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# A comparative study of the geochemical and mineralogical characteristics of the S1 sapropel in the western and eastern Mediterranean

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## Abstract

Sapropels, which are dark sediments with organic carbon content  $>2$  wt%, are common in eastern Mediterranean sections. In some western Mediterranean sites, however, even organic-rich layers (ORLs) are not detected in sections spanning the S1 sapropel deposition event (9500–6000 yr BP). We compare geochemical and mineralogical compositions in cores from the eastern (Ionian Sea) and western (Alboran Sea and South Balearic basin) Mediterranean basins to determine the causes for the lack of ORL deposition during S1 in the western basin. In particular, we investigate whether the differences between the eastern and western sites are due to preservation or productivity variations. Using mineralogical and geochemical data – mineral abundances, major and trace element concentrations and ratios, organic carbon content, Ba and barite accumulations, and sea surface temperature data – along with information about the sedimentary regimes, sedimentation rates, and water depths at these sites, we conclude that the lack of S1 sapropel formation in the western Mediterranean is due to lower export production fluxes in this basin. Accordingly, the response to regional climate changes through time must be different in the eastern and western Mediterranean. Identifying the exact causes for these differences may lead to an understanding of the variations in export production rates in response to basin-wide versus regional climate changes in the Mediterranean region.

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**Keywords:** eastern Mediterranean; western Mediterranean; sapropel S1; productivity; climate

## 1. Introduction

Cyclic deposits of organic-rich layers, with total organic carbon (TOC)  $>2$  wt%, called ‘sapropels’, have long been identified in eastern Medi-

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terranean uplifted and cored marine sections (e.g. Kidd et al., 1978; Rohling and Hilgen, 1991; Rohling, 1994; Thomson et al., 1995, 1999; Nijenhuis et al., 1998; Emeis and Sakamoto, 1998; Wehausen and Brumsack, 1998; Cramp and O'Sullivan, 1999; Emeis et al., 2000a; Nijenhuis et al., 2001). Organic-rich layers (ORLs) have also been observed in western Mediterranean sites in cores from the Ocean Drilling Program (ODP) Leg 161 (Comas et al., 1996). These layers are considered equivalents of the eastern Mediterranean sapropels in higher sedimentation regimes.

Two main models have been put forward to explain the sapropel origin: (1) the 'stagnation model' that calls for external physical processes (temperature, evaporation, circulation) that caused intense vertical gradients of temperature and salinity, which resulted in stable stratification, reduced ventilation of deep water, and anoxia, thus enhanced organic matter preservation (e.g. Vergnaud-Grazzini et al., 1977; Sarmiento et al., 1988; Aksu et al., 1995); and (2) the 'productivity model' that invoked increased export production and rapid supply of organic matter to the sediment, which overwhelmed remineralization, leading to increased organic matter burial and low oxygen in deep waters (e.g. Calvert, 1983; Calvert and Pedersen, 1992). A combination of the two models, bottom water anoxia and increased productivity has also been suggested (e.g. Emeis and Sakamoto, 1998; Emeis et al., 2000a; Warning and Brumsack, 2000).

The application of excess Ba or marine barite accumulation rates, which are paleo-productivity proxies (e.g. Dymond et al., 1992; Paytan et al., 1996), in the sediment interval bearing the most recent sapropel (S1) in the eastern Mediterranean suggests enhanced productivity as the main control for this most recent sapropel deposition (Thomson et al., 1995, 1999; Van Santvoort et al., 1996; Martínez-Ruiz et al., 2000). Increased export of marine organic matter has also been suggested as the main driving force for Pleistocene sapropel formation in the Tyrrhenian Sea (Krishnamurthy et al., 2000). Climatic controls such as enhanced humidity and increased precipitation and runoff that increased the nutrient supply to the basin were invoked to support the elevated

productivity during sapropel deposition periods (e.g. Rossignol-Strick, 1985). Local geographical settings and circulation patterns may, however, have induced various responses to regional climate changes in different Mediterranean basins through time. This is supported by significant differences in the sedimentary records of the eastern and western Mediterranean sapropel event S1 (~9500–6000 yr BP; Mercone et al., 2000).

Here we compare the mineralogical and geochemical characteristics of the S1 sapropel record from sites in the westernmost Mediterranean basins with eastern Mediterranean records. This comparison allows us to determine if the observed differences resulted from variable preservation and post-depositional diagenesis that are related to factors such as sedimentation rates, water depth, and sedimentary redox conditions or whether export production rates varied regionally in response to the basin-wide climate changes.

## 2. Studied areas and site location

Four cores spanning the S1 sapropel deposition have been used in this study, two from the western Mediterranean (Alboran basin and South Balearic basin) and two from the eastern Mediterranean (Ionian basin) (Fig. 1). The sites are characterized by different sedimentary characteristics (sedimentation rates and redox conditions) and water depths (Table 1).

ODP site 976 (36°12.313'N, 4°18.735'W) is located in the Western Alboran basin, and lies on top of a basement horst 60 km off the southern Spanish coast. The Alboran Sea basin (~400 km long and ~200 km wide) is the westernmost basin of the Mediterranean. It has a maximum depth of less than 2000 m and presents a complex seafloor morphology with different sub-basins, ridges, and seamounts (Comas et al., 1999). The basin is positioned between two large converging plates and exhibits a high sedimentation regime. At site 976, a 670 m thick middle Miocene to Pleistocene/Holocene sediment sequence was drilled at 1108 mbsf, which is lying directly on the metamorphic basement (Comas et al., 1996). The sediments consist of nannofossil clay, nanno-



Fig. 1. Map showing the location of the four cores studied spanning the S1 sapropel deposition.

fossil silty clay, sand, silt, calcareous silty clay, and claystone. The upper 5.5 m interval at Hole 976C, which includes the S1 sapropel time interval studied here, comprises poorly and very poorly sorted hemipelagic muds (Alonso et al., 1999) of greenish color. Forty-three samples were analyzed from this 5.5 m interval (see Fig. 3 for sample location).

A second record of the S1 time period from the western Mediterranean, site 274G (37°15.96'N, 00°02.99'W, 2587 m water depth), located further east in the northwestern South Balearic basin, was also studied. The 465 cm long core was taken from the top of a salt diapir and sediments consist of pelagic muds. A visible sapropel layer was recovered at this site in the lower part of the core at 320 cm depth (Martínez-Ruiz et al., in preparation); however, in this work we have focused on the time interval corresponding to S1 sapropel deposition, which is expected to be in the upper section of this core that is composed of calcareous

mud of brownish color. Accordingly, results from the upper 60 cm, sampled at 1.5 cm intervals throughout the upper 60 cm of this core, are presented here.

Two cores recovered in the Ionian Sea basin, core M25 (36°44'75"N, 17°43'05"E, 3376 m water depth; Meteor cruise 1993) (Emeis et al., 2000b; Martínez-Ruiz et al., 2000) and core GL94 (Gendzhik cruise, TTR-Program, 1994, 36°04'75"N, 21°58'03"E, 2687 m water depth) were used as representatives of sites in the eastern Mediterranean basin. Some results from these sites have been previously published by Emeis et al. (2000b) and Martínez-Ruiz et al. (2000). In both these cores, the sediment interval containing the S1 sapropel is identified as a visible dark layer (at 34 and 24 cm depth, respectively) intercalated with light-colored sediments (creamy gray below the sapropel and brownish above it), typical of records of the most recent sapropel in the eastern Mediterranean.

Table 1  
Mineralogical and geochemical characteristics of the S1 sapropel in eastern and western Mediterranean

Core	Location	Water depth (m)	Lithology	Sedim. rate (cm/kyr)	S1 thickness (cm)	CaCO <sub>3</sub> (%)	TOC (wt%)	Presence of pyrite	Presence of barite	Ba (ppm)	Ba/Al	U (ppm)	U/Al
Eastern Mediterranean													
M25	36°44'75"N, 17°43'05"E	3376	Calcareous ooze	~5	12	28	2.40	Yes	Yes	750	133	2.70–15.60	0.37–2.87
GL94	36°04'75"N, 21°58'03"E	2687	Calcareous ooze	~3	6	36	2.94	Yes	Yes	855	217	1.18–8.63	0.29–2.43
Western Mediterranean													
976C	36°12.313'N, 4°18.735'W	1108	Clayey calcareous ooze	~30	1160	23	0.68	Yes	No	345	55	2.77	0.44
274G	37°15.96'N, 00°02.99'W	2587	Calcareous ooze	~4.5	16	50	0.38	No	No	159	34	1.35	0.29

Data from cores M25 and GL94 have been partially published by Martínez-Ruiz et al. (2000).

### 3. Methods

#### 3.1. Mineralogy

Bulk and clay mineral compositions were obtained by X-ray diffraction (XRD) for both bulk and clay mineral analyses. For the latter, the international recommendations compiled by Kisch (1991) were followed. X-ray diffractograms were obtained using a Philips PW 1710 diffractometer with Cu-K $\alpha$  radiation and automatic slit. The estimated semiquantitative analysis error for bulk mineralogy absolute values is 5%, and for clay mineral proportions, error ranges from 5 to 10%. Morphological studies on barite and pyrite were performed using scanning electron microscopy (SEM), and quantitative geochemical microanalyses of clay minerals were obtained by transmission electron microscopy (TEM).

#### 3.2. Barite separation

Barite was separated from bulk samples in order to determine qualitatively if barite is abundant in the sections studied and to compare the size and morphology of the crystals to other barite deposits of different origin (Paytan et al., 2002). This was done using a sequential leaching procedure as described in Paytan et al. (1993, 1996) with a recovery yield around 90%.

#### 3.3. Geochemical analyses

##### 3.3.1. Organic carbon and carbonate measurements

Measurements of organic carbon and carbonate contents were carried out at the Scripps Institution of Oceanography (USCD) and Geologisches Institut (ETH-Zürich). The total inorganic carbon (TIC) was measured using a coulometer. The error for standard calcite determination was  $\pm 0.1\%$ . The total carbon (TC) was measured using a Perkin-Elmer 2400 CHN Elemental Analyzer or a CM 5200 TC Analyzer. Standards and duplicate analyses controlled the measurement and the error was  $\pm 0.05\%$ . The total organic carbon (TOC) content was calculated by subtracting the TIC from the TC values.

### 3.3.2. Major and trace element analyses

Analyses of major elements and Zr from core 274G samples were performed by X-ray fluorescence (XRF) using a Philips PW1404/10 (Analytical Facilities of the University of Granada). The analyses were done using glass discs after fusion with lithium tetraborate. The quality of the analyses was monitored with laboratory and international standards (Govindaraju, 1994), with a precision better than 2% and accuracy of 5%. Major element determinations in samples from site 976 were obtained by atomic absorption spectrometry (AAS) with an analytical error of 2%.

Analyses of trace elements including Ba from the two western sites were performed by inductively coupled plasma-mass spectrometry (ICP-MS) after HNO<sub>3</sub>+HF digestion.

Measurements were performed in triplicate using a Perkin-Elmer Sciex Elan 5000 spectrometer (Analytical Facilities of the University of Granada), with 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). Major and trace element analyses for the eastern Mediterranean sites (M25 and GL94) were performed as described in Martínez-Ruiz et al. (2000). Selected samples from core GL 94 have been reanalyzed for this work using the procedures described for site 976.

### 3.3.3. Isotope analyses

For oxygen and carbon isotope analyses in core 274G, approximately 20 specimens of *Globigerina bulloides* from the fraction > 125 μm, avoiding senescent forms, were separated and thoroughly washed in alcohol. The samples were reacted at 90°C with 100% phosphoric acid on an automated carbonate device connected to a VG-Prism mass spectrometer (Stable Isotope Laboratory at the ETH-Zentrum, Zürich, Switzerland), calibrated with NBS 19, NBS 18 and NBS 20. The results are reported in the conventional ‰ notation with reference to VPDB. Analytical reproducibility of the method, based on repeated standards, is better than ±0.1 ‰ for both carbon and oxygen. Oxygen isotope stratigraphy of the S1 time period at

site M25 has been reported by Emeis et al. (2000b), who also compared this record to that of the Levantine, Ionian and Alboran Sea basins for this same period. Stable isotope analyses were not performed on the other cores studied; however, available data in the literature provide the isotope stratigraphy in the Alboran Sea Basin and Ionian Sea for comparison.

### 3.4. <sup>14</sup>C ages

Age determination using <sup>14</sup>C on selected samples was made in order to identify the depth in the cores corresponding to the S1 time interval (9500–6000 yr BP). The organic fraction of the sediment samples from core 274G was used for accelerator mass spectrometry (AMS) radiocarbon analyses at the Lawrence Livermore National Laboratory AMS Facility (USA). Radiocarbon ages from core M25 were reported by Emeis et al. (2000b), where the visibly identified sapropel layer situated at 34 cm depth was determined to be ~9000–6000 yr BP. At site 976C the time just before S1 deposition (~9700 yr BP) is situated at 2.82 m depth (R. Zahn, personal communication), and at site GL94 the sapropel layer was not dated but the visible S1 sapropel layer was used to assume the age for this time period (see Merccone et al., 2000 for detailed discussion of radiocarbon ages and duration of sapropel S1).

### 3.5. Sea surface temperature (SST) calculations

Paleo-SST was estimated at sites 274G and 976 by means of the modern analog technique, using the square chord distance as the dissimilarity coefficient and the squared chord distance as squared weighting function. The calculation was performed according to the study of González-Donoso and Linares (1998). González-Donoso et al. (2000) reported SSTs at site 976 that have been completed for this study. Paleo-SST studies in the eastern Mediterranean (core M25) were reported by Emeis et al. (2000b) on the basis of alkenone unsaturation ratios. Cacho et al. (2001) also provided a detailed SST reconstruction of the Alboran Sea basin for the last 25 000 years using the U<sub>37</sub><sup>K'</sup> index.



## 4. Results

### 4.1. Western Mediterranean

#### 4.1.1. Site 976

The sediments sampled at site 976 are composed predominantly of clay minerals, calcite and quartz, with trace amounts of dolomite, feldspar and pyrite (Fig. 2). Accessory minerals such as apatite, zircon or biotite are also present in the coarser fraction. No major changes in the relative mineral proportions across the studied interval (0–5.5 mbsf, Hole 976C) were observed and no visible sapropel layer is identified. Calcite content ranges from 25% to 30%, quartz from 15% to 25% and clays from 45% to 60%. The clay mineral associations consist of illite (40–60%), smectite (20–40%), kaolinite and chlorite (each 10–25%); illite/smectite (I/S) mixed layers are also present. TEM analyses revealed that smectites are Al-rich, suggesting a soil-derived origin. The proximity of this site to the Iberian margin led to a high terrigenous input that may have masked any climate-related response of mineral composition; however, slightly lower Zr/Al ratios are evident during the S1 time interval, indicating a possible lower eolian input. Geochemical profiles of major and trace element concentrations and ratios across the S1 time interval (Fig. 3) show slightly elevated Ni/Al, Co/Al and U/Th ratios that suggest relative lower oxygen levels during S1 than in sediments below and above. However, at this site neither a Ba enrichment nor an enrichment in TOC that would suggest paleoproductivity variations are observed (Fig. 4, Table 1). Our barite separation procedure revealed that sediments from this site do not contain any recoverable marine barite (less than 0.001 wt%, which is our detection limit). SSTs show fluctuations (Fig. 5) that can be related to paleoceanographic changes (González-Donoso et al., 2000).

#### 4.1.2. Site 274G

At site 274G, sediments are also composed mostly of calcite (40–55%), clay minerals (30–50%), and quartz (10–25%) (Fig. 2). Lithology is quite uniform across the studied interval and no visible sapropel layer is recognized. The most significant change in the studied interval is an enrichment in quartz at about 29–30 cm depth consistent with higher Zr/Al ratio (Fig. 3) derived from higher detrital input. Clay mineral assemblages consist of illite (50–80%) smectite and I/S mixed-layers (5–25%) chlorite (<5–15%) and kaolinite (5–25%). TEM observations and clay composition obtained from clay particles once again revealed the detrital nature of the clay mineral assemblage. Major and trace element contents show some significant variations that may be related to paleoceanographic changes; for example, a slight decrease in Zr/Al is observed during the S1 deposition period. The bulk mineralogical composition, however, does not indicate major changes across this time (Fig. 2). TOC and Ba contents are low and fluctuate slightly; the average concentrations are around 0.38% and 159 ppm, respectively (Fig. 4, Table 1). Marine barite was not recovered.

Oxygen isotope profiles and SSTs show fluctuations (Fig. 5) that can be related to paleoceanographic changes. Winter SSTs calculated by means of the modern analog technique revealed trends similar to  $\delta^{18}\text{O}$  (Fig. 5). The glacial temperature values are observed at 62.25 cm depth in this core, from this point up to 48.75 cm a warming trend is recognized with cold intervals at 53.25 and 50.25 cm. The temperatures have not fluctuated much from 48.75 cm depth to the core top. Summer SSTs show higher temperature amplitudes in the upper 48.75 cm, suggesting that seasonality was more prominent after the last glacial. In addition to isotope stratigraphy, ages in this core were controlled by radiocarbon dating. Samples at 42–45 and 48–49.5 cm depth correspond to  $8970 \pm 40$  and  $10655 \pm 40$  yr BP, respectively.

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Fig. 2. Concentration (%) of the main mineral components (calcite clays and quartz) and clay mineral proportions (smectite, illite, kaolinite and chlorite) in the clay mineral assemblage at the four cores studied. Illite+chlorite/kaolinite ratio is also represented.

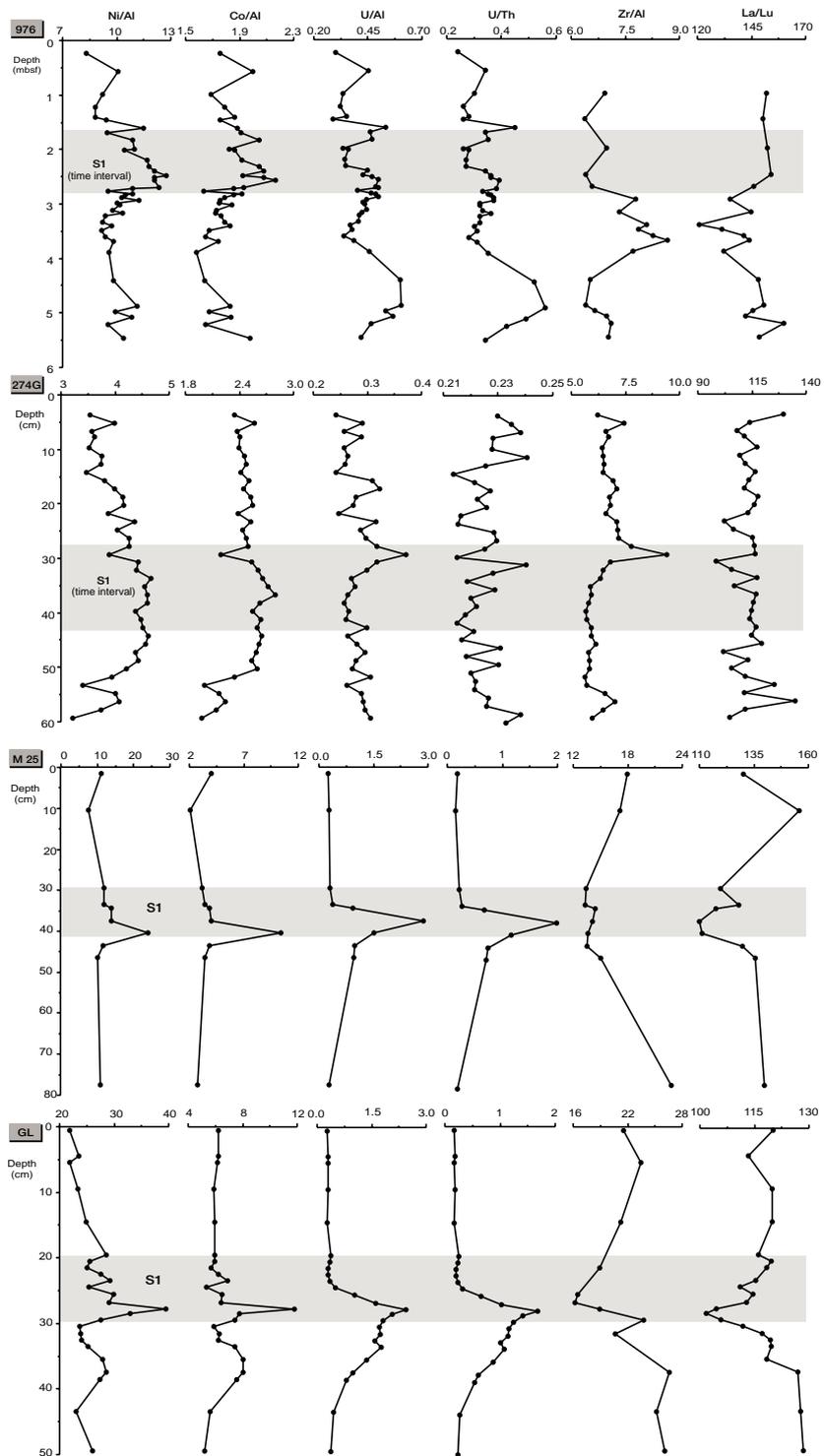


Fig. 3. Trace elements/Al ( $\times 10^4$ ), U/Th and La/Lu ratios versus depth profiles at the four cores studied.

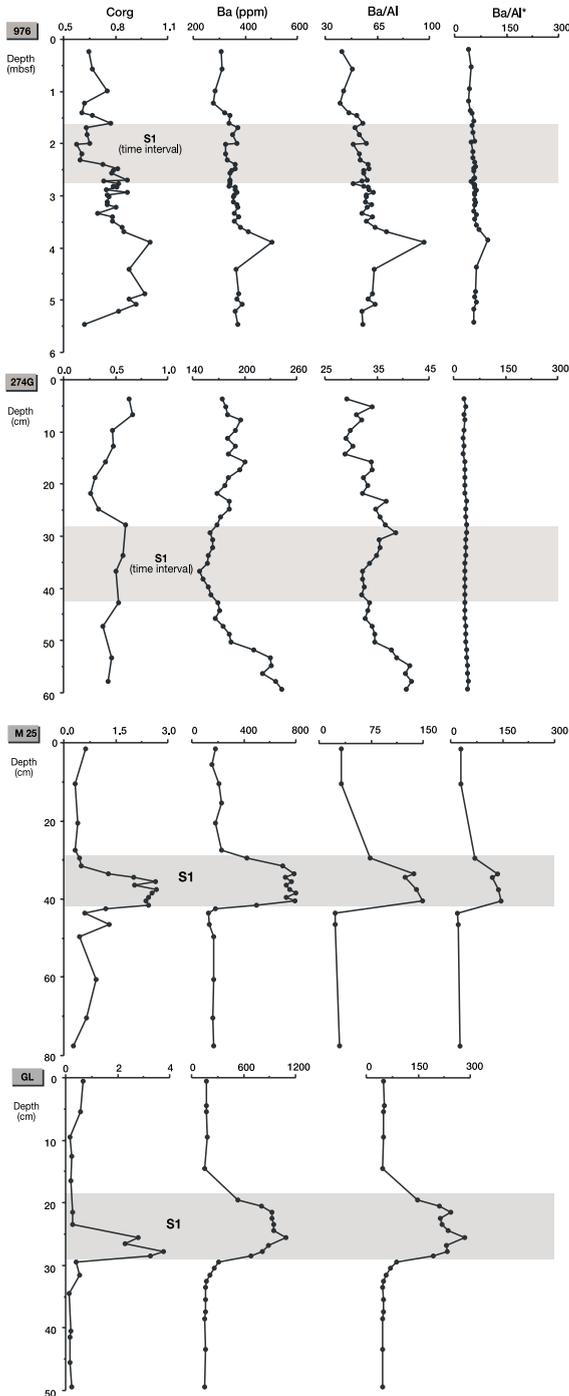


Fig. 4. Concentration versus depth profiles of organic carbon (%), Ba and Ba/Al ( $\times 10^4$ ) ratios at the four cores studied. The Ba/Al\* ratio has also been represented at sites 976, 274G and M25 with the same scale of the maximum ratio (reached at site GL).

#### 4.2. Eastern Mediterranean

Previous analyses from cores M25 and GL94 from the eastern Mediterranean reported by Martínez-Ruiz et al. (2000) show similar facies and bulk mineralogical composition; major mineral phases are also calcite, clay minerals, and quartz (Fig. 2). At these sites, however, a black sapropel layer (S1) at 10 and 5 cm, respectively, is clearly identified. The clay mineral assemblage consists of smectites, illite, chlorite and kaolinite. The sapropel record here is quite similar to that of the S1 sapropel recognized in a wide range of different cores in the eastern Mediterranean (e.g. Thomson et al., 1995, 1999). Mineral composition and detrital element concentrations vary with depth, and significant fluctuations during the S1 sapropel deposition are observed. The concentrations of typical detrital elements decrease at the S1. Lower kaolinite content and higher illite+chlorite content in the sapropel layer suggest a higher fluvial input from the European margin and lower eolian input from the African margin (Martínez-Ruiz et al., 2000). The decreased eolian input from the African margin is further supported by lower Zr/Al ratios and lower La/Lu ratios in the sapropel layer. Mineralogical and detrital-element fluctuations have also been evidenced in other eastern Mediterranean cores (e.g. Calvert and Fontugne, 2001) supporting that sapropel S1 originated during a period of increased humidity, precipitation, and runoff.

Average TOC concentrations in the sapropel layer are 2.4 wt% in core M25 and 2.94% in core GL94 (Table 1, Fig. 4). Ba concentrations are higher than at the western Mediterranean sites and average about 750 and 855 ppm (Table 1), with peaks of 798 and 1084 ppm during sapropel deposition at sites M25 and GL94, respectively. In these cores Ba is enriched in the visible sapropel layer as well as immediately above it, and its content increases up to five times over the background values. It has been demonstrated that this Ba excess is in the form of marine barite crystals, thus supporting that productivity was enhanced (Martínez-Ruiz et al., 2000) (Fig. 6). The marine barite also records the original thickness of the sapropel layer, being a more reliable proxy

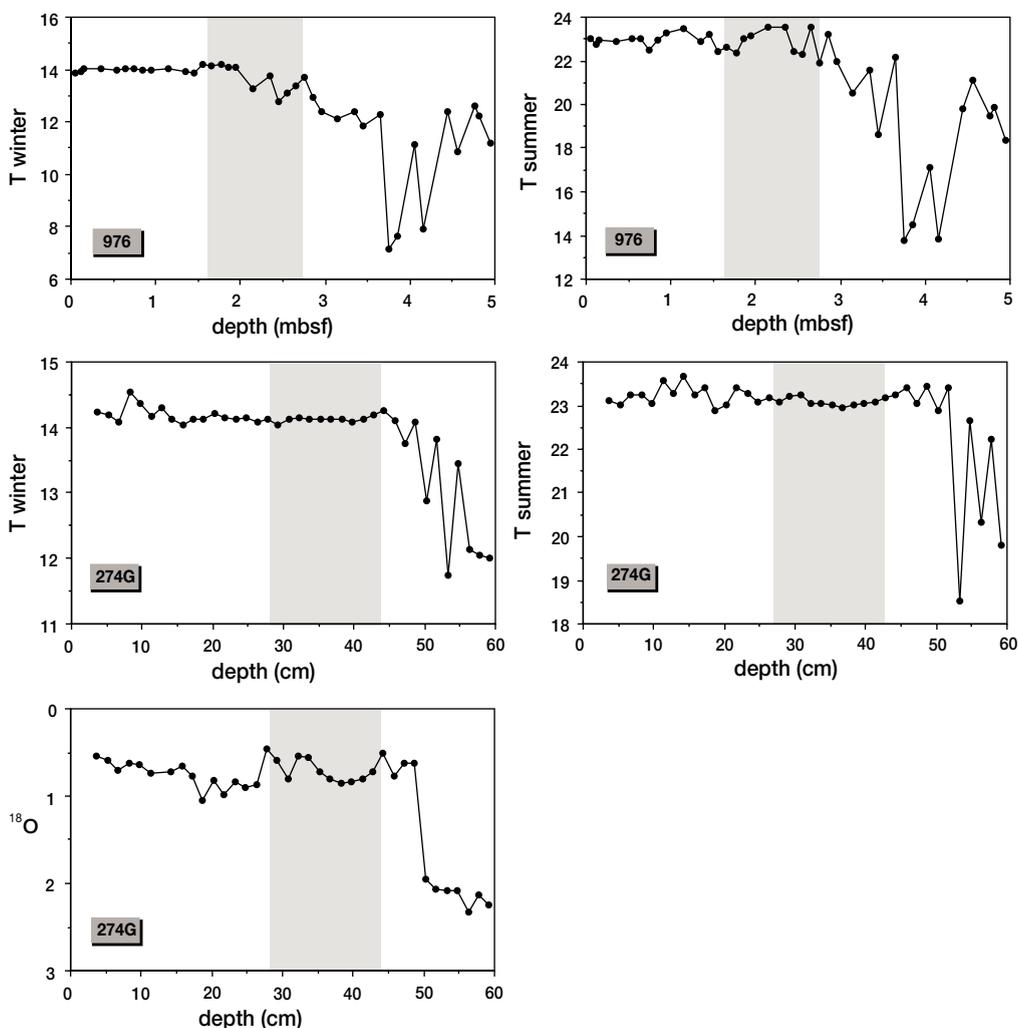


Fig. 5. Winter/summer SSTs at sites 976 and 274G and profile of *Globigerina bulloides*  $\delta^{18}\text{O}$  at site 274G (shaded area corresponds to the S1 time interval).

than the organic carbon record that has been partially erased by oxidation. Barium and barite analyses indicate that carbonates and aluminosilicates carry most of the Ba in the non-sapropel sediments and are also responsible for the background Ba in the sapropel layer. Trace element concentrations (Fig. 3) at these sites show significant variations in response to paleoceanographic changes. Geochemical proxies for oxygen conditions point to decreased oxygenation of bottom waters during S1 deposition but not to anoxic conditions (Martínez-Ruiz et al., 2000).

## 5. Discussion

Two main factors that may have led to the striking differences in organic C and Ba accumulation records across the S1 sapropel ‘time interval’ in the western and eastern Mediterranean are considered: (1) variable preservation of the records in the two basins, reflecting differences in geological setting and/or water depth, or (2) regional climate variations, resulting in considerably higher productivity levels in the east compared to the west basins. The comparison between the four

core records helps to constrain the possible interpretations and suggests that the observed differences are not due to preservation or diagenetic artifacts, but rather represent fluctuations in the export production at the western and eastern Mediterranean basins. Thus, they indicate local and variable responses to the regional climate changes.

The tectonic evolution of the Alboran Sea basin resulted in a high-sedimentation-rate regime since the early Miocene when this extensional basin formed (Comas et al., 1992, 1999). High detrital input to the northwestern Alboran Sea (Ercilla, 1994), where site 976 is located, is reflected by higher detrital clay mineral and quartz contents throughout this sampled site (Fig. 2). For the section studied here, which contains the S1 time interval, sedimentation rate is considerably higher than at the South Balearic basin, site 274G, or at the eastern Mediterranean basin locations studied, sites M25 and GL94 (Table 1). High sedimentation rates dilute the TOC content; although organic-rich layers (ORLs) have been reported in this basin (Comas et al., 1996; Murat, 1999), no true sapropels have been observed. The ORLs are considered the equivalents of eastern Mediterranean sapropels in a high sedimentation regime (Comas et al., 1996; Murat, 1999). However, even an ORL is not recognized during the S1

sapropel time interval at site 976, although it could have been been erased by post-depositional oxidation. Barite or excess Ba accumulations, which have been suggested as more reliable proxies of export production than organic C content (e.g. Dymond et al., 1992; Paytan et al., 1996), have been used to indicate possible enhanced productivity. Nevertheless, no Ba enrichment is observed at site 976 at the appropriate depth range corresponding to the S1 interval, and no marine barite was detected. In addition, no Ba peaks that precipitate at oxidation fronts as a result of Ba remobilization have been observed at this site (Fig. 4).

The absence of a Ba enrichment could be explained by low productivity levels or by post-depositional barite dissolution during extensive sulfate reduction that erased the barite record (e.g. McManus et al., 1998). At site 976 pyrite is abundant in the whole analyzed interval, even replacing foraminifera, suggesting low-oxygen conditions during diagenesis. Furthermore, based on sediment magnetic properties Capotondi and Vigliotti (1999) proposed that the basin was even anoxic during ORL deposition. However, although pyrite is abundant in this core, co-occurrence of pyrite and barite has been observed in eastern Mediterranean S1 sapropel sections (e.g. Passier et al., 1997), suggesting that sulfate reduction conditions did not result in complete barite dissolution. Moreover, at sites with indications for stronger anoxic conditions than at S1, such as at the Pliocene sapropels, the Ba record is also well preserved (e.g. Wehausen and Brumsack, 1998), thus pyrite cannot be used to explain the absence of marine barite at site 976.

Trace element ratios at site 976, such as Ni/Al, Co/Al and U/Th, which when elevated may indicate low redox conditions or anoxia (e.g. Jones and Manning, 1994), are within the range observed in normal terrigenous sediments. Elevated U/Th and U/Al ratios (Table 1), which have also been suggested as indicators of reducing conditions (McManus et al., 1998), are even lower during the sapropel time interval than those at S1 in eastern Mediterranean cores (Fig. 3). Accordingly, the absence of Ba or marine barite in the sediment record at site 976 cannot be explained

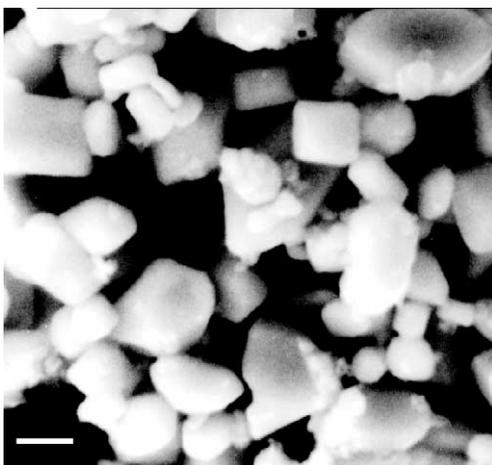


Fig. 6. Scanning electron microscopy (SEM) photograph of barite crystals from S1 layer at core M25.

by low redox conditions that erased the original organic C and barite records.

The absence of a Ba enrichment during S1 deposition at this site could alternatively be explained in terms of differences in the paleoceanographic setting, in particular the water column depth. Site 976 is located at a much shallower depth, 1108 m, than the depths of eastern Mediterranean sites where typical records of S1 have been reported from >2500 m water depths. At this shallower depth site the Ba concentration in the water column and at the sediment–water interface is lower than at the eastern Mediterranean deeper water sites. Because barite preservation and accumulation depends on the Ba content in the water column (e.g. Bishop, 1988; Dymond et al., 1992; Schenau et al., 2001), lower preservation efficiency and possibly complete regeneration has probably occurred at this site, resulting in no Ba enrichment in the sediment record.

To determine whether the absence of TOC and Ba enrichments resulted from dilution due to high sedimentation rates or reduced preservation at shallow depths, respectively, we investigated the S1 deposition interval at a site in the western Mediterranean with water depth and sedimentation rates more similar to the eastern sites, namely site 274G. Site 274G is located in the northeastern part of the South Balearic basin at a depth of 2587 m, which is similar to depths of cores from the eastern Mediterranean, where S1 is recorded as a visible dark layer. Mineral composition and sedimentation rates are similar to eastern Mediterranean basin sites; thus factors controlling barite preservation efficiency are also expected to be similar to the eastern Mediterranean sites (Table 1). Although oxygen isotope stratigraphy and  $^{14}\text{C}$  ages indicate that the core encompasses the S1 time interval, like in the Alboran Sea basin, no visible record of the S1 sapropel is recognized at this site. Both the organic carbon and Ba contents at this site show a much smaller increase in concentration than that reported for eastern Mediterranean S1 cores. The Ba profile does not clearly indicate an increase in concentration during the S1 deposition time interval; however, a very small increasing trend is observed from 42 cm up to 30 cm depth (Fig. 4). Above this interval, the small

Ba peak at  $\sim 29$  cm depth seems to be related to increased detrital input, as suggested by the coincidence with higher Zr/Al ratio (Fig. 3).

At site 274G, the U/Al and U/Th ratios indicate that sediments were not subjected to anoxic diagenesis that may have compromised the Ba record. Accordingly, barite dissolution does not seem to be the reason for the low Ba content; thus, the Ba profiles instead mostly reflect productivity fluctuations.

These data therefore suggest that the lack of TOC and excess Ba enrichments at site 274G, and probably at other western Mediterranean sites, most likely results from lower export production rates in the western basin and is not due to dilution or preservation effects. Regional differences in the response to the climatic fluctuations in the Mediterranean Sea are therefore evident, and the local causes for such different responses require further investigation. Even at the same site in the eastern Mediterranean, when Ba as well as trace-element concentrations of sapropels are compared, as for example in Pliocene sapropels (e.g. Nijenhuis et al., 1998; Wehausen and Brumsack, 1998, 1999), notable geochemical differences are observed down-core. This suggests that productivity, sediment oxygenation, and possibly other oceanographic characteristics varied during sapropel deposition at different sapropel deposition events.

To investigate other parameters that may have been considerably different between the Mediterranean basins and to explore the possible causes for the observed intra-basin differences, we compared the SST at the studied sites. The oxygen isotope record at site M25 during the S1 time period was compared with records from the Levantine, Ionian, and Alboran Sea basins for this same time-interval by Emeis et al. (2000b). This comparison indicated that water mass circulation was not reversed at that time, as also suggested by Stratford et al. (2000) and Paul et al. (2001); hence, changes in the major circulation pattern are not the likely explanation for the increased carbon burial during S1 deposition. These data also showed that SST fluctuations were more prominent in the eastern Mediterranean, while temperatures remained more stable at the Albo-

ran Sea basin through and after S1 deposition (Emeis et al., 2000b). Work by Cacho et al. (2001) that reported increased amplitude of the SST oscillations from the Gulf of Cadiz to the Tyrrhenian Sea also indicates more uniform temperatures in the Alboran Sea basin at this time, compared to those from the eastern Mediterranean. These differences are further supported by data from the central Mediterranean (Ariztegui et al., 2000). At sites 274G and 976, temperatures estimated by modern analog technique (González-Donoso et al., 2000) (Fig. 5) also reveal more stable conditions during the S1 time interval than in the eastern Mediterranean. Some temperature differences are, however, recognized between sites 976 and 274. However, the amplitude of SST oscillations at both sites was not as high as in the Tyrrhenian and eastern Mediterranean basins. As indicated above, oxygen isotopes and SST temperature reconstructions show significant differences between the east and west basins of the Mediterranean. These intra-basin temperature variations further indicate that the different basins did not respond uniformly to the climate changes. The variations in both the temperature and productivity responses at the different basins may have resulted from local changes in circulation and productivity patterns. In fact, some significant regional differences in productivity exist in the modern Mediterranean, as demonstrated by Turley et al. (2000) and Allen et al. (2002).

## 6. Conclusions

The differences in the sedimentary records of the eastern and western Mediterranean S1 sapropel event, in particular those in TOC and Ba enrichments, have resulted from fluctuations in export production fluxes, as evident from our comparison of sites with different sedimentation rates, depths, and redox conditions, rather than from variable preservation of TOC and/or barite. Results presented here suggest that the Mediterranean response to forcing mechanisms such as climate change during S1 sapropel deposition was different in the western and eastern basins. The comparison of the S1 with older sapropels

or the mineralogy and geochemistry records down-core at any of the sites also suggests that climate responses and/or forcing mechanisms may also have varied through time.

Accordingly, regional differences in paleoceanographic conditions at any time interval should be taken into account when paleo-records are interpreted, and regional records cannot be easily extrapolated throughout the Mediterranean. Identifying the exact causes for the different responses in the different basins should be the next step to our understanding of the complexities of this very important region.

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