

# Paleoceanography and Paleoclimatology

### **RESEARCH ARTICLE**

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#### **Special Section:**

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#### **Key Points:**

- Holococcolith preservation is enhanced during seafloor reventilation and benthic foraminiferal repopulation
- A strong correlation between *F.* profunda and Ba/Al supports previous reconstructions that productivity increased in the lower photic zone
- The transition to modern environmental conditions in the eastern Mediterranean Sea is marked by the final decline of high productivity

#### **Supporting Information:**

- Supporting Information S1
- Data Set S1Data Set S2
- Data Set S2
  Data Set S3

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## Reventilation Episodes During the Sapropel S1 Deposition in the Eastern Mediterranean Based on Holococcolith Preservation

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Abstract Organic-rich layers (sapropels), preserved in eastern Mediterranean marine sediment records, represent pronounced perturbations to thermohaline circulation and environmental conditions in the basin, in response to enhanced African monsoon activity and subsequent massive freshwater discharge. During the most recent event, Sapropel S1 formed between 10.8 and 6.1 ka, when freshwater-driven stratification caused seafloor anoxia below ~1,800-m depth, as a result of both failure of deep water formation and enhanced productivity. Here we analyze coccolith assemblages from the open eastern Mediterranean that form a west-east transect across the basin and provide insights on past environmental changes. We focus on holococcoliths, which are specifically produced by coccolithophores as part of their life cycle during the haploid phase. Since holococcolith calcification is characterized by nanocrystals highly susceptible to dissolution, we are testing their potential preservation under different bottom environmental conditions, including the effect of postdepositional oxidation. A comparison with benthic foraminifera assemblages in a core recovered close to Lybia reveals that holococcolith preservation is enhanced during seafloor reventilation and benthic foraminiferal repopulation in the middle to upper part of the record, before the actual sapropel termination. There are two such events of improved deep-water oxygenation in the Aegean and Adriatic Seas at 8.2 and 7.4 ka. The latter episode marks the onset of the transition to restored circulation in the eastern Mediterranean Sea, due to resumption of deep-water formation in the southern Aegean Sea and the conclusion of enhanced biogenic productivity.

#### 1. Introduction

Organic-rich layers, the so-called sapropels, have repeatedly been deposited on the eastern Mediterranean seafloor during precession minima (Hilgen, 1991). Enhanced summer insolation strengthened African monsoon precipitation and led to massive freshwater discharge, especially via the Nile River during S1 and other sapropels, including large fluxes from currently dry river systems along the wider North African margin (Osborne et al., 2008; Rohling et al., 2002, 2004; Rossignol-Strick et al., 1982). Deep water formation was prevented by freshwater buoyancy gain and a distinctive deep chlorophyll maximum (DCM) developed in the lower photic zone [LPZ; Rohling & Gieskes, 1989; Castradori, 1993; Kemp et al., 1999; Meier, 2004; De Lange et al., 2008; Rohling et al., 2015], driving large-scale changes recorded in surface and bottom waters, which are the focus of this current study.

Sapropel S1 is the most recent organic-rich layer and is especially pronounced below 1,800-m depth in the open eastern Mediterranean, with deposition occurring between 10.8 and 6.1 kiloyears ago (ka; De Lange et al., 2008; Grant et al., 2016). Sapropel deposition was interrupted between 8.5 and 7.8 ka in the Aegean and Adriatic Seas (Casford et al., 2003; Rohling et al., 2015). by intermittent bottom water ventilation, as indicated by the repopulation of benthic foraminifera faunas within S1 in the Aegean and Adriatic Seas and on the edge of the basin, offshore Libya and Israel (Jorissen et al., 1993; Casford et al., 2003; Kuhnt et al., 2007; Abu-Zied et al., 2008; Schmiedl et al., 2010; Tesi et al., 2017; Figure 1). The titration of reduced chemical species and the biological oxygen demand after the advection of newly formed bottom water would take ~200 years (Casford et al., 2003). The following reestablishment of bottom anoxia would take ~1,500 years





(Stratford et al., 2000). The short time scales of benthic foraminiferal repopulation events are not consistent with such a long duration and suggest the absence of an extensively anoxic water column. Anoxia may instead have "draped" the seafloor like a thin "blanket," whose occurrence would be governed by the balance between advective oxygen supply and biological and chemical oxygen consumption (Casford et al., 2003).

Here we examine coccolith assemblages in S1 from three short multicores along a west-east transect across the eastern Mediterranean Sea. These cores were previously investigated and elemental proxies provide a precise estimate of the original vertical extent of Sapropel S1 layers, including in the Libya offshore site where benthic foraminifera persistently survived (Casford et al., 2003; Meier, 2004; Möbius et al., 2010). Our study of the three cores in the west-east transect is ideal for assessing potential holococcolith sensitivity to different water column and bottom environmental conditions, to test the effect of postdepositional oxidation and to estimate the existence of vertical (depth) offsets determined by aggressive pore water dissolution.

This study aims to assess paleoenvironmental changes across the eastern Mediterranean transect during Sapropel S1 deposition. We pay special attention to coccolith preservation and selective dissolution of holococcoliths, because coccoliths produced during the holococcolithophore life stage seem to be especially prone to dissolution during early diagenesis (Crudeli et al., 2006; Incarbona & Di Stefano, 2018; Thomson et al., 2004). Different processes that occurred during S1 deposition may have altered the calcite saturation state, which at present is at supersaturated levels throughout the Mediterranean Sea (Schneider et al., 2007): These include: (1) increased primary productivity and water column oxygen shortage affecting the extent and the strength of dissolution and thus the lysocline (Barker, 2016; Paulmier et al., 2011); (2) anoxic remineralization of Corg by sulfate reduction establishes an alkaline environment in interstitial pore waters, below the water/sediment interface (Ten Haven et al., 1987; Thomson et al., 2004); and (3) gypsum precipitation from Ca released by dissolving biogenic carbonate and SO4 released from pyrite oxidation (Calvert, 1983; Cita et al., 1977; Ten Haven et al., 1987) upon postdepositional diffusion of oxygen into the sediment (De Lange et al., 2008; Thomson et al., 1999; Van Santvoort et al., 1996).

### 2. Local Setting

The Mediterranean Sea oceanographic circulation flows through three vertical layers in an overall antiestuarine pattern. Surface waters from the Atlantic Ocean occupy the first 100- to 200-m depth (Modified Atlantic Water, MAW) and undergo severe evaporative salt enrichment while they flow eastward (Millot, 1999; POEM group, 1992). The northern branch of MAW in the Sicily Channel (Atlantic-Ionian Stream) enters the eastern Mediterranean Sea and feeds the Mid-Mediterranean Jet (MMJ; Robinson et al., 1999; Figure 1). MAW describes a large cyclonic gyre into the eastern Mediterranean basin (Pinardi & Masetti, 2000). The MMJ flows to the central Levantine Sea and then it turns northward becoming the Cilician Current and the Asian Minor Current (Malanotte-Rizzoli et al., 2014; Pinardi & Masetti, 2000; POEM group, 1992). Two of our cores 562 and 569 are located within or very close to present day mesoscale anticyclonic gyres; core 563 is close to the MMJ path (Figure 1).

Levantine Intermediate Water forms in winter due to surface cooling and evaporation near Rhodes (Malanotte-Rizzoli & Hecht, 1988). Levantine Intermediate Water flows throughout the Mediterranean basin between 200- and 600-m depths and is a basic requisite for deep water formation. Eastern Mediterranean Deep Water forms in the Adriatic and Aegean Sea and fills the Ionian and Levantine Sea bottom (Figure 1; POEM group, 1992). Deep water formation in the Adriatic and Aegean Seas is promoted by winter heat flux loss, when northerly winds blow (Josey et al., 2011; Rohling et al., 2015).

The eastern Mediterranean Sea is severely oligotrophic. Primary productivity reflects the nutrient depletion (Krom et al., 1991, 2010) and is relatively enhanced in winter and very low in summer due to deepening of the thermocline and nutricline (Allen et al., 2002; D'Ortenzio & D'Alcalà, 2009; Klein & Coste, 1984). Satellite analysis defines the 562, 563, and 569 core sites as "No Bloom" areas, with chlorophyll maxima centered between December and March (D'Ortenzio & D'Alcalà, 2009).

### 3. Material and Methods

Multicores 562 (Gulf of Sirte, 32.774°N, 19.191°E, 1,391-m water depth), 563 (South of Crete, 33.718°N, 23.499°E, 1,881-m water depth), and 569 (Eratosthenes seamount, 33.452°N, 32.576°E, 1,294-m water depth) were recovered during R/V Meteor cruise M51-3 (Figure 1). A short sedimentological description is available in Meier (2004) for cores 562 and 569. Both cores are made of nannofossil ooze with minor amounts of quartz and clay. In all cores, the mismatch between Ba/Al and total organic carbon,  $\delta^{15}$ N15N and amino acid curves clearly testifies to the occurrence of a postdepositional oxygenation front marked by the Mn/Al peak, but there is no conclusive evidence for an S1 base (Meier, 2004; Möbius et al., 2010) (Figure 2). No lithological description is available for Core 563, but even in this case a clear postdepositional oxygenation front is visible from elemental proxies (Möbius et al., 2010; Figure 2).

Coccolith analysis was carried out at 1-cm resolution, between 29 and 4 cm below sea floor (cmbsf) for Core 562, between 30 and 5 cmbsf for Core 563, and between 31 and 9 cmbsf for Core 569. The coccolith analysis was carried out by observation with a polarized microscope at 1,000X magnification. Rippled smear slides were prepared following the standard procedure (Bown & Young, 1998). A mean of 500 specimens within the entire assemblage was identified following the taxonomic concepts for living coccolithophores of Young et al. (2003) and Jordan et al. (2004). Taxa were grouped in "placoliths," "miscellaneous group," "upper photic zone (UPZ) group," "LPZ group," and "holococcoliths" (Di Stefano & Incarbona, 2004; Incarbona et al., 2010). Placoliths include *Emiliania huxleyi*, small placoliths, small *Gephyrocapsa, Gephyrocapsa muellerae*, and *Gephyrocapsa oceanica*. Miscellaneous group includes *Helicosphaera* spp., *Syracosphaera histrica, Pontosphaera* spp., *Calcidiscus leptoporus, Coronosphaera* spp., *Braarudosphaera* spp., *Oolithotus fragilis, Calciosolenia* spp., *Discosphaera tubifera, Rhabdosphaera* spp., and *Umbilicosphaera* spp., LPZ group includes *Florisphaera profunda* and a few specimens of *Gladiolithus flabellatus*. Holococcoliths include all the coccoliths produced during the holococcolithophore life stage.

Placoliths are r-strategist taxa: They grow and reproduce rapidly and bloom after nutrient fertilization (Flores et al., 2000; Incarbona et al., 2010; Young, 1994). Among them, *E. huxleyi* is an opportunistic taxon that dominates today's ocean assemblages (Young, 1994). In the Mediterranean Sea, this taxon blooms in winter and spring, responding to vertical convection that fuels the delivery of nutrients into the photic zone (Di Stefano et al., 2011; Knappertsbusch, 1993). LPZ taxa and the species *F. profunda* peak in response to nutricline deepening within the photic zone (Beaufort et al., 1997; McIntyre & Molfino, 1996; Molfino & McIntyre, 1990b, 1990a). UPZ and Miscellaneous taxa are K-strategists (low division rate) to weakly K-strategists (Incarbona et al., 2010; Young, 1994). Holococcoliths are produced by coccolithophores during their haploid life phase. Although belonging to different species, they behave as a homogeneous group (Oviedo



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**Figure 2.** Downcore variations of geochemical and benthic foraminifera data at 562, 563, and 569 cores plotted versus depth (centimeters below sea floor—cmbsf). Black and dashed lines in Ba/Al and Mn/Al curves, respectively, refer to data from Möbius et al. (2010) and Meier (2004). The vertical dark gray band indicates the extent of visible Sapropel S1. The vertical light gray band indicates the extent of burn down Sapropel S1. TOC = total organic carbon.

et al., 2015), preferring warm and oligotrophic surface waters (D'Amario et al., 2017; Kleijne, 1991; Knappertsbusch, 1993; Oviedo et al., 2015).

#### 4. Results

Coccolith assemblages from the three investigated cores are compatible with those reported from other studies on the eastern Mediterranean Sapropel S1 (Giunta et al., 2003; Incarbona et al., 2011; Incarbona & Di Stefano, 2018; Principato et al., 2003). *E. huxleyi* and *F. profunda* are the dominant taxa (Figures 3 and 4). E. *huxleyi* ranges between 37% and 68% in Core 562, 41% and 65% in Core 563, and 33% and 64% in Core 569, and is, respectively, 51%, 52%, and 48% on average. F. *profunda* ranges between 10% and 53% in Core 562, 13% and 53% in Core 563, 11% and 56% in Core 569, and is, respectively, 30%, 29%, and 33% on average. E. *huxleyi* and F. *profunda* show a similar behavior in the 562 and 563 records, where the latter (former) species increases (decreases) twice, in the lower part of the visible sapropel layer and in the lower part of the oxidized sapropel layer (Figures 3 and 4).

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**Figure 3.** Downcore variations of selected coccolith species at 562, 563, and 569 cores plotted versus depth (centimeters below sea floor—cmbsf). Vertical bars show the 95% confidence level error associated to the counting for each taxon. The vertical dark gray band indicates the extent of visible Sapropel S1. The vertical light gray band indicates the extent of burn down Sapropel S1.

Holococcoliths range between 1% and 16% (6% on average) in Core 562, 1% and 14% (7% on average) in Core 563, and 0% and 16% (5% on average) in Core 569 (Figure 4). They show a large decrease within the Sapropel S1 layer. Most of the holococcolith specimens belong to S. *pulchra HOL* oblonga (*Calyptrosphaera oblonga*), as already observed in late Quaternary Mediterranean sediments (Crudeli et al., 2006; Di Stefano et al., 2015; Incarbona & Di Stefano, 2018). All the other taxa are largely subordinate; they account for less than 5% and do not show significant abundance fluctuations, such as for *S. pulchra* in all three cores and for *Umbellosphaera* spp., *Rhabdosphaera* spp., and *S. histrica* in Core 563 (Figure 3). *Umbellosphaera* spp., *Rhabdosphaera* spp., and S. *histrica* 2018; and decreasing values in the easternmost site 569 (Figure 3).

Subordinate taxa provide useful paleoecological information once grouped following their ecological preference, as described in the previous section (Figure 4). Placoliths and LPZ curves are identical to those from the dominant *E. huxleyi* and *F. profunda* species and their correlation index is  $R^2 = 0.70$ ,  $R^2 = 0.85$ , and  $R^2 = 0.94$ , respectively, for Cores 562, 563, and 569. UPZ and Miscellaneous taxa show opposite trends between the eastern and western sites, following the distribution pattern of some taxa (i.e., *Umbellosphaera* spp. and *Rhabdosphaera* spp. for UPZ and *S. histrica* for Miscellaneous; Figure 4). Less significant seem to be fluctuations and trends of UPZ and Miscellaneous taxa in Core 563 (Figure 4).

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**Figure 4.** Downcore variations of coccolith groups at 562, 563, and 569 cores plotted versus depth (centimeters below sea floor—cmbsf). Vertical bars show the 95% confidence level error associated to the counting for each taxon. The vertical dark gray band indicates the extent of visible Sapropel S1. The vertical light gray band indicates the extent of burn down Sapropel S1.

#### 5. Discussion

#### 5.1. Holococcolith Preservation

There is a remarkable difference between the distribution of holococcoliths and the TOC pattern (as well as those of  $\delta^{15}$ N and the degradation index; Figure 2), which suggests that there has been no influence of post-depositional sapropel oxidation ("burn down," Van Santvoort et al., 1996; Thomson et al., 1999; De Lange et al., 2008) on holococcolith preservation (Figure 5). In other words, holococcoliths were already dissolved or preserved once the oxygen penetrated the water/sediment interface at the end of sapropel deposition.

Benthic foraminiferal peaks within Sapropel S1 of Core 562 (Figure 5) have contributed to formulation of the blanket hypothesis; that is, the occurrence of a thin anoxic layer on the seafloor occasionally displaced by intermittent dense water production and bottom ventilation in the Adriatic and Aegean Seas and in the basin edges (Abu-Zied et al., 2008; Casford et al., 2003; Kuhnt et al., 2007; Triantaphyllou et al., 2016). The comparison between holococcolith and benthic foraminifera abundances reveals the presence of three different steps in the upper part of the record (Figure 5). The oxyphilic benthic foraminifera peak at 17.5 cmbsf (sapropel interruption—Si in Figure 5) correlates with the sapropel interruption in the Adriatic and Aegean Seas centered at about 8.2 ka (Casford et al., 2003), likely due to monsoon activity weakening and/or northerly air outbreaks that led to surface cooling and temporary deep water formation (Casford et al., 2003;

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**Figure 5.** Downcore variations of coccolith taxa, geochemical, and benthic foraminifera data at 562, 563, and 569 cores plotted versus depth (centimeters below sea floor—cmbsf). Black and red lines in the benthic foraminifera plot, respectively, indicate absolute numbers of specimens and oxyphilic taxa percentage values. Si marks the sapropel interruption in the Adriatic and Aegean Sea. Vertical dashed lines mark the transition to modern environmental conditions in the eastern Mediterranean Sea. The vertical dark gray band indicates the extent of visible Sapropel S1. The vertical light gray band indicates the extent of burn down Sapropel S1. TOC = total organic carbon.

Mercone et al., 2001; Rohling et al., 1997, 2015, 2019). A small, but statistically significant (Figure 4), peak in holococcoliths is found in the oxidized S1 in all cores and attests to improved preservation in coincidence with the reventilation episode at 8.2 ka (Figure 5). Above 13.5 cmbsf, a peak in the absolute number of benthic foraminiferal specimens is again associated with improved holococcolith preservation. This horizon, which occurred well before the end of sapropel deposition, is especially relevant because it also indicates the final decline of a distinct DCM combined with high primary productivity, as visible in the F. profunda and Ba/Al patterns (Figure 5). Thus, this level highlights the beginning of the transition from sapropel to modern environmental conditions in the eastern Mediterranean Sea, characterized by oligotrophic conditions with a short phytoplankton bloom (placolith-bearing species among coccolithophores) centered around winter/early spring (Auliaherliaty et al., 2009; D'Ortenzio & D'Alcalà, 2009; D'Amario et al., 2017; Oviedo et al., 2015; Ziveri et al., 2000). The subsequent step at 10.5 cmbsf, at the end of Sapropel S1, led to persistent oxygen availability on the seafloor, repopulation of oxyphilic benthic foraminifera assemblages, and the preservation of holococcoliths that were resistant to prediagenetic dissolution (Kleijne, 1991). The sequence described above is perfectly compatible with the occurrence of distinct reventilation episodes at 8.2 and 7.4 ka in the Aegean and Adriatic Seas, before the termination of sapropel deposition at 6.6-6.3 ka (Filippidi et al., 2016). Both the 8.2- and 7.4-ka events

AGU 100 would be caused by cool and arid conditions that led to improved deep-water oxygenation and benthic foraminiferal repopulation.

The three steps are identified in the upper part of the holococcolith record in Cores 563 and 569 (Figure 5). The only exception concerns an apparently missing holococcolith peak in Core 569 at around the 8.2-ka event, which might be explained by the fact that this site is deeper than the 1,800-m depth limit below which persistent anoxia dominated throughout S1 (De Lange et al., 2008).

Benthic foraminifera are usually present throughout the Sapropel S1 layer in the Aegean Sea and the Adriatic Sea (Abu-Zied et al., 2008; Casford et al., 2003; Jorissen et al., 1993; Kuhnt et al., 2007; Schmiedl et al., 2010), which indicates a continuous supply of (seasonal to interannual) oxygen from today's deep water formation sites that did not reach the open eastern Mediterranean Sea in sufficient volume. However, the three steps described above are still recognizable in the open eastern Mediterranean in terms of minor differences in benthic foraminifera assemblages, abundances, and derived oxygen indices on the eastern Mediterranean margin (Levantine Sea cores SL 112 and LC31; Schmiedl et al., 2010). This suggests the occurrence of a discrete number of oxygen availability phases across the open eastern Mediterranean Sea since the sapropel interruption, in sites that were above or close to the 1,800-m depth limit of permanent anoxia. Although detailed chronological constraints remain to be established for these events, the sequence of improved deep water oxygenation in the Adriatic and Aegean Seas (Filippidi et al., 2016) may provide a suitable explanation for this phenomenon.

Holococcoliths have a distinct preference for warm and oligotrophic water (Oviedo et al., 2015) and may be able to adapt to ongoing Mediterranean climate change, where surface water would be characterized by relatively high calcite saturation state, high temperature, stratification, and nutrient limitation (D'Amario et al., 2017). In accordance with their ecological preference, holococcoliths are especially abundant in eastern Mediterranean water samples (D'Amario et al., 2017; Oviedo et al., 2015). Even though the Mediterranean waters are supersaturated with respect to calcite (Schneider et al., 2007), holococcolith diversity and abundance are reduced in surface sediments (Kleijne, 1991; Knappertsbusch, 1993), because of disaggregation into microcrystals and lysocline/seafloor dissolution.

Holococcolith dissolution within S1 may be explained by prediagenetic (lysocline) dissolution. The vertical lysocline extent and the calcite saturation state are affected by processes acting during sapropel deposition, including productivity variations and oxygen shortage (Barker, 2016; Paulmier et al., 2011). Since primary productivity was higher during S5 deposition than during S1 deposition, and since anoxia extended toward shallow levels near the base of the photic layer (Rohling et al., 2006, 2015), a different pattern of coccolith selective preservation might be expected in S5 than in S1. However, the coccolith distribution pattern during S5 is identical to S1, with no or rare holococcoliths and the preservation of delicate umbelliform species (i.e., *D. tubifera* and *Umbellosphaera* spp.; Principato et al., 2006), which suggests that lysocline dissolution was ineffective or negligible in explaining holococcolith absence in sapropel layers.

Late Quaternary sapropels are associated with high concentrations of aragonite, alternating with high-Mg calcite in underlying and overlying marls, both thought to be early diagenetic products (Calvert & Fontugne, 2001; Thomson et al., 2004). During S1 deposition, anoxic remineralization of  $C_{org}$  by sulfate reduction would have enhanced sediment pore water alkalinity and thus enhanced diagenetic aragonite precipitation (Thomson et al., 2004). However, the only study dealing with interstitial sapropel waters indicates that the pH was significantly lower than in surrounding marls, due to anaerobic bacterial activity (Ten Haven et al., 1987). The role of bacterial activity in driving different seafloor preservation was identified through comparison of sediment trap and surface sediment coccolith assemblages in the Gulf of California (Ziveri & Thunell, 2000). There, a considerable number of species are lost (dissolved), and coccoliths show etching and fragmentation, on the anoxic seafloor due to organic acid production by bacteria and subsequent acidification of the water/sediment interface or of the top centimeters of the sediment column. In contrast, coccoliths are well preserved and the taxonomic composition of coccolithophores is much more similar to that observed in trap samples where bottom conditions are aerobic.

Scanning electron microscope observation of coccoliths shows a prevalence of overgrowths in marls and a prevalence of fragmentation/etching in S1 sediments (Crudeli et al., 2004; Crudeli & Young, 2003). This further supports that oxygen availability on the seafloor is key to holococcolith preservation in marls and

even within sapropel layers after episodes of reventilation. The F. profunda and Ba/Al decrease that marks the transition to modern eastern Mediterranean environmental conditions is widely recorded and attributed to a productivity decline in the photic zone, with limited to no impact of the seafloor oxygenation state.. The abrupt decrease of F. profunda is seen throughout the Ionian, Adriatic, Aegean, and Levantine Seas (Giunta et al., 2003; Incarbona et al., 2011; Incarbona & Di Stefano, 2018; Principato et al., 2003; Triantaphyllou et al., 2009; Triantaphyllou et al., 2009; Triantaphyllou et al., 2010; Triantaphyllou et al., 2016). In all three cores 562, 563, and 569, this horizon resides 3-4 cm below the end of S1 deposition (Figure 5). Assuming that the base of the sapropel is very close to the base of sediment recovery at Sites 562 and 563 and that S1 formed between 10.8 and 6.1 ka (Grant et al., 2016), we infer that the transition lasted about 750-1,000 years. This duration estimate is much longer than a previous estimate of 100-200 years for reoxygenation of the water column below 1,500 m (Casford et al., 2003). However, the latter is likely an underestimate because it ignores the inventory of reduced chemical species in the water column that would need to be overcome, as well as the oxygen demand involved in reoxidation (burn down) of the sapropel after reoxygenation of the overlying water column (Casford et al., 2003). Alternatively, the recovery of seafloor oxygenation may have suffered from a lower rate of dense water production, and consequently limited oxygen supply, relative to that involved in modern Eastern Mediterranean Deep Water circulation. In any case, the 750-1,000 years taken by the transition is compatible with the interval between restored deep water formation in the Aegean Sea (7.4 ka) and the end of sapropel deposition (6.3 ka; Filippidi et al., 2016).

#### 5.2. DCM and Sapropel Productivity

In all three 562, 563, and 569 cores, there is an evident *F. profunda* abundance increase within the Sapropel S1 layer (Figure 5), which points to a deep nutricline and a distinctive DCM. DCM development has been reported in all microfossil groups (Castradori, 1993; Kemp et al., 1999; Meier, 2004; Rohling & Gieskes, 1989) and is thought to be the reason for increased productivity and increased biogenic barite accumulation in sapropels (Rohling et al., 2015; Rohling & Gieskes, 1989). This is corroborated by the similarity between the *F. profunda* and Ba/Al profiles from the three cores (Figure 5;  $R^2 = 0.65$  in Core 562,  $R^2 = 0.63$  in Core 563, and  $R^2 = 0.82$  in Core 569). The dinoflagellate species *Leonella granifera*, which is used as a proxy for water stratification as a result of increased river input (Meier, 2004; Vink, 2004), shows the same pattern as *F. profunda* and Ba/Al in Cores 562 and 569 (Meier, 2004).

*F. profunda* has been used as a proxy for paleoproductivity; more specifically, it was found to be inversely related to primary productivity in many low-latitude ocean settings (Beaufort et al., 1997; Hernández-Almeida et al., 2019). This contrasts with enhanced productivity as inferred here for Sapropel S1 by comparison with Ba/Al values. However, the behavior of *F. profunda* in response to vertical column dynamics (stratification, upwelling, and vertical convection) and in relation to productivity is not straightforward. There is a high correlation of organic carbon export and *F. profunda* fluxes in sediment traps of the Bay of Bengal and the Alboran Sea (Bárcena et al., 2004; Stoll et al., 2007). An extensive review of the *F. profunda* abundance and primary productivity relationship in all the oceans led to the conclusion that, with very few local exceptions, there is no inverse correlation in the Mediterranean Sea (Hernández-Almeida et al., 2019).

Looking at the spatial distribution of single signals, *F. profunda*, Ba/Al, and *L. granifera* (Meier, 2004) seem to be quite different in the three sites. Among others, the Ba/Al is a perfect bell-shaped curve in Core 569 and is asymmetric in 562 and 563 (Figure 5). *F. profunda* shows a single abundance decrease in the lower-middle S1 in 562 and 563 cores and high-frequency variability in 569 (Figure 5). This suggests that, although the DCM and high productivity are widespread features in the eastern Mediterranean Sea, local signals were superimposed, likely due to mesoscale oceanographic activity and surface and subsurface water dynamics. For instance, Site 562 is close to the mesoscale anticyclone in the Gulf of Sirte, while Site 569 is close to the Shikmona Gyre, and the Nile River freshwater discharge directly affects Site 569. This local overprinting is supported by different trends in single species and groups, such as miscellaneous and UPZ taxa (Figures 3 and 4).

#### 6. Conclusions

Coccolith assemblages from three cores along a west-east transect across the open eastern Mediterranean Sea have been investigated. Data from the most recent sapropel layer (S1) reveal development of a distinct DCM, indicated by increased *F. profunda* abundance, a coccolith species that thrives in the deep photic zone. A



strong correlation between *F. profunda* and Ba/Al in all cores supports previous reconstructions that productivity increased in the LPZ (Castradori, 1993; Kemp et al., 1999; Meier, 2004; Rohling & Gieskes, 1989).

Comparison with previously published records of total organic carbon,  $\delta^{15}N$ , degradation index, Ba/Al, and Mn/Al proves conclusively that there was no influence of postdepositional sapropel oxidation on holococcolith preservation. Sapropel S1 holococcolith peaks in Core 562 are associated with benthic foraminiferal repopulation episodes. The first episode can be correlated with sapropel interruption in the Adriatic and Aegean Seas. The second episode marks the onset of the transition to modern environmental conditions in the eastern Mediterranean Sea, coinciding with the final decline of high productivity. These two events are also visible in our other cores, except for the event associated with sapropel interruption in Core 563, which is explained by the fact that this core was recovered from a site below the depth of permanent anoxia (De Lange et al., 2008). The two events are also compatible with reports of cool and arid conditions at 8.2 and 7.4 ka in the Aegean and Adriatic Seas (Filippidi et al., 2016).

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#### References

- Abu-Zied, R. H., Rohling, E. J., Jorissen, F. J., Fontanier, C., Casford, J. S. L., & Cooke, S. (2008). Benthic foraminiferal response to changes in bottom-water oxygenation and organic carbon flux in the eastern Mediterranean during LGM to Recent times. *Marine Micropaleontology*, 67(1–2), 46–68. https://doi.org/10.1016/j.marmicro.2007.08.006
- Allen, J. I., Somerfield, P. J., & Siddorn, J. (2002). Primary and bacterial production in the Mediterranean Sea: A modelling study. Journal of Marine Systems, 33-34, 473–495. https://doi.org/10.1016/S0924-7963(02)00072-6
- Auliaherliaty, L., Stoll, H. M., Ziveri, P., Malinverno, E., Triantaphyllou, M. V., Stravrakakis, S., & Lykousis, V. (2009). Coccolith Sr/Ca ratios in the eastern Mediterranean: Production versus export processes. *Marine Micropaleontology*, 73(3–4), 196–206. https://doi.org/ 10.1016/j.marmicro.2009.10.001
- Bárcena, M. A., Flores, J. A., Sierro, F. J., Pérez-Folgado, M., Fabres, J., Calafat, A., & Canals, M. (2004). Planktonic response to main oceanographic changes in the Alboran Sea (Western Mediterranean) as documented in sediment traps and surface sediments. *Marine Micropaleontology*, 53(3–4), 423–445. https://doi.org/10.1016/j.marmicro.2004.09.009
- Barker, S. (2016). Dissolution of deep-sea carbonates. In S. A. Elias (Ed.), Paleoceanography, Physical and chemical proxies. Elsevier. https:// doi.org/10.1016/B978-0-12-409548-9.09717-7.

Beaufort, L., Lancelot, Y., Camberlin, P., Cayre, O., Vincent, E., Bassinot, F., & Labeyrie, L. (1997). Insolation cycles as a major control of equatorial Indian Ocean primary production. Science, 278(5342), 1451–1454. https://doi.org/10.1126/science.278.5342.1451

- Bown, P. R., & Young, J. R. (1998). Techniques. In P. R. Bown (Ed.), *Calcareous nannofossil biostratigraphy* (pp. 16–28). London: Chapman and Kluwer Academic. https://doi.org/10.1007/978-94-011-4902-0\_2
- Calvert, S. E. (1983). Geochemistry of Pleistocene sapropels from the eastern Mediterranean. Oceanologica Acta, 6, 255-267.
- Calvert, S. E., & Fontugne, M. R. (2001). On the late Pleistocene-Holocene sapropel record of climatic and oceanographic variability in the eastern Mediterranean. *Paleoceanography*, 16(1), 78–94. https://doi.org/10.1029/1999PA000488
- Casford, J. S. L., Rohling, E. J., Abu-Zied, R. H., Fontanier, C., Jorissen, F. J., Leng, M. J., et al. (2003). A dynamic concept for eastern Mediterranean circulation and oxygenation during sapropel formation. *Palaeogeography Palaeoclimatology Palaeoecology*, 190, 103–119. https://doi.org/10.1016/S0031-0182(02)00601-6
- Castradori, D. (1993). Calcareous nannofossils and the origin of Eastern Mediterranean sapropel. Paleoceanography, 8(4), 459–471. https://doi.org/10.1029/93PA00756
- Cita, M. B., Vergnaud Grazzini, C., Robert, C., Chamley, H., Ciaranfi, N., & D'Onofrio, S. (1977). Paleoclimatic record of long deep sea core from the eastern Mediterranean. *Quaternary Research*, 8(2), 205–235. https://doi.org/10.1016/0033-5894(77)90046-1
- Crudeli, D., & Young, J. R. (2003). SEM-LM study of holococcoliths preserved in eastern Mediterranean sediments (Holocene/Late Pleistocene). Journal Nannoplankton Research, 25(1), 39–50.
- Crudeli, D., Young, J. R., Erba, E., De Lange, G. J., Henriksen, K., Kinkel, H., et al. (2004). Abnormal carbonate diagenesis in Holocene-late Pleistocene sapropel-associated sediments from the Eastern Mediterranean; Evidence from *Emiliania huxleyi* coccolith morphology. *Marine Micropaleontology*, 52(1-4), 217–240. https://doi.org/10.1016/j.marmicro.2004.04.010
- Crudeli, D., Young, J. R., Erba, E., Geisen, M., Ziveri, P., de Lange, G. J., & Slomp, C. P. (2006). Fossil record of holococcoliths and selected hetero-holococcolith associations from the Mediterranean (Holocene-late Pleistocene): Evaluation of carbonate diagenesis and palaeoecological-palaeoeconographic implications. *Palaeogeography Palaeoclimatology Palaeoecology*, 237(2–4), 191–212. https://doi.org/ 10.1016/j.palaeo.2005.11.022
- D'Ortenzio, F., & D'Alcalà, M. R. (2009). On the trophic regimes of the Mediterranean Sea: A satellite analysis. *Biogeosciences*, 6(2), 139–148. https://doi.org/10.5194/bg-6-139-2009
- D'Amario, B., Ziveri, P., Grelaud, M., Oviedo, A., & Kralj, M. (2017). Coccolithophore haploid and diploid distribution patterns in the Mediterranean Sea: Can a haplo-diploid life cycle be advantageous under climate change? *Journal of Plankton Research*, 39(5), 781–794. https://doi.org/10.1093/plankt/fbx044
- De Lange, G. J., Thomson, J., Reitz, A., Slomp, C. P., Principato, M. S., Erba, E., & Corselli, C. (2008). Synchronous basin-wide formation and redox-controlled preservation of a Mediterranean sapropel. *Nature Geoscience*, 1(9), 606–610. https://doi.org/10.1038/ngeo283
- Di Stefano, A., Foresi, L. M., Incarbona, A., Sprovieri, M., Vallefuoco, M., Iorio, M., et al. (2015). Mediterranean coccolith ecobiostratigraphy since the penultimate Glacial (the last 145,000years) and ecobioevent traceability. *Marine Micropaleontology*, 115, 24–38. https://doi.org/ 10.1016/i.marmicro.2014.12.002
- Di Stefano, E., & Incarbona, A. (2004). High-resolution palaeoenvironmental reconstruction of ODP Hole 963D (Sicily Channel) during the last deglaciation based on calcareous nannofossils. *Marine Micropaleontology*,
- 52(1-4). https://doi.org/10.1016/j.marmicro.2004.04.009
- Di Stefano, E., Incarbona, A., Bonomo, S., & Pelosi, N. (2011). Coccolithophores in water samplesand fossil assemblages in sedimentary archives of the Mediterranean Sea: A review.

Filippidi, A., Triantaphyllou, M. V., & De Lange, G. J. (2016). Eastern-Mediterranean ventilation variability during sapropel S1 formation, evaluated at two sites influenced by deep-water formation from Adriatic and Aegean Seas. *Quaternary Science Reviews*, 144, 95–106. https://doi.org/10.1016/j.quascirev.2016.05.024

Flores, J. A., Bárcena, M. A., & Sierro, F. J. (2000). Ocean-surface and wind dynamics in the Atlantic Ocean off Northwest Africa during the last 140 000 years. *Palaeogeography Palaeoclimatology Palaeoecology*, 161(3–4), 459–478. https://doi.org/10.1016/S0031-0182(00)00099-7 Giunta, S., Negri, A., Morigi, C., Capotondi, L., Combourieu-Nebout, N., Emeis, K. C., et al. (2003). Coccolithophorid ecostratigraphy and

multi-proxy paleoceanographic reconstruction in the Southern Adriatic Sea during the last deglacial time (Core AD91-17). *Palaeogeography Palaeoclimatology Palaeoecology*, 190, 39–59. https://doi.org/10.1016/S0031-0182(02)00598-9

Grant, K. M., Grimm, R., Mikolajewicz, U., Marino, G., Ziegler, M., & Rohling, E. J. (2016). The timing of Mediterranean sapropel deposition relative to insolation, sea-level and African monsoon changes. *Quaternary Science Reviews*, 140, 125–141. https://doi.org/ 10.1016/j.quascirev.2016.03.026

Hernández-Almeida, I., Ausín, B., Saavedra-Pellitero, M., Baumann, K.-H., & Stoll, H. M. (2019). Quantitative reconstruction of primary productivity in low latitudes during the last glacial maximum and the mid-to-late Holocene from a global *Florisphaera profunda* calibration dataset. *Quaternary Science Reviews*, 205, 166–181. https://doi.org/10.1016/j.quascirev.2018.12.016

Hilgen, F. J. (1991). Astronomical calibration of Gauss to Matuyama sapropels in the Mediterranean and implication for the Geomagnetic Polarity Time Scale. *Earth and Planetary Science Letters*, 104(2-4), 226–244. https://doi.org/10.1016/0012-821x(91)90206-w

Incarbona, A., & Di Stefano, E. (2018). Calcareous nannofossil palaeoenvironmental reconstruction and preservation in sapropel S1 at the Eratosthenes Seamount (Eastern Mediterranean). Deep-Sea Research Part II: Topical Studies in Oceanography, 164, 206–215. https://doi.org/10.1016/j.dsr2.2018.10.004

Incarbona, A., Ziveri, P., di Stefano, E., Lirer, F., Mortyn, G., Patti, B., et al. (2010). The impact of the Little Ice Age on coccolithophores in the central Mediterranea Sea. *Climate of the Past*, 6(6), 795-805. https://doi.org/10.5194/cp-6-795-2010

Incarbona, A., Ziveri, P., Sabatino, N., Manta, D. S., & Sprovieri, M. (2011). Conflicting coccolithophore and geochemical evidence for productivity levels in the Eastern Mediterranean sapropel S1. *Marine Micropaleontology*, 81(3–4), 131–143. https://doi.org/10.1016/j. marmicro.2011.09.003

Jordan, R. W., Cros, L., & Young, J. R. (2004). A revised classification scheme for living haptophytes, edited by M. V Triantaphyllou. *Micropaleontology*, 50(Suppl\_1), 55–79. https://doi.org/10.2113/50.Suppl\_1.55

Jorissen, F. J., Asioli, A., Borsetti, A. M., Capotondi, L., de Visser, J. P., Hilgen, F. J., et al. (1993). Late Quaternary central Mediterranean biochronology. *Marine Micropaleontology*, 21(1–3), 169–189. https://doi.org/10.1016/0377-8398(93)90014-O

Josey, S. A., Somot, S., & Tsimplis, M. (2011). Impacts of atmospheric modes of variability on Mediterranean Sea surface heat exchange. Journal of Geophysical Research, 116, C02032. https://doi.org/10.1029/2010JC006685

Kemp, A. E. S., Pearce, R. B., Koizumi, I., Pike, J., & Rance, S. J. (1999). The role of mat-forming diatoms in the formation of Mediterranean sapropels. *Nature*, 398(6722), 57–61. https://doi.org/10.1038/18001

Kleijne, A. (1991). Holococcolithophorids from the Indian-Ocean, Red-Sea, Mediterranean-Sea and North-Atlantic Ocean. Marine Micropaleontology, 17(1–2), 1–76. https://doi.org/10.1016/0377-8398(91)90023-Y

Klein, P., & Coste, B. (1984). Effects of wind-stress variability on nutrient transport into the mixed layer. Deep-Sea Research Part I: Oceanographic Research Papers, 31(1), 21–37. https://doi.org/10.1016/0198-0149(84)90070-0

Knappertsbusch, M. (1993). Geographic distribution of living and Holocene coccolithophores in the Mediterranean Sea. Marine Micropaleontology, 21(1–3), 219–247. https://doi.org/10.1016/0377-8398(93)90016-Q

Krom, M. D., Emeis, K. C., & Van Cappellen, P. (2010). Why is the Eastern Mediterranean phosphorus limited? Progress in Oceanography, 85(3-4), 236–244. https://doi.org/10.1016/j.pocean.2010.03.003

Krom, M. D., Kress, N., Brenner, S., & Gordon, L. I. (1991). Phosphorus limitation of primary productivity in the eastern Mediterranean-Sea. Limnology and Oceanography, 36(3), 424–432. https://doi.org/10.4319/lo.1991.36.3.0424

Kuhnt, T., Schmiedl, G., Ehrmann, W., Hamann, Y., & Hemleben, C. (2007). Deep-sea ecosystem variability of the Aegean Sea during the past 22 kyr as revealed by Benthic Foraminifera. *Marine Micropaleontology*, 64(3-4), 141–162. https://doi.org/10.1016/j. marmicro.2007.04.003

Malanotte-Rizzoli, P., Artale, V., Borzelli-Eusebi, G. L., Brenner, S., Crise, A., Gacic, M., et al. (2014). Physical forcing and physical/biochemical variability of the Mediterranean Sea: A review of unresolved issues and directions for future research. Ocean Science, 10(3), 281–322. https://doi.org/10.5194/os-10-281-2014

Malanotte-Rizzoli, P., & Hecht, A. (1988). Large-scale properties of the eastern Mediterranean: a review. Oceanologica Acta, 46(6-7), 1199–1235. https://doi.org/10.1016/S0967-0645(99)00020-X

McIntyre, A., & Molfino, B. (1996). Forcing of Atlantic equatorial and subpolar millennial cycles by precession. Science, 274(5294), 1867–1870. https://doi.org/10.1126/science.274.5294.1867

Meier, K. J. S. (2004). Different nutrient sources forcing increased productivity during eastern Mediterranean S1 sapropel formation as reflected by calcareous dinoflagellate cysts. *Paleoceanography*, *19*, PA1012. https://doi.org/10.1029/2003PA000895

Mercone, D., Thomson, J., Abu-Zied, R. H., Croudace, I. W., & Rohling, E. J. (2001). High-resolution geochemical and micropalaeontological profiling of the most recent eastern Mediterranean sapropel. *Marine Geology*, 177(1–2), 25–44. https://doi.org/10.1016/S0025-3227 (01)00122-0

Millot, C. (1999). Circulation in the western Mediterranean Sea. Journal of Marine Systems, 20(1-4), 423-442. https://doi.org/10.1016/S0924-7963(98)00078-5

Möbius, J., Lahajnar, N., & Emeis, K. C. (2010). Diagenetic control of nitrogen isotope ratios in Holocene sapropels and recent sediments from the Eastern Mediterranean Sea. *Biogeosciences*, 7(11), 3901–3914. https://doi.org/10.5194/bg-7-3901-2010

Molfino, B., & McIntyre, A. (1990a). Nutricline variation in the equatorial Atlantic coincident with the Younger Dryas. Paleoceanography, 5(6), 997–1008. https://doi.org/10.1029/PA005i006p00997

Molfino, B., & McIntyre, A. (1990b). Precessional forcing of nutricline dynamics in the equatorial atlantic. *Science*, 249(4970), 766–769. https://doi.org/10.1126/science.249.4970.766

Osborne, A. H., Vance, D., Rohling, E. J., Barton, N., Rogerson, M., & Fello, N. (2008). A humid corridor across the Sahara for the migration of early modern humans out of Africa 120,000 years ago. Proceedings of the National Academy of Sciences of the United States of America, 105(43), 16,444–16,447. https://doi.org/10.1073/pnas.0804472105

Oviedo, A., Ziveri, P., Álvarez, M., & Tanhua, T. (2015). Is coccolithophore distribution in the Mediterranean Sea related to seawater carbonate chemistry? Ocean Science, 11(1), 13–32. https://doi.org/10.5194/os-11-13-2015

Paulmier, A., Ruiz-Pino, D., & Garçon, V. (2011). CO<sub>2</sub> maximum in the oxygen minimum zone (OMZ). *Biogeosciences*, 8(2), 239–252. https://doi.org/10.5194/bg-8-239-2011 Pinardi, N., & Masetti, E. (2000). Variability of the large scale general circulation of the Mediterranean Sea from observations and modelling: A review. *Palaeogeography Palaeoclimatology Palaeoecology*, 158(3–4), 153–173. https://doi.org/10.1016/S0031-0182(00)00048-1
 POEM group (1992). General-circulation of the eastern Mediterranean. *Earth Science Reviews*, 32(4), 285–309. https://doi.org/10.1016/0012-8252(92)90002-B

Principato, M. S., Crudeli, D., Ziveri, P., Slomp, C. P., Corselli, C., Erba, E., & de Lange, G. J. (2006). Phyto- and zooplankton paleofluxes during the deposition of sapropel S1 (eastern Mediterranean): Biogenic carbonate preservation and paleoecological implications. *Palaeogeography Palaeoclimatology Palaeoecology*, 235(1–3), 8–27. https://doi.org/10.1016/j.palaeo.2005.09.021

Principato, M. S., Giunta, S., Corselli, C., & Negri, A. (2003). Late Pleistocene-Holocene planktonic assemblages in three box-cores from the Mediterranean Ridge area (west-southwest of Crete): Palaeoecological and palaeoceanographic reconstruction of sapropel S1 interval. *Palaeogeography Palaeoclimatology Palaeoecology*, 190, 61–77. https://doi.org/10.1016/S0031-0182(02)00599-0

Robinson, A. R., Sellschopp, J., Warn-Varnas, A., Leslie, W. G., Lozano, C. J., Haley, P. J., et al. (1999). The Atlantic Ionian stream. Journal of Marine Systems, 20(1–4), 129–156. https://doi.org/10.1016/S0924-7963(98)00079-7

Rohling, E. J., Cane, T. R., Cooke, S., Sprovieri, M., Bouloubassi, I., Emeis, K. C., et al. (2002). African monsoon variability during the previous interglacial maximum. *Earth and Planetary Science Letters*, 202(1), 61–75. https://doi.org/10.1016/S0012-821X(02)00775-6

Rohling, E. J., & Gieskes, W. W. (1989). Late Quaternary changes in Mediterranean intermediate water density and formaton rate. Paleoceanography, 4(5), 531-545. https://doi.org/10.1029/PA004i005p00531

Rohling, E. J., Hopmans, E. C., & Damsté, J. S. S. (2006). Water column dynamics during the last interglacial anoxic event in the Mediterranean (sapropel S5). *Paleoceanography*, 21, PA2018. https://doi.org/10.1029/2005PA001237

Rohling, E. J., Jorissen, F. J., & De Stigter, H. C. (1997). 200 Year interruption of Holocene sapropel formation in the Adriatic Sea. Journal of Micropalaeontology, 16(2), 97–108. https://doi.org/10.1144/jm.16.2.97

Rohling, E. J., Marino, G., & Grant, K. M. (2015). Mediterranean climate and oceanography, and the periodic development of anoxic events (sapropels). Earth Science Reviews, 143, 62–97. https://doi.org/10.1016/j.earscirev.2015.01.008

- Rohling, E. J., Marino, G., Grant, K. M., Mayewski, P. A., & Weninger, B. (2019). A model for archaeologically relevant Holocene climate impacts in the Aegean-Levantine region (easternmost Mediterranean). *Quaternary Science Reviews*, 208, 38–53. https://doi.org/10.1016/j. quascirev.2019.02.009
- Rohling, E. J., Sprovieri, M., Cane, T., Casford, J. S. L., Cooke, S., Bouloubassi, I., et al. (2004). Reconstructing past planktic foraminiferal habitats using stable isotope data: A case history for Mediterranean sapropel S5. *Marine Micropaleontology*, *50*(1–2), 89–123. https://doi. org/10.1016/S0377-8398(03)00068-9

Rossignol-Strick, M., Nesteroff, W., Olive, P., & Vergnaud-Grazzini, C. (1982). After the deluge: Mediterranean stagnation and sapropel formation. *Nature*, 295(5845), 105–110. https://doi.org/10.1038/295105a0

Schmiedl, G., Kuhnt, T., Ehrmann, W., Emeis, K.-C., Hamann, Y., Kotthoff, U., et al. (2010). Climatic forcing of eastern Mediterranean deep-water formation and benthic ecosystems during the past 22 000 years. *Quaternary Science Reviews*, 29(23-24), 3006–3020. https:// doi.org/10.1016/j.quascirev.2010.07.002

Schneider, A., Wallace, D. W. R., & Körtzinger, A. (2007). Alkalinity of the Mediterranean Sea. *Geophysical Research Letters*, 34, L15608. https://doi.org/10.1029/2006GL028842

Stoll, H. M., Arevalos, A., Burke, A., Ziveri, P., Mortyn, G., Shimizu, N., & Unger, D. (2007). Seasonal cycles in biogenic production and export in Northern Bay of Bengal sediment traps. Deep-Sea Research Part II: Topical Studies in Oceanography, 54(5–7), 558–580. https:// doi.org/10.1016/j.dsr2.2007.01.002

Stratford, K., Williams, R. G., & Myers, P. G. (2000). Impact of the circulation on Sapropel Formation in the eastern Mediterranean. Global Biogeochemical Cycles, 14(2), 683–695. https://doi.org/10.1029/1999GB001157

Ten Haven, H. L., De Lange, G. J., & McDuff, R. E. (1987). Interstitial water studies of Late Quaternary Eastern Mediterranean sediments with emphasis on early diagenetic reactions and evaporitic salt influences. *Marine Geology*, 75(1-4), 119–136. https://doi.org/10.1016/0025-3227(87)90099-5

Tesi, T., Asioli, A., Minisini, D., Maselli, V., Dalla Valle, G., Gamberi, F., et al. (2017). Large-scale response of the Eastern Mediterranean thermohaline circulation to African monsoon intensification during sapropel S1 formation. *Quaternary Science Reviews*, 159, 139–154. https://doi.org/10.1016/j.quascirev.2017.01.020

Thomson, J., Crudeli, D., De Lange, G. J., Slomp, C. P., Erba, E., Corselli, C., & Calvert, S. E. (2004). Florisphaera profunda and the origin and diagenesis of carbonate phases in eastern Mediterranean sapropel units. *Paleoceanography*, 19, PA3003. https://doi.org/10.1029/ 2003PA000976

- Thomson, J., Mercone, D., De Lange, G. J., & Van Santvoort, P. J. M. (1999). Review of recent advances in the interpretation of eastern Mediterranean sapropel S1 from geochemical evidence. *Marine Geology*, 153(1-4), 77-89. https://doi.org/10.1016/S0025-3227(98)00089-9
- Triantaphyllou, M. V., Antonarakou, A., Dimiza, M. D., & Anagnostou, C. (2010). Calcareous nannofossil and planktonic foraminiferal distributional patterns during deposition of sapropels S6, S5 and S1 in the Libyan Sea (Eastern Mediterranean). Geo-Marine Letters, 30(1), 1–13. https://doi.org/10.1007/s00367-009-0145-7
- Triantaphyllou, M. V., Antonarakou, A., Kouli, K., Dimiza, M., Kontakiotis, G., Papanikolaou, M. D., et al. (2009). Late Glacial-Holocene ecostratigraphy of the south-eastern Aegean Sea, based on plankton and pollen assemblages. *Geo-Marine Letters*, 29(4), 249–267. https:// doi.org/10.1007/s00367-009-0139-5

Triantaphyllou, M. V., Gogou, A., Dimiza, M. D., Kostopoulou, S., Parinos, C., Roussakis, G., et al. (2016). Holocene Climatic Optimum centennial-scale paleoceanography in the NE Aegean (Mediterranean Sea). *Geo-Marine Letters*, 36(1), 51–66. https://doi.org/10.1007/ s00367-015-0426-2

Triantaphyllou, M. V., Ziveri, P., Gogou, A., Marino, G., Lykousis, V., Bouloubassi, I., et al. (2009). Late Glacial-Holocene climate variability at the south-eastern margin of the Aegean Sea. *Marine Geology*, 266(1–4), 182–197. https://doi.org/10.1016/j.margeo.2009.08.005

Van Santvoort, P. J. M., De Lange, G. J., Thomson, J., Cussen, H., Wilson, T. R. S., Krom, M. D., & Ströhle, K. (1996). Active post-depositional oxidation of the most recent sapropel (S1) in sediments of the eastern Mediterranean Sea. *Geochimica et Cosmochimica Acta*, 60(21), 4007–4024. https://doi.org/10.1016/S0016-7037(96)00253-0

Vink, A. (2004). Calcareous dinoflagellate cysts in South and equatorial Atlantic surface sediments: diversity, distribution, ecology and potential for palaeoenvironmental reconstruction. *Marine Micropaleontology*, 50(1-2), 43–88. https://doi.org/10.1016/S0377-8398(03) 00067-7

Young, J. R. (1994). Functions of coccoliths. In A. Winter, & W. G. Siesser (Eds.), Coccolithophores (pp. 63–82). Cambridge: Cambridge Univ. Press.

Young, J. R., Geisen, M., Cros, L., Kleijne, A., Sprengel, C., Probert, I., & Østergaard, J. (2003). A guide to extant coccolithophore taxonomy. Journal Nannoplankton Research, 1, 1–125. Ziveri, P., Rutten, A., De Lange, G. J., Thomson, J., & Corselli, C. (2000). Present-day coccolith fluxes recorded in central eastern Mediterranean sediment traps and surface sediments. *Palaeogeography Palaeoclimatology Palaeoecology*, 158(3–4), 175–195. https://doi. org/10.1016/S0031-0182(00)00049-3

Ziveri, P., & Thunell, R. C. (2000). Coccolithophore export production in Guaymas Basin, Gulf of California: response to climate forcing. Deep-Sea Research Part II, 47(9–11), 2073–2100. https://doi.org/10.1016/S0967-0645(00)00017-5