through time at the four locations, showing values mostly between 5 and 10 for background "normal"pelagic sediment (carbonate ooze), and increasing up to 25 in the sapropels (see Figs. 4 and 5). The highest TOC/TN ratios are found at Site 967, whereas the lowest are found on the bathymetrically elevated Site 966.

4 Discussion

4.1 Paleoproductivity proxies

4.1.1 δ^{13}C patterns and paleoceanographic significance

The δ^{13}C of organic matter can reveal important information about ocean productivity, although a wide variety of factors can affect the isotope signal for C_{org}, such as surface temperature, vital effects, nutrient uptake (e.g., Kump and Arthur, 1999; Meyers, 1997), nutrient recycling (e.g., van Breugel et al., 2005), or even massive biomass burning (Finkelstein et al., 2006). Organic δ^{13}C values in our samples range from −26‰ and −19‰, (Fig. 4), which mostly correspond to organic matter of marine origin, although some terrestrial influence might be argued for the more negative values. The possibility of land-derived influence is potentially applicable particularly for samples from Site 967, which is under the distal plume of the Nile River discharge. This river can deliver large amounts of detrital material to this location during intensified monsoon periods (Rossignol-Strick, 1985). However, δ^{13}C values smaller than −23‰ are common across the Eastern Mediterranean, especially in low TOC sections. The more negative values are consistent with an oligotrophic setting in which C availability does not limit algal vital fractionation. In contrast, periods of higher productivity result in depletion of ^{12}C from increased uptake, which can lead to less negative $\delta^{13}C_{org}$ values

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(e.g., Meyers, 1997). This pattern of a slight increase in $\delta^{13}C_{org}$ values during periods of higher productivity is the general response found in analyzed sapropels and is particularly evident at the base of the sapropel layers. However, this classic high-productivity isotopic trend is not evident at Site 967. Instead, cores recovered at this deep Levan-

5   tine sub-basin location exhibit the most negative $\delta^{13}C_{org}$ values and the most erratic trends in our sample suite. A possible explanation is that extensive organic matter recycling in the surface ocean limited the ^{13}C enrichment associated with net uptake (e.g., Arnaboldi and Meyers, 2006; Menzel et al., 2003; Meyers and Arnaboldi, 2008; Struck et al., 2001). In this scenario, increased continental runoff lowered the salin-

10   ity of the surface ocean and created a strongly stratified water column that impeded sinking of organic matter and discouraged vertical mixing. Oxidation of the isotopically light organic carbon could then occur within the lower part of the photic zone, where it would be re-assimilated by photosythesizers. The near-surface recycling of marine organic carbon during times of fluvial dilution of the surface ocean would potentially be

15   augmented by delivery of terrestrial organic matter adding to the low isotope signal. In any case, a shift toward heavier isotopic composition is visible at the base of the TOC-enriched layers at Site 967, which is a classical indication of a general increase in ^{12}C removal in the form of marine organic matter during initiation of sapropel deposition.

4.1.2   Paleoproductivity evidence from nitrogen concentrations

20   The concentration of total nitrogen in sediment can be a proxy of organic matter production, provided that an insignificant amount of inorganic N is adsorbed to clay minerals (e.g., Calvert, 2004; de Lange, 1992; Freudenthal et al., 2001). We verified that the percentage of inorganic N in our sediments is insignificant using the correlation method described by Nijenhuis and de Lange (2000), Calvert (2004), and Arnaboldi and Mey-

25   ers (2006) in which the concentrations of TOC are plotted against those of TN. The correlation is extremely good ($R > 0.9$ for all cores, see Fig. 7) with an intersection essentially at the y axis around and even below detection limit (see Fig. 7). Although this

intersection point is not exactly zero, the amount of inorganic N is negligible, as C:N ratios of low TOC samples are within the range of previous studies (e.g., Meyers and Arnaboldi, 2005) and in agreement with expected Redfield ratios.

Because organic N is also susceptible to post-depositional oxidation similar to or-
ganic carbon, its use for paleoproductivity reconstruction is subject to the same restric-
tions. Nonetheless, the correlation between TN and TOC gives us confidence that all of the N in the sediment is associated with or derived from organic matter, and so our δ^{15}N analyses will reflect purely N_{org}. Moreover, Higgins et al. (2010) recently veri-
fied that the δ^{15}N values in preserved sapropels are a pristine signal, not altered by
diagenesis.

4.1.3 δ^{15}N patterns in sapropel sequences

The N_{org} isotopic composition can be used as an indicator for the origin of organic mat-
ter (e.g., Knicker and Hatcher, 2001; Meyers, 1997; Rinna et al., 2002; Schubert and Calvert, 2001) and, more importantly, for evaluating nutrient cycles in the water column
(e.g., Altabet et al., 1999; Altabet and Francois, 1994; Freudenthal et al., 2001; Karl et al., 2002; Pantoja et al., 2002; Voss et al., 1996).The Mediterranean is presently an oligotrophic sea, characterized by low concentrations of macro-nutrients such as P and N in surface waters, (e.g., Astraldi et al., 2002; Bethoux, 1989; Struck et al., 2001). This shortage of nutrients, as a whole and of P specifically, is particularly dramatic in
the Eastern Basin, being distant from the Atlantic Ocean, the present main source of renewal water and its nutrients to the basin. An important regional nutrient source to the Eastern Mediterranean is the Nile River (e.g., Diester-Haass et al., 1998; Jenkins and Williams, 1984; Rossignol-Strick, 1985; Weldeab et al., 2003a). This riverine input and its significance as a nutrient source has fluctuated over time as cyclic variations
in the monsoon system influenced runoff from its catchment. Specifically, increased nutrients and fresh water supply from the Nile have coincided in time with precessional minima associated with sapropel formation (e.g., Hilgen, 1991; Rohling and Hilgen,

1991; Rossignol-Strick, 1985). With respect to N, nitrogen fixation and possibly atmospheric deposition are currently important sources for bioavailable N to the oligotrophic Mediterranean, although their significance is also variable over space and time.

Organic matter in all the sapropels exhibits a shift to low δ^{15}N values at the four locations (Fig. 4). This signature is unlikely a result of diagenesis as under suboxic-anoxic water column conditions the expected trend of organic matter degradation is an increase in δ^{15}N due to remineralization which is associated with an increase in TOC/TN ratios (e.g., Karl et al., 2002; Lehmann et al., 2002; Meyers and Arnaboldi, 2005; Nakatsuka et al., 1997). Higgins et al. (2010) also rejected the possible diagenetic overprinting by measuring chlorin δ^{15}N. Instead, the possible explanations for the dramatic decrease in δ^{15}N values in the sapropels are: (a) incomplete nutrient utilization under nutrient excess conditions (e.g., Calvert et al., 1992), (b) an external source of light N such as river discharge or atmospheric deposition (e.g., Krom et al., 2004; Mara et al., 2009), and (c) an ecosystem change in which a bloom of nitrogen-fixing primary producers occurs (e.g., Arnaboldi and Meyers, 2006; Milder et al., 1999; Pantoja et al., 2002; Sachs and Repeta, 1999; Struck et al., 2001).

The evidence for increased productivity based on the high TOC and Ba concentrations of the sapropels is strong. We may therefore reject the hypothesis of incomplete nitrogen utilization as nitrogen would be in higher demand when productivity is high. Fluvial delivery is also unlikely as an extraordinary excess of nutrients would have to be delivered to lower the δ^{15}N values, particularly considering the amount of organic carbon accumulated in the sapropels (Sachs and Repeta, 1999). Increase in atmospheric deposition on nitrogen is also unlikely as it is expected that less dust would be mobilized during wetter climate precessional minima. In addition much of the atmospheric nitrogen sources today are anthropogenic and thus atmospheric deposition was not as important in pre-anthropogenic times. Accordingly we believe that nitrogen fixation is the main source of the bioavailable nitrogen with low isotope values in surface waters (e.g., Altabet and Francois, 1994; Kuypers et al., 2004). This process would incorporate dissolved atmospheric dinitrogen (δ^{15}N=0‰) into the marine system, lowering the

isotopic composition (e.g., Altabet, 1999; Karl et al., 2002; Meyers, 1997; Pantoja et al., 2002). The extremely light N isotopic composition suggests a change in the photoautotrophic community to a primarily N-fixing biota, probably associated with a decrease in eukaryote phytoplankton activity during sapropel deposition times (e.g., Pantoja et al., 2002; Sachs and Repeta, 1999). Nitrogen fixing cyanobacteria, cyanobacterial mats and/or diatom-hosted cyanobateria, (see review by Karl et al., 2002; Kemp et al., 1999), produced organic matter that is isotopically very light in nitrogen. This phenomenon would favor low δ^{15}N values, and at the same time, it would provide extra bioavailable nitrogen for other primary producers. Nitrogen fixation is often limited by Fe, Mo and/or P concentrations (Karl et al., 2002). However, although river runoff would not be able to supply enough N to support the observed increase in productivity, it may have been capable of supplying oligoelements, such as Fe, in quantities sufficient to induce higher productivity and N-fixation by cyanobacteria and archaea.

The extra input of freshwater from the Nile would decrease salinity in the upper part of the water column. Lower salinity is known to enhance Mo reactivity and availability, in the form of MoO_4^{-2}, whereas P can easily be recycled by efficient scavenging in the water column (Karl et al., 2002) or reductive dissolution at the sediment-water interface (e.g., Slomp et al., 2004). All these factors, along with an increase in sea surface temperature (e.g., Emeis et al., 2000b; Lourens et al., 1992), allowed the maintenance of blooms of N-fixing organisms and associated biota.

The shift towards low δ^{15}N values is evident across the whole region in the Quaternary sequences and parallels or precedes the increase in export production indicated by Ba$_{bio}$ MARs (e.g., Dehairs et al., 1987; Gallego-Torres et al., 2007; Weldeab et al., 2003a). The Pliocene sapropels show mutually similar trends across the basin. δ^{15}N values exhibit a progressive decrease from the onset of sapropel formation upwards, but not always parallel to Ba/Al enrichments. In fact, it is common to find a lighter N-isotopic composition preceding the productivity maxima, indicating that maximum N fixation was followed by an increase in total export production. As a whole, low δ^{15}N values coincide well with increased organic carbon concentrations, in agreement with

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other sapropel studies (e.g., Calvert et al., 1992; Meyers and Arnaboldi, 2005; Milder et al., 1999; Struck et al., 2001). We thus infer that blooms of nitrogen-fixing biota were a central factor in creating the higher surface productivity that led to sapropel formation.

4.1.4 Paleoproductivity patterns based on Ba concentration

Ba concentrations and Ba/Al ratios have been used for paleoproductivity reconstructions in a wide variety of marine environments (e.g., Dymond et al., 1992; Eagle et al., 2003; McManus et al., 1999; Paytan, 1997; Weldeab et al., 2003a). Greater TOC concentration in our sapropel sequences is consistently linked to an increase in Ba_{bio}. Although Ba_{bio} cannot be used to quantitatively determine export productivity, (e.g., Averyt and Paytan, 2004; Gingele and Dahmke, 1994; Kasten et al., 2001; McManus et al., 1994, 1998), it has been widely and successfully applied as a semi-quantitative indicator for enhanced marine productivity in the Mediterranean (e.g., Dehairs et al., 1987; Diester-Haass et al., 1998; Emeis et al., 2000a; Weldeab et al., 2003a). Furthermore, it has been shown that Ba content generally permits a better reconstruction of the duration of enhanced paleoproductivity than TOC, because barite is less sensitive to postdepositional oxidative destruction (e.g., Paytan and Kastner, 1996; Thomson et al., 1995). In Mediterranean sapropels, TOC destruction is evidenced by oxidation fronts in the form of high Fe and Mn layers above sapropel and low TOC concentrations in the upper parts of the sapropel, whereas high Ba concentrations typically remain preserved (e.g., Gallego-Torres et al., 2007, 2010; Larrasoana et al., 2003b; Martínez-Ruiz et al., 2000; Thomson et al., 1995, 1999).

TOC and Ba_{bio} MAR's are calculated assuming constant LSR's for each i-cycle (see Table 1). This assumption might conflict with the accepted "isochronous sapropel model" (e.g., De Lange et al., 2008; Rohling et al., 2006). However, assuming isochronous sapropel boundaries implies shifts in LSR's of up to 90% higher or up to 45% lower from background to sapropel sediments. Nijenhuis and De Lange (2000) proved the inconsistency of such shifts. This problem was earlier addressed by Van

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Oss et al. (1994). Owing to the necessity of selecting one hypothesis, constant LSR's were assumed.

An increase in Ba_{bio} concentration appears in all the sapropel layers we studied. Although the amounts of these increases in concentration may vary among the layers, they always accompany the shift to higher TOC content and higher TOC-MAR at the base of the sapropels. However, as mentioned before, we clearly observe a disconnect between concentrations of Ba (unaltered signal for increased productivity) and TOC (partly oxidized) at the top of the Quaternary S1 sapropel at the four study locations (different gray shadings, Figs. 2 and 4) and, to a lesser extent, in some Pleistocene sapropels, (Gallego-Torres et al., 2007, 2010). This offset, attributed to post-depositional oxidation of the organic matter at the top of the sapropel layer, as described by Van Santvoort et al. (1996) (see also Martínez-Ruiz et al., 2000; Thomson et al., 1995), indicates that the real duration of increased productivity (thus, sapropel formation) was longer than evident from the easily oxidized organic matter.

As a whole, the Pleistocene sapropels, ranging in age from 81 ky to 217 ky, exhibit the highest export production levels of the studied sections, as represented by the highest Ba_{bio}-MAR, although TOC concentrations are lower than during the Pliocene.

The Pliocene sapropels at Sites 964 and 969 differ in two important ways from the Quaternary sapropels in the Eastern Mediterranean transect. The increase in productivity is again indicated by increases in Ba_{bio} and TOC-MARs, but the sapropels generally lack oxidation fronts. In fact, a reversed offset between TOC and Ba/Al is evident in i-cycles 282 and 284 (Site 964 and 969, see Figs. 3 and 5). These sapropels originally developed as a result of an increase in export production. TOC accumulated and was preserved, reaching very high concentrations although productivity was less than in some of the Pleistocene sapropels. Organic matter continued to accumulate after the return to normal productivity, probably due to the presence of anoxic bottom waters that favored its preservation. Anoxia associated with sulfate reduction in the sediments evidently degraded barite and diminished the Ba contents of the upper parts of these sapropels (e.g., Arndt et al., 2009). These differences suggest that

deep-water circulation in the Eastern Mediterranean during the middle Pliocene was slower than in the Quaternary, leading to poorer deep-water ventilation.

4.2 Sapropel expression across the Eastern Basin through time

Our results reveal basin-wide patterns, temporal variations, and spatial differences in the history of sapropel deposition in the Eastern Mediterranean Sea over the past 3 My. The general trend towards lighter N-isotopic composition in the sapropel layers is clear but not particularly strong during the deposition of the Holocene S1 sapropel (i-cycle 2). The most plausible explanation for this weak signal is a minor increase in nitrogen-fixing cyanobacteria population and overall marine productivity. We find an important offset between deep-water Site 967 and shallow-water Site 966 for i-cycle 8. At Site 967, a well developed sapropel was deposited during that time span, with TOC values reaching up to 3.3%, and high productivity marked by a distinct peak in Ba/Al and a minimum in δ^{15}N. This layer also shows evidence of postdepositional oxidation of the organic matter at the top of the sapropel while increased paleoproductivity is still evident from the Ba/Al peak. At the same time, deposition on the top of the Eratosthenes seamount (Site 966) produced a poorly developed sapropel that is now described as a Ghost Sapropel (Emeis et al., 2000a). The signals of Ba$_{bio}$, TOC and δ^{15}N are weak, with maximum TOC of only 1.1%, may not even qualify as a true sapropel (Kidd et al., 1978). These values suggest less organic matter recycling in the water column due to the shallower water depth, or greater degradation of the organic matter after deposition (e.g., Freudenthal et al., 2001; Kienast et al., 2005; Lehmann et al., 2002). Same-age sapropel development in other Eastern Basin (Emeis et al., 2000a), is weak or absent. Thus we postulate that the i-cycle 8 sapropel is restricted to the easternmost Mediterranean, most likely related to direct influence of the Nile River (see Fig. 1). The shift to wetter climate associated with periods of sapropel deposition was less intense and/or did not occur basin-wide during this time (81 ka).

The remaining Pleistocene and Pliocene sapropels show similar and essentially concordant trends across the basin: a progressive decrease of δ^{15}N values from the onset

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of sapropel formation upwards, frequently preceding Ba/Al enrichment. At the top of the Holocene S1 sapropel in the four study locations (Figs. 2 and 4), post-depositional oxidation does not permit us to assess whether N-fixation continued during the whole high productivity phase. The Ba-MARs during S1 deposition are equivalent for Sites 964 and 969, whereas at Site 966 the MAR is considerabl[=]ower and at Site 967 it is relatively higher. The same pattern is seen in TOC-MARs. Sites 966 and 967 are geographically proximate to each other, but they are located in very different water depths (926 m b.s.l. vs. 2555 m b.s.l.). Export production, which is a surface ocean process, is expected to be similar at these sites. The difference in Ba MARs may be instead related to the degree of barite saturation and thus its preservation in the water column, which is depth dependent (e.g., Paytan and Griffith, 2007; van Beek et al., 2006). In any case, for the same insolation cycle, the relatively shallow Site 966 exhibits the lowest TOC and Ba MARs of the four sites (Fig. 3). Therefore, it appears that greater water depth favors the burial and preservation of organic matter as proposed by Murat and Got (2000) and refined by de Lange et al. (2008), although it is not a factor influencing the mechanism of sapropel formation itself. Sapropels on the top of Eratosthenes Seamount, although possessing lower TOC values, are characterized by all of the same features as those in the deep basin (increase in Ba/Al and Ba-MAR, lower δ^{15}N, higher TOC/TN). These proxies point toward sapropel formation induced by basin wide increased surface productivity, at least during the period between i-cycles 20 and 2, where we are able to compare similar layers across the basin.

Analyzing Figs. 2 and 4, we observe that the duration of some sapropels (e.g., S5 to S7) appears to become longer from west to east. This pattern may indicate either a progressively shorter increased productivity event towards the west or an increase in sedimentation rates associated with sapropel forming conditions. A similar problem was addressed by Nijenhuis and De Lange (2000) and recently Katsouras et al. (2010) showed that S1 developed later in the Aegean Sea compared to the Lybian coast, by an offset of up to 0.9 ky. We do not have sufficient information (particularly, absolute dating) to resolve this issue. However, we are inclined to believe that this pattern results

from differences in sedimentation rates inasmuch as the paleoceanographic conditions that favored increased productivity were approximately stable and concordant across the basin.

This pattern allows us to conclude that the same climatic factors (warm/wet periods during summer insolation maxima and enhanced monsoon activity) that triggered increased fluvial discharge and amplified nutrient input also favored the establishment of N-fixing bacteria. This combination of factors ultimately induced sapropel formation.

4.3 Diagenesis

The combination of TOC/TN ratios and δ^{13}C and δ^{15}N values has been used to determine the origin of the organic matter in marine sediments (e.g., Bouloubassi et al., 1999; Meyers, 1997; Oldenburg et al., 2000; Rullkötter, 2000) by distinguishing between contributions from marine algae, marine cyanobacteria, lacustrine algae, and continental C_3–C_4 plants, as summarized by Meyers (1997). These parameters are plotted in Fig. 8, where we show the TOC/TN, δ^{13}C and δ^{15}N data for the 35 sapropels we analyzed. Holocene sediments plot close to the marine algae end member, with minor deviations coinciding with the highest TOC values. Pleistocene samples show a nearly bimodal distribution on the TOC/TN-δ^{13}C plot. The great majority of low TOC samples fall in the marine domain, whereas samples from within the sapropel shift towards composition that emulates C_3 terrestrial plants. Only a few samples present low TOC concentrations and high TOC/TN ratios, and they are found mostly in sediments from Site 967 that may receive a greater continental influence due to its location. A similar trend is observed for Pliocene sapropels. In contrast, the δ^{15}N vs. δ^{13}C plot systematically shows a marine algae composition for non-sapropel samples and a typical marine cyanobacteria composition for sapropel samples.

Although TOC/TN vs. δ^{13}C plots could be interpreted as resulting from an influence of continental input (i.e., C_3 plants), the δ^{15}N vs. δ^{13}C graphs suggest that the sapropels are dominated by marine organic matter, and other independent evidence such

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as large values of the Rock-Eval Hydrogen Index (Bouloubassi et al., 1999; Emeis et al., 1996) and an abundance of marine biomarker molecules (Rinna et al., 2002) supports this interpretation. Nitrogen isotopic composition is only slightly or not at all affected in preserved organic matter (Higgins et al., 2010), whereas under conditions of high surface productivity, the typical TOC/TN value of the exported organic matter is higher than the typical algal signal, partly due to selective remineralization of N and N-rich molecules below the euphotic zone and/or at the sediment surface (e.g., Twichell et al., 2002). According to Freudenthal et al. (2001) (see also Macko et al., 1994), TOC/TN ratios would increase when remineralization and preferential degradation of amino acids (isotopically heavy) occurs along the water column. Similar results were obtained in sediment traps by van Mooy et al. (2002). Selective remineralization of amino acids could simultaneously yield negative δ^{15}N values and higher TOC/TN values of deposited organic matter. The increase in TOC/TN can also partly be caused by denitrification under a suboxic environment (Karl et al., 2002) that is easily achieved under highly productive waters. These diagenetic changes support the conclusions made by Arnaboldi and Meyers (2006) on similar sediments in the Eastern Mediterranean. We observed that this increase in TOC/TN ratio is more extreme during the Pliocene, in agreement with a highly restricted water column oxygenation for this period as postulated by Passier et al. (1999, 1996), Böttcher et al. (2003), Warning and Brumsack (2000), Larrasoaña et al. (2003a), Weldeab et al. (2003a, b).

Lighter N-isotopic composition of organic matter mirrors organic-rich levels, but it does not extend above oxidized sapropels to parallel the increase in productivity. Since nitrogen fixation seems to be crucial for sapropel formation, changes in export productivity (Ba$_{bio}$) should run parallel to N-fixing activity (δ^{15}N), because both reflect primary production. However, the post burial burn-down oxidation may affect this signal. Specifically, oxidation of deposited organic matter preferentially consumes ^{14}N, so that the remaining organic matter in the sediment becomes enriched in ^{15}N thus altering the δ^{15}N signal. Higgins et al. (2010) postulate that the N isotope signal is not affected by oxidation of decaying organic matter, although the resolution of their analyses is not

high enough to discriminate oxidation fronts. However, if we accept their hypothesis, we may infer that the increase of δ^{15}N values immediately on top of sapropels S1 or S7 (light shading in Fig. 4) is due to better oxygenation of the overlying water column while high productivity conditions still prevailed.

5 Summary and conclusions

Based on the observations and interpretations obtained from δ^{15}N, δ^{13}C, TOC, Ba$_{bio}$ and MAR's, we present the following paleoceanographic reconstruction. The remarkably lighter N isotopic compositions of the sapropel layers indicate periods of nitrogen fixation and thus, amplified cyanobacterial productivity (probably associated with bacterial mats) in the water column. Although N-fixation is frequently associated with oligotrophic basins, in the case of Eastern Mediterranean sapropels it created a highly productive environment. This increase in N-fixing biota and bacterial primary productivity increased export production and is reflected in major increases in TOC and Ba$_{bio}$ MARs. The change in mode of productivity is fueled by nutrient input (such as P, Fe or Mo), most likely through riverine discharge and by a warming environment with higher SST and lower SSS (Emeis and Weissert, 2009; Emeis et al., 2000b). These climatically driven productivity events affected the entire Eastern Mediterranean, independent of water depth. Differences in sapropel expression depend on water depth, related to winnowing, deep water circulation and/or SO$_4^{-2}$ saturation.

Our results allow us to distinguish between the importance of organic matter production and its preservation in forming the sapropel layers. TOC-MAR and Ba$_{bio}$ MAR do not show a direct correlation with C$_{org}$ concentration and Ba/Al ratio, respectively. Some upper Pleistocene sapropels, such as S5 (i-cycle 12) have lower TOC concentrations but higher TOC and Ba$_{bio}$ MAR's than older equivalents, indicating that both marine productivity and detrital sedimentation dramatically increased during the late Pleistocene. Opposite to this trend, early Pleistocene and late Pliocene sapropels accumulated under markedly lower sedimentation rates and therefore exhibit higher Ba

concentrations but lower MARs than upper Pleistocene equivalents. In other words, greater productivity does not directly result in higher TOC accumulation (Fig. 9). These late Pliocene and early Pleistocene relatively smaller increases in productivity correspond to limited water mass circulation due to more restricted water inflow from the
5   Atlantic than in late Pleistocene times; water mass circulation may have even reversed (estuarine circulation, e.g., Bottcher et al., 2003; Wehausen and Brumsack, 1999) favouring bottom waters stagnation. This interpretation implies that organic carbon concentration in these layers is equally influenced by both preservation and productivity. Variations in deep water circulation are also responsible for different diagenetic
10 imprints on TOC, TOC/TN ratio and δ^{15}N signals.

Humidity maxima also contribute to the intensity of productivity increase by magnifying fluvial nutrient input into the basin. Higher humidity signifies stronger river runoff, higher nutrient supply from the continent and, at the same time, increased detrital input that would increase sedimentation rates. If we consider the increase in African de-
15 rived nutrient input as climatically controlled (in turn defined by insolation cycles), the maximum increase in fluvial input should correspond to i-cycles 12 to 20, which show the greatest maximum summer insolation (500 to 520 W/m^2) according to Emeis et al. (1996) and Lourens et al. (2004). Sampled sapropels from i-cycles 152 to 182 correspond to insolation peaks that remain around 500 W/m^2 (Larrasoana et al., 2003a)
20 or below, for i-cycles 270 to 286. Thus, detrital and nutrient input would be the highest at maximum insolation (i.e., late Pleistocene). This prediction is supported by our results that reveal relatively low TOC concentration compared to older equivalents and, at the same time, the very high TOC and Ba$_{bio}$-MARs found at all four sites, for example during i-cycle 12. The relative sizes of the increases in sedimentation rates and
25 productivity rates are evidently related to the amplitudes of the precessional insolation and humidity maxima.

A remarkable increase in TOC/TN ratios, related to denitrification processes, suggests intense oxygen consumption below the euphotic zone. The δ^{15}N signal, although mostly representing a primary signal, might be shifted to somewhat larger values by

diagenetic oxidation that is evident in diminished TOC concentrations at the tops of sapropel layers because of oxidative burndown.

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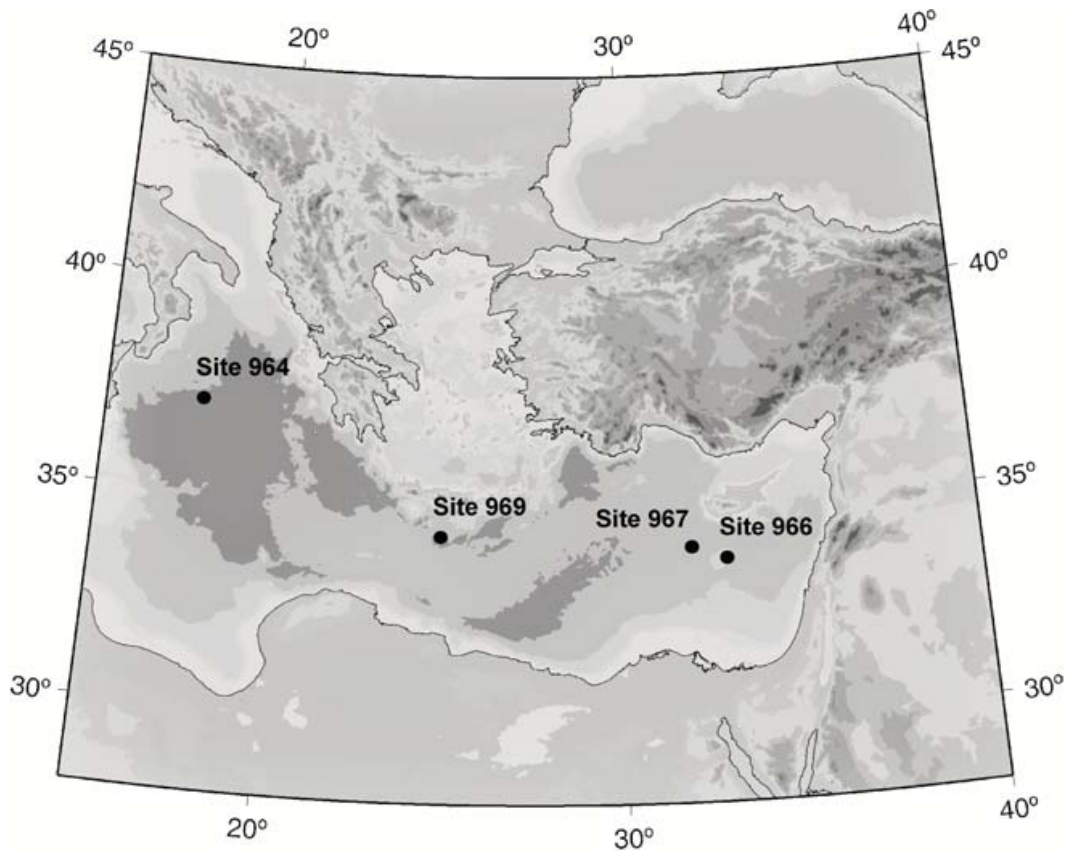
Table 1. Four-site paleoproductivity proxy sapropel sequences.

Sample location	I-Cycle	Age[*] sapropel midpoint (ka)	Depth (m b.s.f.)	Depth (m c.d.)	LSR (cm/ky)
Site 964, Ionian Basin (3658 m b.s.l.)					
Hole 964A	i-c 2	7.75	0.73	0.73	4.14
Hole 964A	i-c 12	124	7.71	7.81	5.93
Hole 964A	i-c 16	172	11.12	11.22	6.00
Hole 964A	i-c 18	195	11.99	12.09	4.04
Hole 964A	i-c 20	217	12.62	12.72	3.02
Hole 964A	i-c 272	2828	76.73	98.21	2.55
Hole 964A	i-c 282	2943	79.64	101.12	2.41
Hole 964A	i-c 284	2965	80.19	101.67	2.87
Hole 964A	i-c 286	2989	80.93	102.41	2.50
Site 966, Eratosthenes Seamount (926 m b.s.l.)					
Hole 966B	i-c 2	8.26	0.27	0.27	3.90
Hole 966B	i-c 8	81	2.36	2.36	2.60
Hole 966B	i-c 12	124	3.31	3.31	2.35
Hole 966B	i-c 16	172	4.36	4.36	2.19
Hole 966B	i-c 18	195	4.78	4.78	2.24
Hole 966B	i-c 20	217	5.45	5.45	2.04
Site 967, Levantine Basin (2555 m b.s.l.)					
Hole 967D	i-c 2	7.94	1.17	1.17	5.36
Hole 967D	i-c 8	81	4.32	4.28	5.64
Hole 967D	i-c 10	102	5.65	5.58	5.90
Hole 967D	i-c 16	172	10.57	9.79	4.67
Hole 967D	i-c 170	1736	47.76	52.96	2.20
Hole 967C	i-c 172	1757	48.21	53.41	2.58
Hole 967C	i-c 176	1808	49.35	54.55	1.92
Hole 967C	i-c 178	1829	49.89	55.09	2.42
Hole 967C	i-c 180	1851	50.35	55.55	2.30
Hole 967C	i-c 182	1872	50.87	56.07	2.18
Site 969, Mediterranean Ridge (2200 m b.s.l.)					
Hole 969A	i-c 2	7.98	0.27	0.27	4.39
Hole 969A	i-c 10	102	2.64	2.42	4.36
Hole 969A	i-c 12	124	3.92	3.41	4.24
Hole 969A	i-c 16	172	5.65	4.94	2.62
Hole 969A	i-c 18	195	6.16	5.48	2.64
Hole 969A	i-c 152	1564	27.05	34.05	2.80
Hole 969A	i-c 160	1642	28.54	36.19	2.75
Hole 969A	i-c 280	2921	50.74	73.25	1.88
Hole 969E	i-c 284	2965	51.48	73.96	2.37

[*] Ages are from Lourens et al. (1996) and de Kaenel et al. (1999) and are based on the orbital calculations. S1 age is based on De Lange et al. (2008).

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Fig. 1. Location map for the 4 studied sites. Site 964 (Ionian basin) is the deepest studed location. 966 is located on a pelagic high, the Eratosthenes Seamount (see text for details).
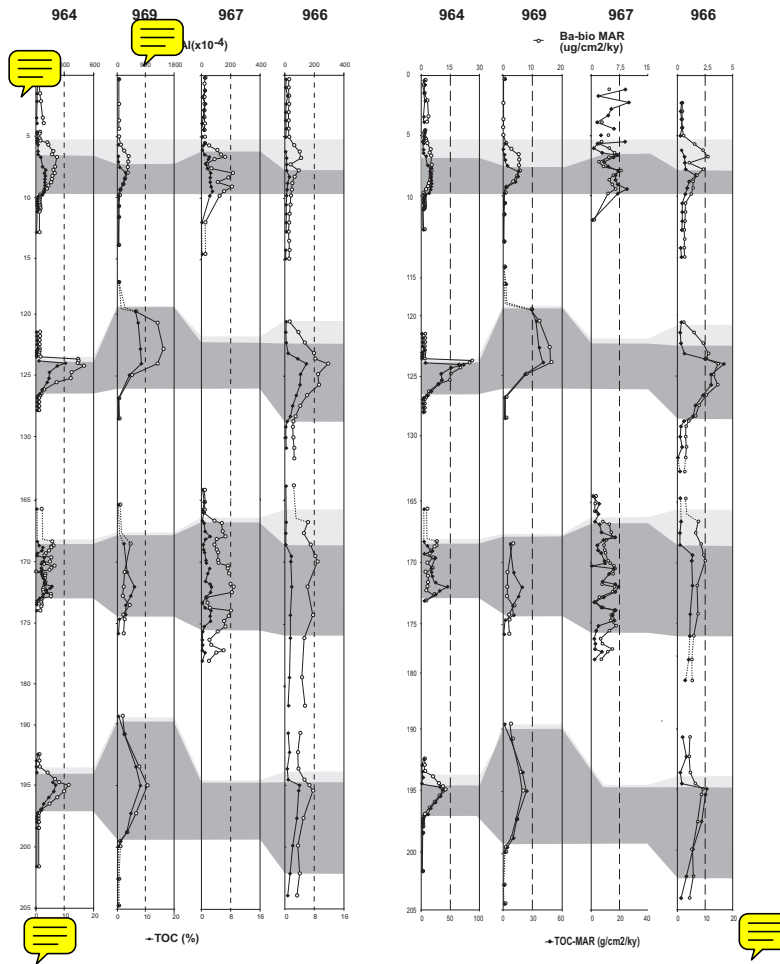
Fig. 2. Comparison of TOC and Ba/Al vs. TOC-MAR and Ba$_{bio}$ MAR through the late Quaternary on the four studied sites. Dark shade corresponds to visible sapropel layer. Light shade represents oxidized sapropel.

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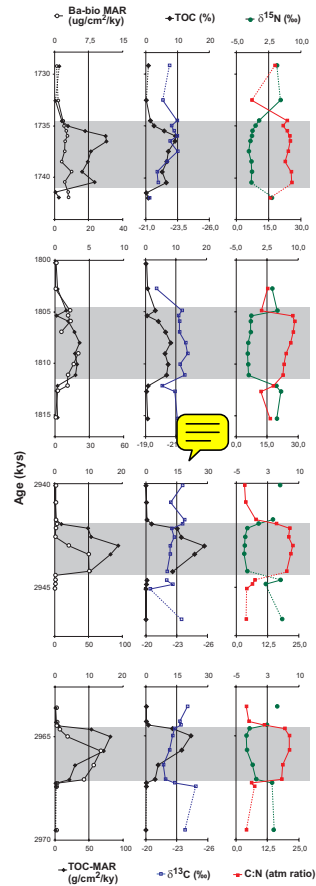
Fig. 3. Geochemical signal and TOC-Ba$_{bio}$ Mass Accumulation Rates, C:N and C-N isotopic composition for representative Pliocene sapropels from Sites 967 and 964. Note different scales for TOC and Ba-MAR's. Shaded areas correspond to sapropel layers.
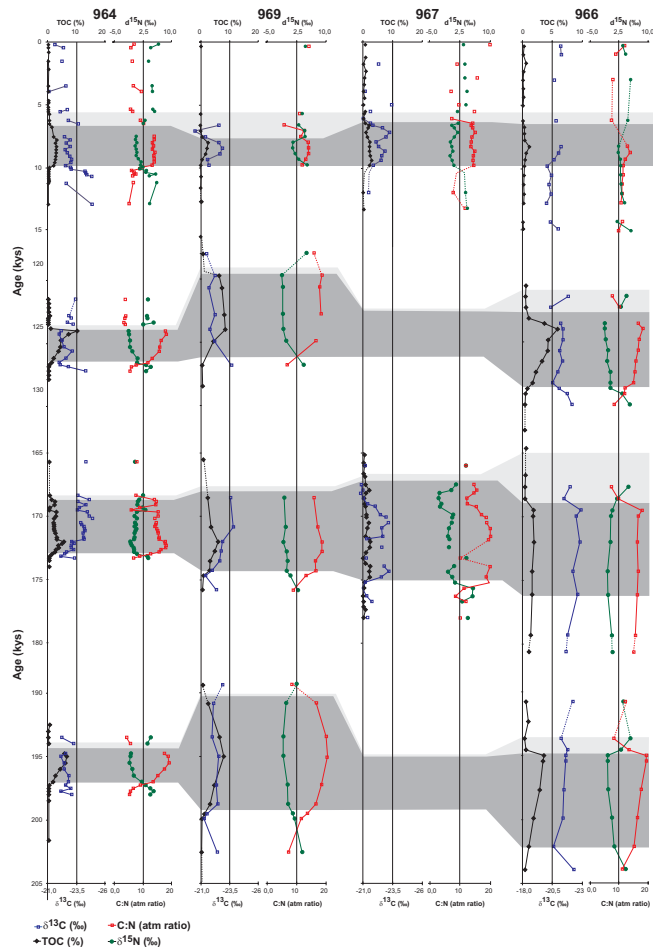
Fig. 4. Variations of TOC, Ba_bio-MAR, N and C isotopic composition and C:N ratios across the Eastern Mediterranean during late Quaternary.
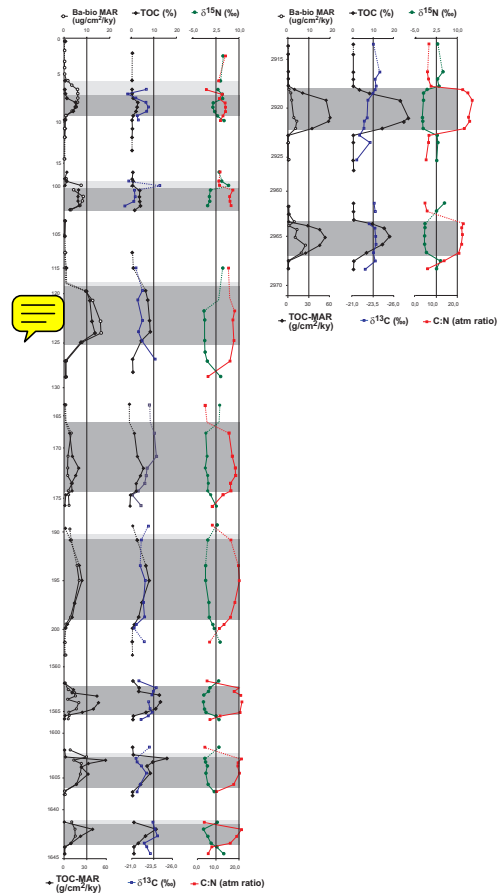
Fig. 5. Temporal evolution of the depositional conditions from Pliocene to Holocene represented by TOC, Ba-bio-MAR, N and C isotopic composition and C:N ratio on the Eastern Mediterranean Ridge (Site 969).

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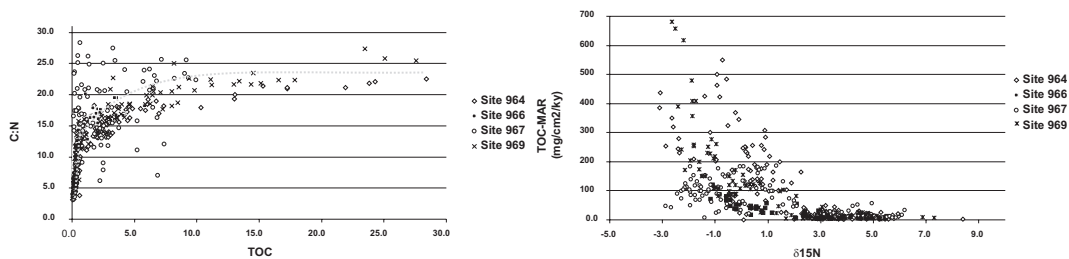
Fig. 6. C:N, TOC and δ^{15}N relationships in the studied sections.
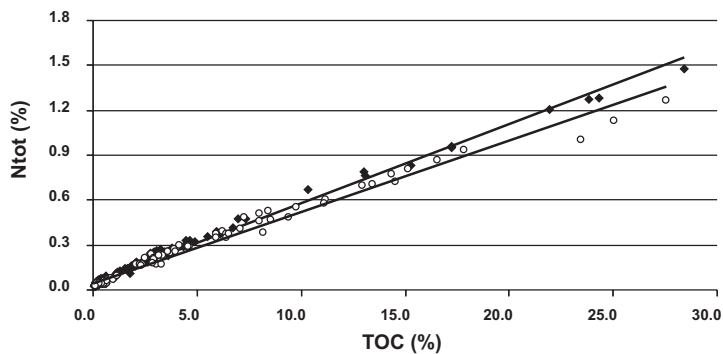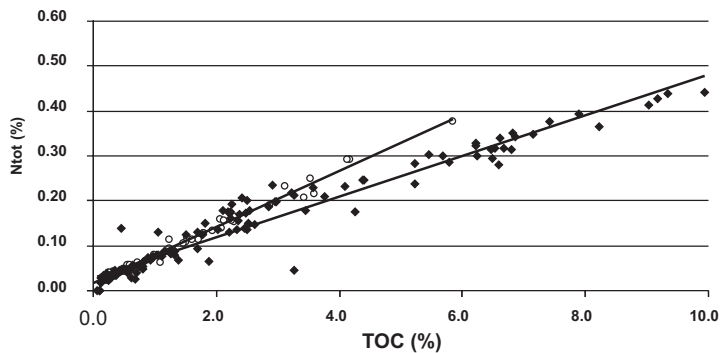
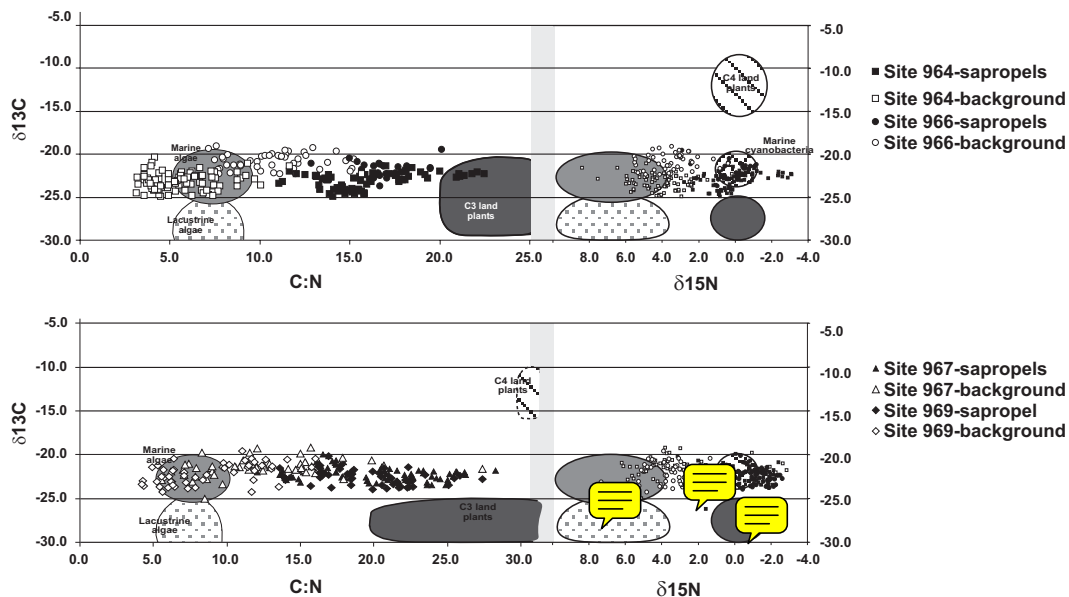**Fig. 7.** Total Nitrogen to TOC correlation. Very high correlation rate indicates that we may consider $N_{tot}=N_{org}$.

Fig. 8. Origin of the organic matter contained in the sampled sapropels as a function of δ^{15}N, δ^{13}C and C:N ratios.
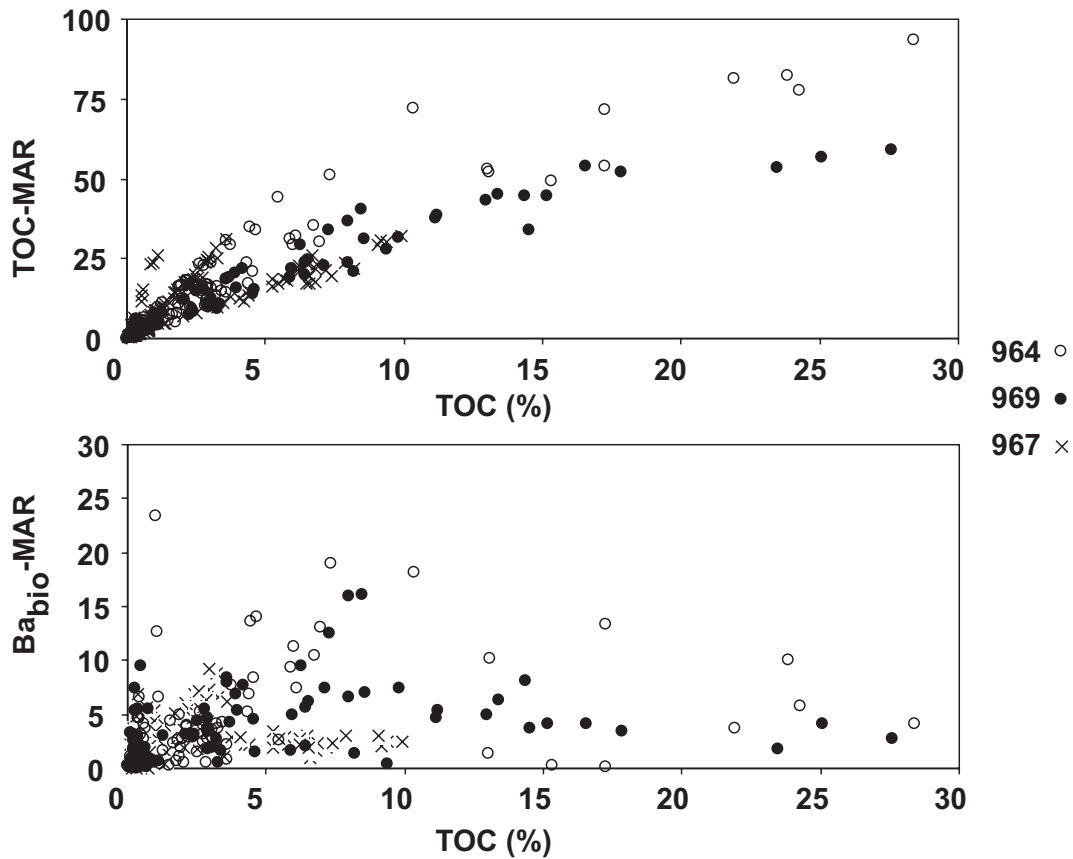
Fig. 9. Correlation between TOC vs. TOC-MAR and between TOC vs. Ba_{bio}-MAR for Sites 964, 969 and 967. Maximum TOC values do not correspond with highst Ba_{bio}-MAR and viceversa.