Pliocene–Holocene evolution of depositional conditions in the eastern Mediterranean: Role of anoxia vs. productivity at time of sapropel deposition

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Abstract

A multiproxy geochemical study of nine sapropel layers from ODP Hole 964A, ODP Leg 160 in the eastern Mediterranean spanning the Pliocene–Holocene time interval provides new insights into the evolution of sapropel deposition. Paleoenvironmental proxies were used for reconstruction of productivity (Ba derived from marine barite), oxygen conditions (trace metal ratios) and sedimentary regime (clay minerals, detrital elements). These proxies reveal a significant increase in river runoff relative to decreasing aeolian input during sapropel deposition over the whole time interval. Ba excess supports the argument that a significant increase in export productivity is the main triggering mechanism for sapropel deposition, although preservation also played an important role. Furthermore, major differences exist in depositional conditions, including both oxygenation and productivity since the Pliocene. Productivity fluctuated substantially and was higher during the Pliocene and Pleistocene than during the Holocene; at the same time decreasing oxygen availability parallels the enhanced productivity. Dysoxic to anoxic conditions appear to coincide with marine productivity maxima, thus suggesting that oxygen depletion may be linked to greater consumption rather than restricted circulation. This correspondence supports the hypothesis that productivity fluctuations resulting from climate oscillations were the main cause of enhanced organic matter contents and also a main controlling factor for reduced oxygen availability.
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Keywords: Sapropel; Eastern Mediterranean; Redox proxies; Productivity; Anoxia

1. Introduction

Sapropel deposition in the eastern Mediterranean has been the subject of intense debate for decades, (Kidd et al., 1978). It has been argued that increased organic carbon content is the consequence of stagnation-enhanced preservation of organic material fluxes. Evidence in favour of the stagnation model is frequently based on faunal assemblages or biomarkers (e.g., Rohling and Hilgen, 1991; Menzel et al., 2002; Negri et al., 2003), or on the concentration of trace elements and sulphide-forming metals, (e.g., Rossignol-Strick, 1985; Nolet and Corliss, 1990). Alternatively, marine surface productivity has also been considered the main cause of higher organic matter contents. Ba excess and

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other productivity proxies, (e.g., Emeis et al., 1991; Strohle and Krom, 1997; Emeis et al., 2000b; Warning and Brumsack, 2000; Martinez-Ruiz et al., 2003; Menzel et al., 2003; Paytan et al., 2004), as well as the nitrogen isotopic composition of organic matter (e.g., Meyers and Arnaboldi, 2005; Meyers and Bernasconi, 2005), indicate an increase in productivity during sapropel deposition. The combination of both processes has also been invoked and a consensus is now emerging that both productivity and preservation played an important role (e.g., Calvert and Fontugne, 2001; Rinna et al., 2002; Filippelli et al., 2003).

In any of the scenarios, it is accepted that sapropels originated as a response to astronomically forced climate cycles (Hilgen, 1991) that affected the basin by altering paleoceanographic conditions. However, the ultimate reason for the accumulation and preservation of organic matter is still a matter of debate. Enhanced precipitation and wetter conditions (Rossignol-Strick, 1985) imply a higher continental runoff into the basin, thus providing the Mediterranean system with more freshwater and land-derived nutrients (e.g., Lourens et al., 1992; Aksu et al., 1995; Emeis et al., 2000a; Nijenhuis and de Lange, 2000; Casford et al., 2003; Weldeab et al., 2003a), both of which could be factors that promoted sapropel formation. On the one hand, freshwater could cause stratification of the water column, thus preventing oxygenation of the seafloor. At the same time, nutrients would allow increased productivity and export production, which may have overwhelmed oxygenation rates and resulted in organic matter accumulation in the sediments.

These two possible explanations are at the core of a major debate understanding sapropel formation. With the aim of clarifying the main cause of TOC accumulation and preservation in the Mediterranean sedimentary record (e.g., Mangini and Schlosser, 1986; Murat and Got, 2000), and also reconstructing the conditions of the basin at the time of sapropel deposition, and the evolution of these TOC enrichment events, nine sapropel layers from ODP core 964A (Ionian Basin) spanning from the Pliocene to Holocene were analyzed at high resolution. Within this high-resolution approach, we first applied mineralogical and geochemical proxies to determine sedimentological and climatic conditions (e.g., Hamroush and Stanley, 1990; Krom et al., 1999; Frumkin and Stein, 2003). We then used productivity proxies, such as TOC-Mass Accumulation Rates and Ba/Al and biogenic barite (e.g., Dehairs et al., 1987; Paytan et al., 2002, 2004), previously proven to be reliable in this area (e.g., Thomson et al., 1995; Passier et al., 1996; Thomson et al., 1999;

Martínez-Ruiz et al., 2000; Paytan et al., 2004). Finally, we also discuss a set of compiled redox proxies (e.g., Jones and Manning, 1994; Thomson et al., 1995; Holser, 1997; Bottcher et al., 2003; Powell et al., 2003; Rimmer, 2003) and compare their behaviour over time, bearing in mind their possible diagenetic redistribution and alteration processes (e.g., Jung et al., 1997; Crusius and Thomson, 2003).

2. Materials and methods

Pelagic sediments including sapropel layers from the Pliocene–Holocene time interval were sampled in ODP cores recovered at Site 964 during Leg 160. This Site is located in the Pisano Plateau near the Ionian Abyssal Plain on a small bathymetric high at a depth of 3650 m (see Fig. 1 for location). An excellent record of sapropel deposition in the Ionian Basin was obtained at this location in six drill holes. The lithostratigraphic section recovered at these holes shows little down core variations and consists predominantly of nannofossil clay, clayey nannofossil ooze and nannofossil ooze with some intervals of clay and foraminiferal sand (Emeis et al., 1996). Within this section, numerous sapropel layers occur with variable characteristics (e.g., from massive to laminated, from sharp color boundaries to gradual contacts) and with a variable TOC content.

According to the scope of this study, we selected sapropels from different time periods in order to establish the oxygenation/productivity evolution of the eastern Mediterranean since the Early Pliocene. Sapropel layers were sampled continuously at 2 cm intervals, and more detailed sampling down to mm scale was performed on selected boundaries.

Analyzed sapropel intervals are summarized below. We followed the nomenclature according to the description provided by Emeis, Robertson, Ritcher (1996) in the ODP 160 Initial Reports and Emeis et al. (2000a), eventually modified by Lourens (2004), as well as our own description and sampling:

– Quaternary sapropels: S1, S3, S5 and S6 are defined at this location as thick-bedded, greater than 5 cm in thickness, dark olive gray to black in color and often laminated. S1 is the only Holocene sapropel, deposited during insolation cycle 2 (8.5 kyr, Lourens, 2004). Pleistocene sapropels S3, S4, S5 and S6 correspond, respectively, to insolation cycle 12, 16, 18 and 20. The ages of these levels, following Lourens (2004), calibration, are; S3=124 kyr; S5=195 kyr; S6=216 kyr. S4 is a composite sapropel of 4 distinct dark layers separated by light-colored sediment with
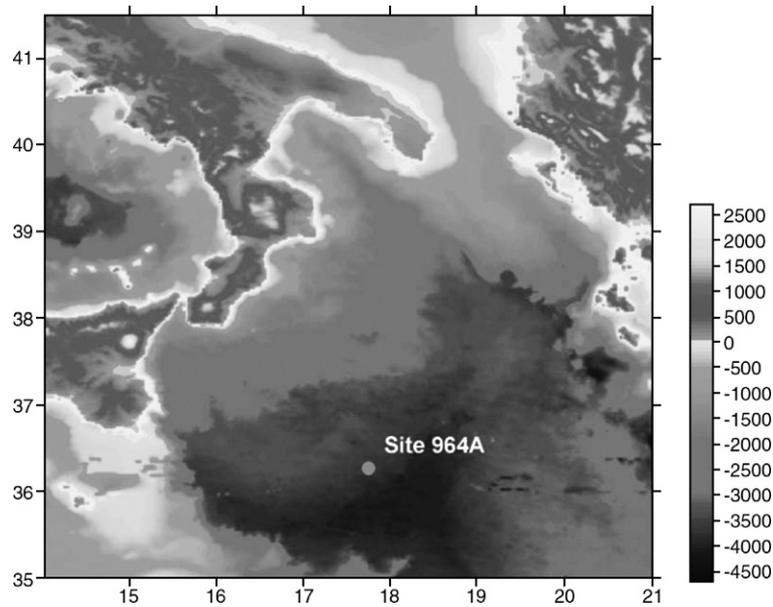
Fig. 1. Location map for the studied core, ODP Leg 160, Site 964 Hole A.

a total thickness of 58 cm. The calculated age at the top of this sapropel is approximately 172 kyr.

– Pliocene sapropels: sampled intervals are generally thinner, darker in color, with a higher TOC content, some displaying faint lamination. S49, defined as thin-bedded sapropels and thus less than 5 cm thick, is dated 2.828 Ma, corresponding to insolation cycle 272. Sapropel S52 (not described in the ODP Initial Reports) is defined by Emeis et al. (2000a), and was deposited during insolation cycle 282, with a calibrated age of 2.943 Ma. S53 (according to Emeis et al., 2000a) is a composite sapropel, with 2 distinct intervals of TOC enrichment. The age for this sapropel is 2.965 Ma, during insolation cycle 284. Finally, S55, described in ODP Initial Report as a sapropel, was analyzed, but it appeared to be a ghost sapropel, in agreement with Emeis et al. (2000a).

These ages are referred to the sapropels's correlative 3 kyrs lagged insolation maxima, calibrated on the sapropel mid-point, as explained on Emeis et al. (2000b), and Lourens (2004) (see also Larrasoaña et al., 2003).

The samples taken from these intervals were dried and ground in an agate mortar, homogenized and prepared for geochemical and mineralogical analyses. Representative sample portions were used to determine bulk and clay mineralogy, TOC and N contents as well as major and trace element concentrations. Sr isotopic composition and detailed mineralogical analyses by high-resolution electron microscopy (transmission and scanning) were also performed on selected samples.

TOC and N measurements were made using a Perkin–Elmer Elemental analyzer at the Stable Isotope Laboratory (Stanford University). Samples were acidified with H_2SO_3 to eliminate inorganic carbon. Major elements (Al, Ca, Mg, Fe, Mn, K) were determined by atomic absorption spectrometry at the Analytical Facilities of the University of Granada. Trace elements were measured with an ICP-MS Perkin–Elmer Sciex Elan 5000 spectrometer (CIC; Analytical Facilities of the University of Granada), using Re and Rh as internal standards. These analyses were carried out after HNO_3 and HF digestion. 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). Strontium isotope analyses were done in the CIC, University of Granada, Sr was separated using ion exchange columns (BIORAD AG 50 W8 200–400 resins). Isotopic composition was then determined with a Finnigan MAT 262, using WSE as standard, with an estimated precision better than 0.0026% and reproducibility higher than 0.0007%. Bulk and clay mineralogy were determined using a Phillips PW1710 difractometer in the Mineralogy Department, University of Granada, and resulting difractograms were interpreted using XPowder software (Martin-Ramos, 2004). Samples were prepared following the recommendations by Kirsch (1991). In order to determine the chemical composition of clay minerals, selected samples were suspended in ethanol, the finest fraction was recovered onto a gold grid, and particles were analyzed under high-resolution

TEM (STEM PHILIPS CM20, CIC, University of Granada). For the morphological description of barite, selected samples were observed under FESEM (LEO Gemini 1530, CIC, University of Granada) using backscattered and secondary electron images. Mineral phase composition was determined by an X-Ray dispersion microanalysis coupled to the device.

3. Paleoenvironmental conditions and detrital input

The paleoceanographic conditions leading to sapropel deposition have been a subject of debate for decades. There is now a consensus that the climate setting, humidity conditions and subsequent changes in river runoff at the time of sapropel deposition were major factors in sapropel formation. (Rossignol-Strick, 1985; Rohling and Hilgen, 1991; Lourens et al., 1992; Aksu et al., 1995; Nijenhuis and de Lange, 2000; Casford et al., 2003) Different proxies have been used to reconstruct paleoenvironments and climate in Mediterranean regions. Mineral compositions, as well as the concentrations and ratios of detrital elements, have suggested that precipitation and runoff increased during those periods (e.g., Krom et al., 1999; Wehausen and Brumsack, 1999; Warning and Brumsack, 2000; Calvert and Fontugne, 2001; Bottcher et al., 2003). In order to validate such a scenario over the Pliocene–Holocene interval, fluctuations in kaolinite and palygorskite content, along with La/Lu, Zr/Al and Sr^{87}/Sr^{86} ratios, have been used to reconstruct fluvial and aeolian input and runoff during the Pliocene and the Quaternary.

Both the Zr/Al and La/Lu ratios have been extensively used as proxies for aeolian input in the Mediterranean area (Gallet et al., 1998; Wehausen and Brumsack, 1999; Martínez-Ruiz et al., 2000). The La/Lu ratio is used to discriminate the input from the African margin, (Hamroush and Stanley, 1990) and displays higher values when the main source of sediments is from the African craton. This ratio averages around 120

during the deposition of most of the "normal pelagic sediments", but decreases to 115 or less within sapropel layers and can be as low as 75 in some Pliocene sapropels. Zr/Al ratios range from 1.2 to 1.8, with typically lower values within sapropels (see Table 1), indicating diminished aeolian input from the African tropical region, (e.g., Rossignol-Strick, 1985; Rohling and Hilgen, 1991) and a general increase towards the top of the TOC-enriched sediment layer. This decrease in aeolian dust is due to an increase in monsoon activity, that produces higher humidity, and thus, more abundant soil-derived detrital material and riverine denudation. During drier periods, environments similar to the present day Sahara desert develop, and sediment can be more easily mobilized and transported by aeolian processes during windstorms. Results from both proxies indicate wetter conditions during sapropel deposition in this particular area. Average values reported for these proxies are shown in Table 1. We observed that the highest contrasts in Zr/Al between sapropel and "normal marine" layers are found in the Pliocene, when the lowest La/Lu ratio is also detected. This could mean that the most intense monsoon activity (according to the above-mentioned authors) is reached during this period. The striking differences in these ratios in the Quaternary also point to a noticeable variability for the humidity (from La/Lu ratio of 80 to 148) and aeolian input in the basin (Zr/Al ranges from 0.8 to 2.7). The Sr^{87}/Sr^{86} ratio is lower within the sapropel as compared to non-sapropel layers (see Table 1). Krom et al. (1999); (see also Frumkin and Stein, 2003), determined the different isotopic ratios found in the material transported by Saharan winds and by the Nile river, and concluded that lower Sr^{87}/Sr^{86} originates from the riverine detrital material. Thus, the interpretation of lower aeolian input is also supported by Sr-isotope data. Aeolian input fluctuations are also indicated by variations in the mineralogical composition. Fibrous minerals, as well as high kaolinite content, have been associated with

Table 1
Average values of sedimentary, detrital, redox and palaeoproductivity proxies during different time periods

| Age		Ba/Al (10^{-4})	Zr/Al (10^{-4})	La/Lu	$U_{authigenic}$	V/Cr	V/Sc	Sr^{87}/Sr^{86}
Holocene	Maximum	31.1	2.2	132.9	8.1	3.2	24.6	0.710975
	Average	20.7	1.2	118.5	1.8	1.7	11.3	
	Minimum	7.7	0.9	105.2	−0.9	1.2	7.5	0.709459
Pleistocene	Maximum	49.8	2.7	148.1	35.5	5.1	49.6	
	Average	24.7	1.4	120.6	4.9	2.0	13.5	
	Minimum	10.4	0.8	80.3	−0.2	1.3	7.0	
Pliocene	Maximum	86.5	3.5	117.2	54.2	12.2	163.7	
	Average	26.7	1.5	92.0	5.6	3.3	34.3	
	Minimum	16.2	1.0	63.7	−0.6	1.3	6.3	

Complete data table is available online.
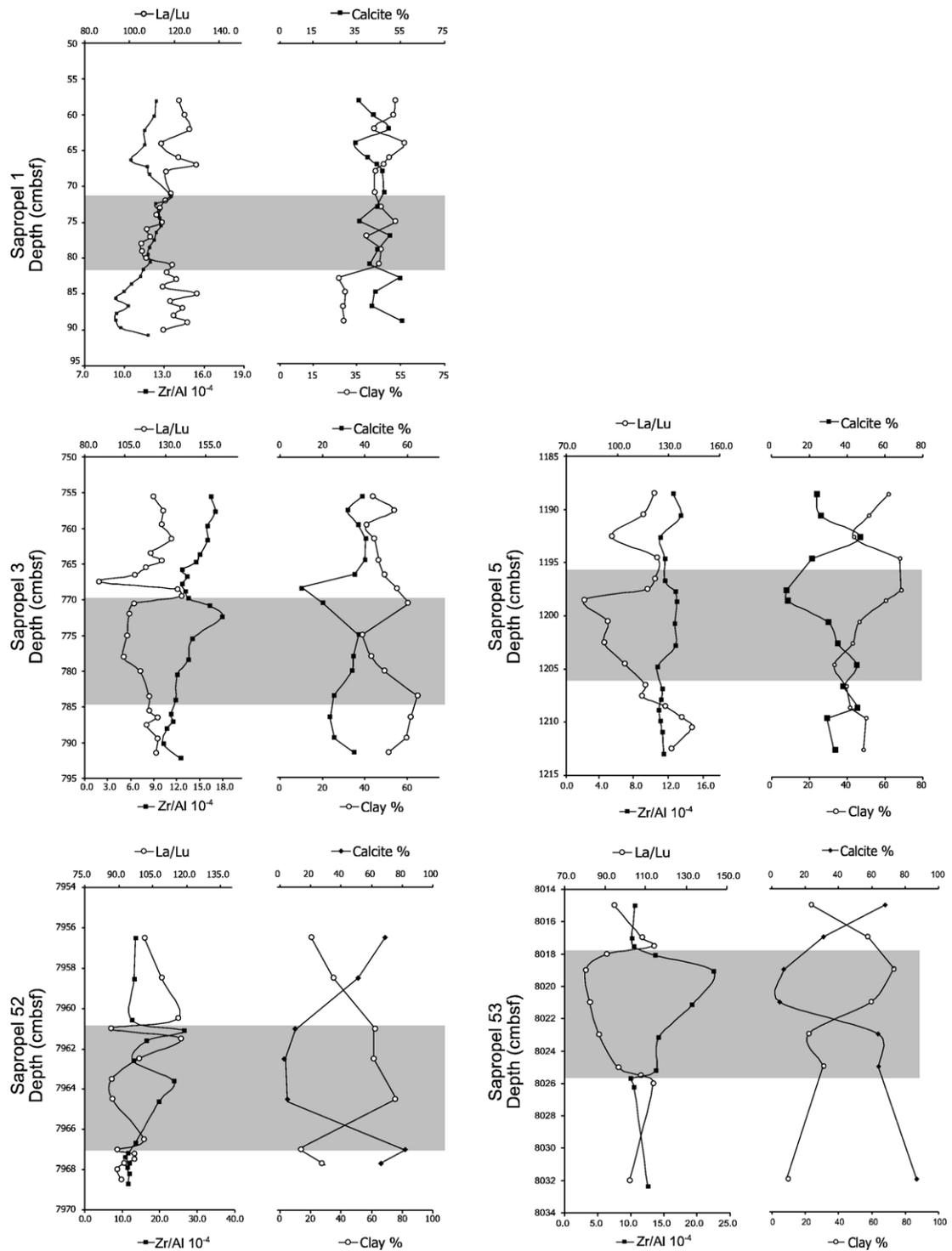
Fig. 2. Trends of the mineralogical and geochemical proxies applied to the determination of the sedimentary regime and climatic implications at the time of deposition. Zr/Al ratio shows variation of aeolian input. La/Lu indicates variations in detrital input from the African craton. Shaded area corresponds to the sapropel.

aeolian input in the Mediterranean area (e.g., Diester-Haass et al., 1998), while riverine origin is indicated by increased smectite and chlorite incoming mainly from the southern and northern continents, respectively (e.g., Maldonado and Stanley, 1981; Rossignol-Strick, 1985; Hamroush and Stanley, 1990; Krom et al., 1999; Martinez-Ruiz et al., 2003). Geochemically, at Site 964, this is reflected by an increase in K/Al and Mg/Al, as interpreted by Nijenhuis et al. (2001) or Wehausen and Brumsack (2000). Both the bulk sediment and the clay fraction present higher concentrations of smectite, relative to illite and lower kaolinite content in the TOC-enriched sections (see Fig. 2). The decrease in carbonate content cannot be totally accounted for calcite dissolution, as discussed by Thomson et al. (2004); (see also Crudeli et al., 2004; Meyers and Arnaboldi, 2005; Crudeli et al., 2006). Thus, it must be interpreted as the consequence of a global palaeoceanographic change in the basin. Furthermore, fibrous minerals (i.e., palygorskite and sepiolite, recognized and described using high-resolution TEM techniques) mostly appear in "normal" pelagic sediments, and are virtually absent in sapropel layers. All of the above-mentioned observations reaffirm the idea that sapropels were deposited during a period of increased rainfall and riverine fluxes. This deduction becomes more robust when we compare our results to similar studies carried out in other Mediterranean areas, such as Eratosthenes Seamount or Mediterranean Ridge, where Wehausen and Brumsack (1999, 2000) concluded that sapropel formation depends on fluviatile input, based on Ti, Fe, Mg or K to Al ratio evolution.

4. Export production fluxes during sapropel deposition

The interpretation of TOC enrichments in marine sediments raised the question of their origin in terms of enhanced export production or preservation, and put marine productivity at the center of a long debate, (e.g., Dehairs et al., 1987; Pedersen and Calvert, 1990; Calvert and Pedersen, 1993; Martínez-Ruiz et al., 2000; Filippelli et al., 2003; Pichevin et al., 2004; Meyers and Bernasconi, 2005). Some consensus exists at present regarding the potential combination of both factors to form these TOC-rich sediments. However, productivity fluctuations through time questioned the relative importance of preservation vs. export production. To further investigate productivity changes with time during sapropel deposition, marine barite and Ba/Al ratios have been used to establish export production fluxes (e.g., Thomson et al., 1995; Martínez-Ruiz et al., 2000; Rutten and de Lange, 2002; Martinez-Ruiz et al.,

2003). The use of Ba excess over crustal abundance as a productivity proxy is based on the correlation between the fluxes of excess Ba and organic matter in sinking particulate matter (e.g., Bishop, 1988; Dymond et al., 1992; Dymond and Collier, 1996; Paytan and Kastner, 1996; Eagle et al., 2003). This association is also supported by the observations that Ba-rich sediments usually underlie areas of high biologically productive and surface sediment barite accumulation rates correlate with upper water column productivity (Dehairs et al., 1987; Paytan, 1997; McManus et al., 1998, 1999; Eagle et al., 2003). The use of this proxy also assumes that Ba excess is related to barite crystals that originated in the water column (Paytan et al., 2002). Although Ba excess must be interpreted with care and does not allow for quantitative estimates of export production (e.g., McManus et al., 1994, 1998; Averyt and Paytan, 2004), successful paleoproductivity reconstructions using Ba excess in marine Pliocene and Pleistocene sediments from Mediterranean basins have demonstrated that widespread deposition of sapropels resulted from enhanced export production fluxes (e.g., Thomson et al., 1999; Martínez-Ruiz et al., 2000; Nijenhuis and de Lange, 2000; Weldeab et al., 2003b; Paytan et al., 2004). The reliability of this proxy to confirm enhanced productivity is additionally supported by the S isotope composition of barite crystals separated from sapropel intervals. The S isotopic composition of the sapropel barite samples is consistent with the expected water column values. This indicates that the origin of these crystals is in the water column and, consequently, that they are related to increased carbon export (Paytan et al., 2004). Barite crystals in sapropels also show sizes and morphologies similar to those described in the water column (Dehairs et al., 1987) or collected in sediments
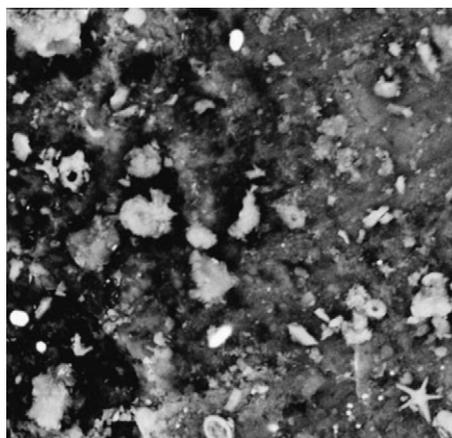

Fig. 3. SEM backscattered electron image of a sediment sample from sapropel S54. Light white crystals are marine barite.
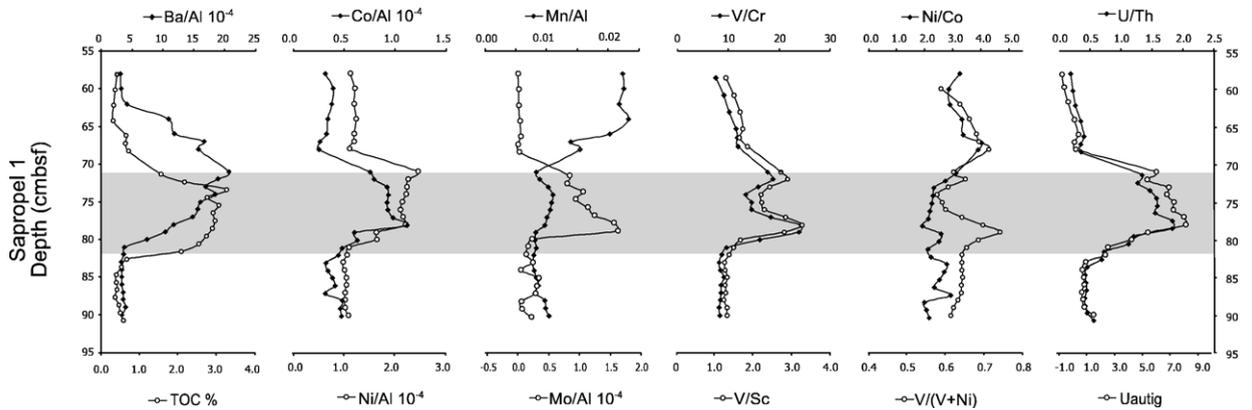
Fig. 4. Geochemical proxies indicating productivity (Ba/Al×10^{-4}), redox-sensitive elements (Ni/Al, Mo/Al, Co/Al), diagenetic remobilization of Mn and redox conditions (V/Cr, V/Sc, V/(V+Ni), U/Th and U$_{authigenic}$) during deposition, compared to the TOC (%) content of the sediments, for Holocene sapropel S1. Shaded area corresponds to the sapropel.

underlying areas of increased productivity (Paytan et al., 1993; Ginsele and Dahmke, 1994; Paytan, 1997). (See Fig. 3)

Ba excess shows two distinct patterns over the time span represented by the studied samples. In Quaternary sapropels, the maximum productivity as indicated by

Ba/Al ratio expands over the top of the TOC-enriched level. The offset between high organic carbon content and high Ba (thus productivity) is due to post-depositional oxidation of organic matter. The much greater stability of Ba against diagenetic remobilization makes Ba/Al ratio a more robust indicator for marine
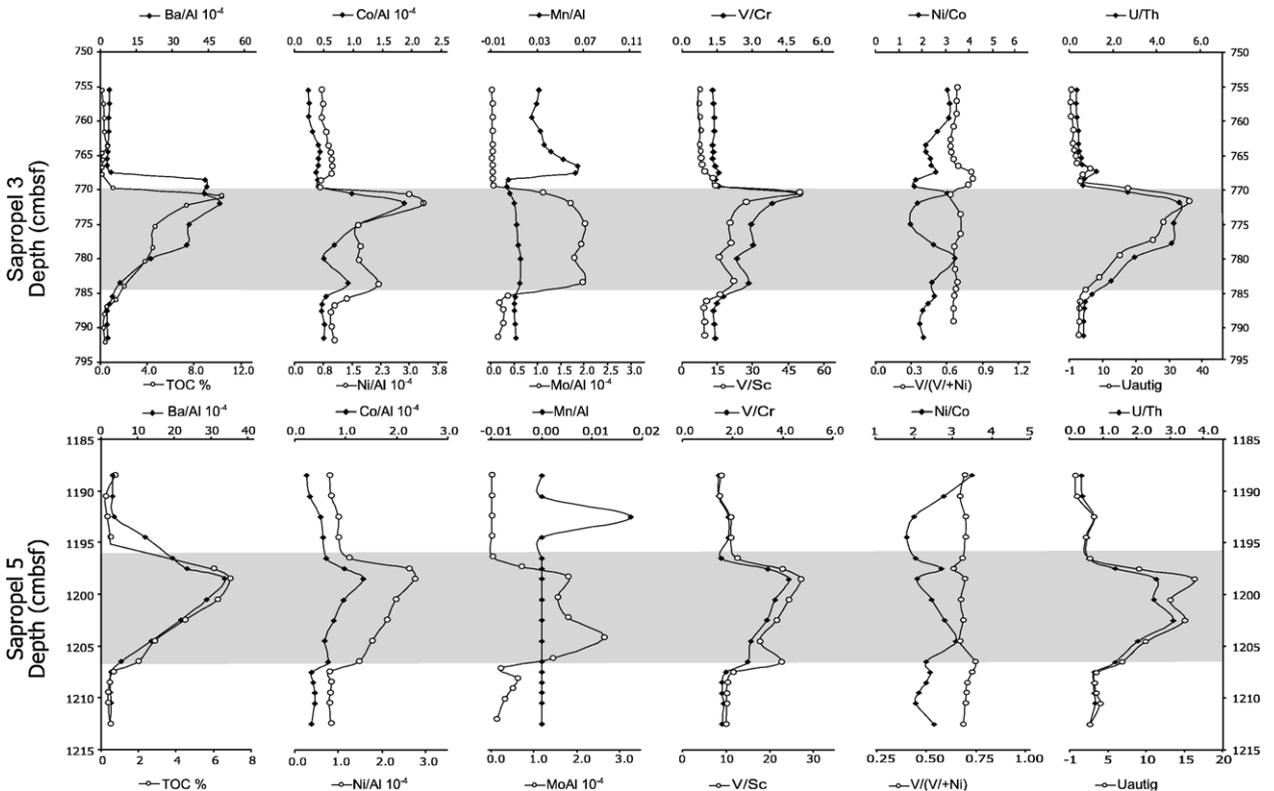

Fig. 5. Geochemical proxies indicating productivity (Ba/Al×10^{-4}), redox-sensitive elements (Ni/Al, Mo/Al, Co/Al), diagenetic remobilization of Mn and redox conditions (V/Cr, V/Sc, V/(V+Ni), U/Th and U$_{authigenic}$) during deposition, compared to the TOC content of the sediments, for Pleistocene sapropel S3 and S5. Shaded area corresponds to the sapropel.

palaeoproductivity than TOC. (e.g. Thomson et al., 1999; Martínez-Ruiz et al., 2000, 2003; Nilsen et al., 2003; Powell et al., 2003). The onset of the formation of the sapropel approximately coincides with the first increase in Ba excess. In contrast, in Pliocene sapropels, which have much higher Ba contents, the Ba enrichments are confined to the present day detectable black layer (Figs. 4 and 6). This reveals that Quaternary sapropel levels were more extensively altered after deposition, as further shown by the penetration of oxidation fronts marked by Mn and Fe peaks (e.g., van Santvoort et al., 1996; Thomson et al., 1999).

Although the Ba/Al ratio is not quantifiable, there are striking differences between values from Holocene to Pliocene, as we see in Table 1 or Figs. 4–6. During the Early Pliocene, this ratio reaches values of up to 4 times the maximum for the Holocene. TOC and TOC-Mass Accumulation Rates (TOC-MAS) values are equally higher in the Early Pliocene, when compared to sapropel S1 (see Fig. 7). However, it is during the Pleistocene that sapropel levels show the highest Ba and C_{org} MAR values. It may thus be assumed that the increase in export production during sapropel deposition was in fact much greater during the Early Pliocene and Late Pleistocene. Equally high values are described in the literature (e.g., Emeis et al., 1996; Nijenhuis and de Lange, 2000; Struck et al., 2001; Meyers and Arnaboldi, 2005; Arnaboldi and Meyers, 2006) for similar levels on different sites within the basin. After insolation cycle 12 the system suffered an abrupt change, and consequently S1 shows a relatively minor productivity increase, (e.g., Martínez-Ruiz et al., 2000; Murat and Got, 2000). This might be related to a particularly high nutrient input associated to extreme humidity in the weather system of the region, as we have detected for the same periods, and the dramatic climatic change that characterizes the Holocene. The relationship between paleoproductivity and TOC content in the sediment seems evident, although other factors, such as bottom water oxygenation, will be discussed below.

5. Geochemical proxies for oxygen conditions

Increased preservation of the organic carbon due to low oxygen conditions has been used for decades as the scenario most appropriate for sapropel origin. When
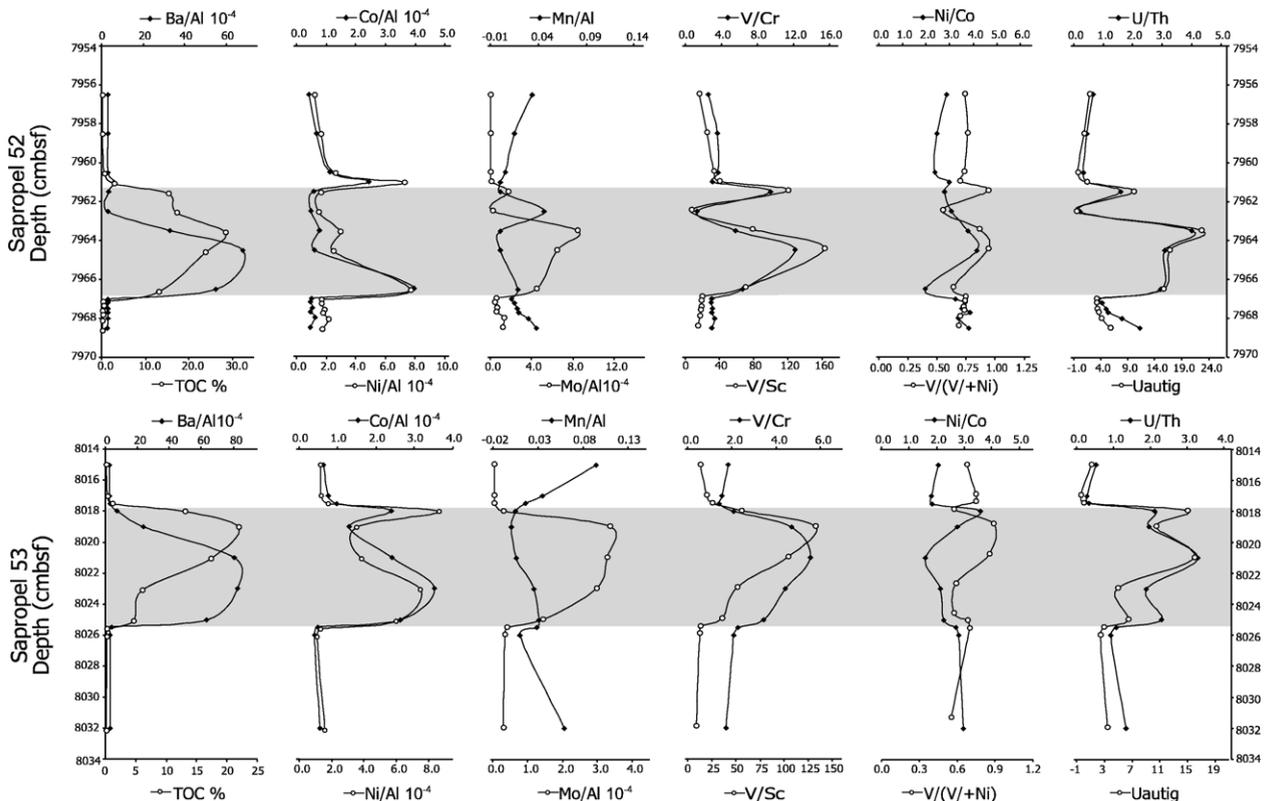

Fig. 6. Geochemical proxies indicating productivity (Ba/Al×10^{-4}), redox-sensitive elements (Ni/Al, Mo/Al, Co/Al), diagenetic remobilization of Mn and redox conditions (V/Cr, V/Sc, V/(V+Ni), U/Th and U$_{authigenic}$) during deposition, compared to the TOC content of the sediments, for Pliocene sapropel S52 and S53. Shaded area corresponds to the sapropel.
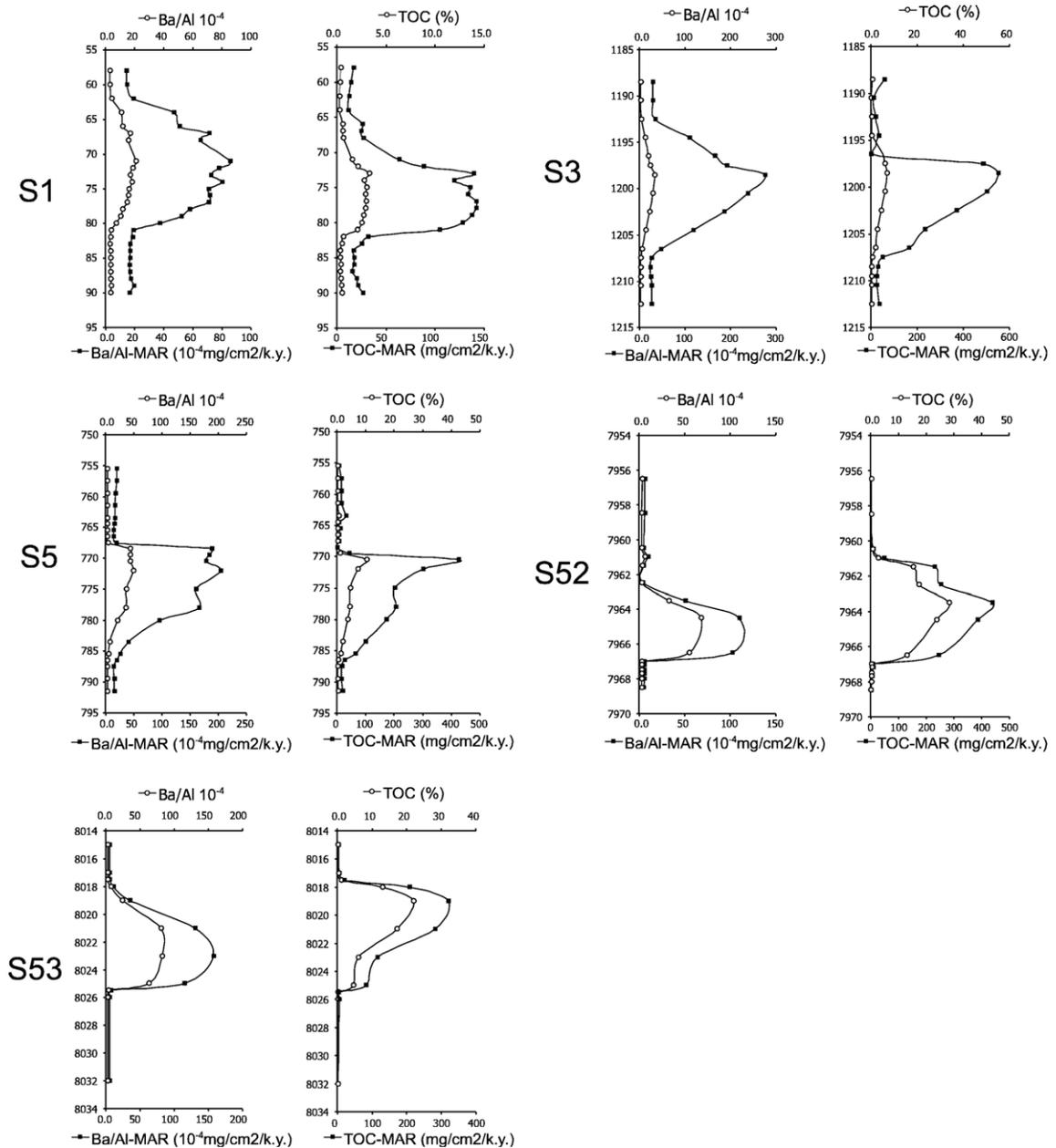
Fig. 7. TOC (mg/cm^2/k.y.) and Ba/Al (10^{-4} mg/cm^2/k.y.) Mass Accumulation Rates for selected sapropels S1, S3, S5, S52 and S53.

Calvert et al. (1992, 1996) proposed the alternative productivity hypothesis, the oxygen conditions at the time of sapropel deposition were further investigated on the basis of different redox proxies. A wide variety of geochemical indices and element/Al ratios have been used as indicators of the redox conditions. Those proxies include Mn, U, V, Ni, Cr and Mo contents (e.g., Calvert and Pedersen, 1993; Jones and Manning, 1994; Calvert et al., 1996; Holser, 1997; Nijenhuis et al., 1999; Nijenhuis and de Lange, 2000; Powell et al., 2003;

Ivanochko and Pedersen, 2004), as well as other indices, such as U$_{authigenic}$, U/Th, Ni/Co, V/Cr, V/(V + Ni) and V/Sc (e.g., Wignall and Myers, 1988; Calvert and Pedersen, 1993; Jones and Manning, 1994; Schovsbo, 2001), as summarized in Table 2.

An enrichment in redox sensitive elements is observed in all of the sampled sapropels. However, a number of clear differences appear when comparing Pliocene and Quaternary sapropels. The high concentrations of trace elements, such as V, Cr, U and Mo, are far

Table 2
Summary of conditions defined by selected redox proxies, (see text for references)

Proxy	Oxic	Disoxia	Anoxia
$U_{authigenic}$			>12
U/Th		0.75 to 1.25	>1.25
Ni/Co		5 to 7	>7
V/Cr		2.0 to 4.25	>4.25
V/(V+Ni)			>0.84
V/Sc	<9.1		

more noticeable in Pliocene levels than in younger equivalents and thus follow a trend similar to that of Ba/Al. Most redox proxies present very similar fluctuation profiles, showing increased values within the TOC-enriched sediments. The exceptions are the (V/V+Ni) and Ni/Co ratios, whose trends are unclear.

The youngest sapropel, S1, summarized in Fig. 4, presents a clear enrichment in Mo, Cr or Ni. This enrichment suggests a low oxygen concentration within the sediment, but is not diagnostic of anoxia in the water column. Of all the examined proxies, only the U/Th ratio is indicative of oxygen-depleted bottom waters (i.e., U/Th > 1.25). The other selected proxies do not imply an anoxic water column during S1 sapropel formation, thus suggesting that only dysoxic conditions were reached. It is worthy of note that there is no evidence of a lack of oxygen at the onset of this sapropel (bottom of the layer).

U-based proxies suggest that the deposition conditions of sapropel S3 were slightly more anoxic than S1 (see Fig. 5). The U/Th ratio points to an intermediate dysoxic environment during deposition of the central part of the sapropel, and oxic bottom waters above and below it. However, contradictory results are obtained when using other proxies, such as Ni/Co or V/Sc. Whereas Ni/Co values are indicative of continuous oxygen availability during S3 formation, V/Sc ratios indicate reducing conditions.

Results from sapropel S4, which is a composite sapropel with alternating laminae of less than 1% TOC and as high as 5%, also indicate similar discrepancies among different proxies. $U_{authigenic}$ and V/Cr suggest a constant oxic environment, whereas V/Sc indicates the opposite scenario. V/(V+Ni), U/Th ratio and Ni/Co values point to reduced oxygenation, (full record is available online). The depositional environment portrayed by the redox proxies is mostly oxygenated, partly oxygen-impoverished at times. Increasing anoxia corresponds to higher organic carbon content.

Oxic conditions also prevailed during sapropel S5 deposition (see Fig. 5) according to V/(V+Ni) and Ni/

Co records. Again, $U_{authigenic}$ and V/Cr display very similar behavior, suggesting normal oxygen availability on the top and bottom of the layer, and dysoxic average conditions, at points anoxic towards the middle. U/Th and V/Sc also correlate relatively well, but V/Sc is suggestive of mostly anoxic conditions, even during the onset of sapropel formation.

For sapropel S6, all proxies except the U/Th ratio indicate oxic to dysoxic conditions. U/Th points to complete anoxia during most of the deposition of this bed. In summary, most of these oxygen proxies suggest that Quaternary sapropels were deposited in generally oxygenated environments with only short-term restricted oxygenation, while only U/Th ratios seem to suggest very low oxygenation at certain times and intervals.

The conditions evidenced by the same set of redox proxies in Pliocene sapropels are notably different. Thus, in sapropel S49 oxygenation is clearly lower than in the Quaternary equivalents. It is worth noting that right beneath the high TOC bed, a layer of virtually no oxygenation is defined by most of the proxies used and no organic matter is preserved in the sediment at this depth. Some discrepancies also arise when using different proxies: V-based proxies indicate anoxia, the U/Th ratio mainly suggests a dysoxic environment, whereas Ni/Co and $U_{authigenic}$ values oscillate within the oxic range.

The next level within the Pliocene interval sampled downcore, S52, presents the highest organic carbon contents analyzed for this work (28% TOC, see Fig. 6). This maximum coincides with high Ba/Al ratios and all redox proxies indicating an anoxic environment, with the exception of the Ni/Co ratio, which increases but does not reach anoxic values. $U_{authigenic}$, V/(V+Ni) and V/Cr support reduced oxygen availability at the base of the sapropel layer, while oxygen would be completely consumed during the deposition of the sapropel. Of particular interest is the sudden decrease in the values of all redox proxies coinciding with a maximum in Mn.

Redox proxies indicate similar depositional conditions for sapropel S53. The onset of organic matter accumulation occurs under oxic to dysoxic conditions, and only the V/Sc ratio indicates anoxia at that level (see Fig. 6). Towards the top of the bed, all proxy values except that of Ni/Co indicates anoxia. The V/Sc values suggest that the absence of oxygen expand several centimeters over the top of the sapropel. The increase in productivity suggested by Ba/Al ends slightly before the anoxic conditions, as indicated by the redox proxies.

For the oldest sampled sapropel, S54, results are again similar: an oxic to dysoxic onset, evolving to anoxia during the later stages of formation. V/Sc situates

the whole sapropel in anoxic bottom waters. Other proxies ($U_{authigenic}$, V/(V + Ni), U/Th, and V/Cr) clearly point to increasing anoxia during the deposition interval and no available oxygen at the top of the layer. In general, Pliocene sapropels were deposited under low oxygenation conditions or even complete anoxia, but co-occurring increased productivity at these time intervals is also supported by Ba proxies.

In summary, Quaternary sapropels show only partial anoxic or dysoxic conditions, whereas Pliocene ones fall into more complete anoxic conditions. This is consistent with the higher export production during Pliocene sapropel deposition.

6. Evaluation of redox proxies

Comparison of different proxies commonly used to establish oxygen conditions (e.g., Jones and Manning, 1994; Powell et al., 2003), has also enabled the evaluation and validation of such proxies. Certain discrepancies are evident between the various proxies with respect to the implied level of anoxia. This makes it necessary to corroborate which proxies are reliable, considering both synsedimentary and diagenetic processes that affect the distribution of redox sensitive elements (McManus et al., 2005).

Most of the selected proxies follow a coherent evolution except Ni/Co, and to a lesser extent V/(V + Ni). The rest of the proxies display highly similar profiles, although very little agreement can be appreciated when they are translated into quantitative estimates for the degree of anoxia reached during sapropel deposition. This suggests that these proxies may be used qualitatively within the same location. However, quantitative determinations are difficult. As mentioned above, the Ni/Co ratio displays a random-like pattern, always hovering in the oxic condition field. Although no evidence of substantial sulfate reduction is found in these sapropels (Paytan et al., 2004), the evidence for reduced oxygen availability at least for the Pliocene sapropels is obvious (e.g., Passier et al., 1996, 1999). The Ni/Co ratio does not reflect these conditions. Since Ni and Co are very sensitive to diagenetic remobilization, we suggest that Ni/Co is not a very reliable proxy for determining paleo-redox conditions in the paleoceanographic context of sapropel deposition.

The rest of the selected proxies can be divided into two groups: one defines clear limits among oxic, dysoxic and anoxic fields; the other defines a limit between presence and absence of oxygen in seawater (see Table 2). U/Th and V/Cr ratios correspond to the first group. Indeed, these two proxies generally coincide in both their tendencies and the range of oxygenation defined by their values. The second group of proxies includes $U_{authigenic}$, V/(V + Ni), and V/Sc and does not define clear limits but rather general conditions. All three show very similar profiles, although V/Sc generally reaches high values, which suggest more extreme conditions compared to the other two. As proposed by Powell et al. (2003), the V/Sc ratio is not so well delimited; a reevaluation and new quantification of the behaviour of this elemental ratio should be considered.

Our data suggest that a detailed and global comparison among oxygen proxies would be necessary to obtain a more accurate definition of the fields of anoxia vs. oxic conditions. It is also worth noting that very high concentrations of organic matter in the sediment are strongly associated with extreme values of certain element ratios, such as V/Sc or U/Th. This supports the link among TOC contents, redox conditions and the concentrations of certain elements. This could be the consequence of a direct association (adsorption etc.) with organic matter. In fact, uranium may complex with dissolved fulvic acid in hemipelagic sediments, as has been explained by Nagao and Nakashima (1992), and the relationship of U with organic matter in the sediment has been described in different paleoceanographic studies (e.g., Klinkhammer and Palmer, 1991; Baturin, 2002; Kochenov and Baturin, 2002). If we compare TOC-MAR and Ba/Al-MAR (see Fig. 7), for Pleistocene and for Pliocene sapropels, we observe that it was actually higher during the Pleistocene, although TOC and redox proxies values are lower. This could mean that Pliocene anoxia (or low dissolved oxygen concentration) was in fact a main controlling factor for sapropel formation, and that the threshold for redox proxy sensitivity should be corrected to MAR.

7. Preservation of the geochemical record

It is known that post-depositional processes redistributed redox sensitive elements and thus altered the signal recorded at the time of deposition. This alteration provides information about early diagenesis in the sediment, but may also help to define sediment ventilation conditions during and immediately after deposition (e.g., Rutten et al., 1999; Gallego-Torres et al., 2004; Morford et al., 2005). Mn is frequently used as an indicator of oxidation of the sediment–water interface, since it precipitates as oxy-hydroxides when oxygen is available and constitutes a clear mark of the oxidation front (e.g., Thomson et al., 1995, 1999; Powell et al., 2003). Other redox sensitive elements, such as Ni and Co are also redistributed when oxygen levels in pore

waters are low enough to reduce them. Once in solution, these elements may undergo diffusive losses through the sediment column until oxic conditions are encountered again. In Quaternary sapropels, Mn is a key element used to define the oxidation front that consumed the organic matter originally present in the sediment (e.g., Thomson et al., 1995, 1999). The Holocene sapropel shows a clear and pronounced oxidation front evidenced by a Mn peak which marks the thickness of the oxidized sapropel (e.g., Thomson et al., 1999; Martínez-Ruiz et al., 2000; Zonneveld et al., 2001; Nilsen et al., 2003; Powell et al., 2003). Also used as redox proxies, V, Cr, Mo and Co may be re-mobilized and re-precipitated with Mn oxy-hydroxides within the oxidation front, thus generating a double peak in such elements. Similar diffusion processes are expected in Pleistocene sapropels. Indeed, the oxidation front penetrates into the high productivity level, as shown by the location of the Mn peak (see Figs. 4 and 5). In Pliocene sapropels, Ni, Co, Cr and Mo show a similar distribution to that of Quaternary equivalents. In sapropel S52, as described above, redox proxies undergo a sudden decrease coinciding with the Mn maximum, thus suggesting an oxic event, although no decrease in TOC is observed. In general, during the Pliocene there are no indications of oxidation fronts that would suggest the consumption of the upper part of the sapropels, as shown in Fig. 6.

8. Forcing mechanisms for sapropel deposition: the roles of productivity and anoxia

By comparing all of the reported sets of proxies, we can discuss the triggering mechanism for the enhanced accumulation of organic carbon in these sediments. As mentioned above, sapropels appear to be linked to cyclical variations in the climate, (e.g., Hilgen, 1991), as corroborated by detrital input. The ultimate reason for the formation of organic-enriched levels would be the effect of this climate change on the basin. With this scope in mind, we have evaluated the relations among the productivity and redox proxies, especially around the limits of the sapropel. In all the studied sections the relation between the paleoproductivity and redox proxies is clearly visible. Sampled sapropels frequently present a maximum in the value of low oxygenation proxies, such as $U_{authigenic}$, U/Th, or V/Cr, and coincide with Ba excess. This is particularly clear in Pliocene sapropels, although an offset can be seen between the two signals in certain cases, in some of which productivity typically leads to anoxia. This fact point to an anoxic environment induced by total oxygen consumption, the latter resulting from a massive input of organic matter.

If we focus on the conditions represented by the top and bottom limits of the layers studied, it can be observed that the base of the TOC-enriched level coincides with the increase in productivity in all of the sampled sapropels. As for the top of the sapropels, two distinct patterns are visible. The sapropels deposited during the Holocene and most of the Pleistocene present a peak in Ba/Al that expands over the top of the high TOC layer. Combined with the Mn peak, this provides evidence for a thicker original sapropel, later oxidized in the uppermost part. On the other hand, Ba enrichment in Pliocene layers is constrained to the sapropels themselves, and in some cases TOC-enriched sediments expand after the Ba (productivity) maximum. No burn-down front is detectable.

By analyzing the redox proxies in a similar way, no clear anoxic conditions are observed at the base of the sapropels, but rather a progressive depletion of oxygen. Since maximum values of redox proxies are reached mostly coinciding with maximum productivity or with a slight offset, the range of values indicating reduced oxygen concentration (or absence) are constrained to the sapropel layer in most cases, although these conditions may sometimes extend on the top of the sapropel, mirroring the Ba/Al ratio, as seen in sapropel S1 (Fig. 4).

It can thus be inferred that productivity, which is induced by climate cycles, was the main triggering factor controlling sapropel formation. In most cases, this increase in productivity could account for oxygen depletion in bottom waters, due to exceptionally high oxygen consumption, as evidenced by "burn-down" oxidation fronts in Quaternary sapropels. In Pliocene layers, absent or limited oxygen is also linked to very high productivity, although these conditions prevail after productivity returns to normal values, thus implying either lags in the response of deep water oxygen or reduced ventilation of bottom waters.

9. Conclusions

The integration of multi-proxy data makes it possible to reach a set of conclusions regarding sapropel deposition in the eastern Mediterranean within the Pliocene–Holocene time interval. Ba excess derived from marine barite supports the argument that a significant increase in export productivity is the main triggering mechanism for sapropel deposition. As regards oxygen conditions, redox proxies show that Quaternary sapropels were deposited under oxic to dysoxic bottom water conditions, while Pliocene levels display lower concentrations of oxygen, reaching anoxic environments. Post-depositional alteration mostly affected Quaternary sapropels and obliterated the TOC signal in the sediment. Thus,

TOC values are not a reliable indicator for productivity variation, since organic matter is frequently oxidized at a very high rate. As geochemical redox proxies indicative of low oxygen correlate with increased marine productivity, low oxygen conditions may be a consequence of high organic matter fluxes and oxygen consumption at depth, instead of the triggering mechanism for an increased preservation due to stagnation. The use of different oxygen proxies evidenced that the results provided by U/Th, $U_{authigenic}$, V/Cr and V/(V+Ni) are relatively consistent. The V/Sc ratio displays very similar tendencies, although a re-calibration of the meaning of the values will be required in order for this proxy to be consistent with the others. The Ni/Co ratio has not been proven to be useful or reliable within the analyzed paleoceanographic setting.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.palaeo.2006.10.008.

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