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Eastern-Mediterranean ventilation variability during sapropel S1 formation, evaluated at two sites influenced by deep-water formation from Adriatic and Aegean Seas

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A B S T R A C T

Present-day bottom-water ventilation in the Eastern Mediterranean basin occurs through deep-water convection originating from the two marginal basins, i.e. Adriatic and Aegean Seas. In the paleo record, long periods of enhanced deep-water formation have been alternating with shorter periods of reduced deep-water formation. The latter is related mainly to low-latitude humid climate conditions and the enhanced deposition and preservation of organic-rich sediment units (sapropels). This study focuses on sedimentary archives of the most-recent sapropel S1, retrieved from two sites under the direct influence of the two deep-water formation areas. Restricted oxygen conditions have developed rapidly at the beginning of S1 deposition in the Adriatic site, but bottom-water conditions have not persistently remained anoxic during the full interval of sapropel deposition. In fact, the variability in intensity and persistence of sedimentary redox conditions at the two deep-water formation sites is shown to be related to brief episodes of climate cooling. In the Adriatic site, sapropel deposition appears to have been interrupted twice. The 8.2 ka event, only recovered at the Adria site, is characterized by gradually increasing suboxic to possibly intermittently oxic conditions and decreasing C_{org} fluxes, followed by an abrupt re-establishment of anoxic conditions. Another important event that disrupted sapropel S1 formation, has taken place at ca. 7.4 cal ka BP. The latter event has been recovered at both sites. In the Adriatic site it is followed by a period of sedimentary conditions that gradually change from suboxic to more permanently oxic, as deduced from the Mn/Al pattern. Using the same proxy for suboxic/oxic sedimentary redox conditions, we observe that conditions in the Aegean Sea site shift to more permanently oxic from the 7.4 ka event onwards. However, at both sites the accumulation and preservation of enhanced amounts of organic matter have continued under these suboxic to intermittently oxic sedimentary conditions. It seems thus, that after 7.4 cal ka BP sapropel-like surface or deep-chlorophyll-maximum conditions including enhanced productivity continued, whereas bottom-water conditions were at least intermittently oxic. The latter is related to decreasing precipitation, i.e. run-off, and thus a progressive development and deepening of deep-water formation. The shallower Aegean site, would be affected earlier by such deepening ventilation than the slightly deeper Adriatic site. Finally, termination of sapropel S1 formation as deduced from diminished organic matter contents and Ba/Al, appears to have occurred almost simultaneously in the two areas, namely at 6.6 ± 0.3 and 6.3 ± 0.5 cal ka BP in Adriatic and Aegean sites, respectively.

1. Introduction

1.1. Circulation in the Mediterranean Sea

The present-day Eastern Mediterranean is a well-ventilated and oligotrophic system [Bethoux, 1989; Wu and Haines, 1996] following a density-driven, anti-estuarine circulation pattern. The

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low-latitude climate-related excess evaporation and mid-latitude originating cold spells result in frequent deep-water formation. This occurs in the two northern-most marginal seas of the Eastern Mediterranean, i.e. the Adriatic and Aegean Seas [Schlitzer et al., 1991]. In view of this subtle interaction between two climate zones, the Mediterranean region is one of the most suitable areas for high-resolution paleoclimatic studies. Its geographic and oceanographic setting contributes to the enhanced imprint and preservation of climatic perturbations associated with mid- and low-latitude climate conditions.

1.2. Deposition of sapropel S1

Periods of precession minima/insolation maxima are characterized by increased humid conditions associated with the intensification of N. African monsoonal activity [Rossignol-Strick, 1985; Hilgen, 1991]. It is only during these humid periods that distinctly organic-rich units, called sapropels, have been deposited and preserved basin wide in a repetitive pattern [Olausson, 1961; Kidd et al., 1978; Emeis and Shipboard Scientific Party, 1996; Emeis et al., 1998].

Deposition of the most-recent sapropel S1 coincides with the development of the Last African Humid phase [De Menocal et al., 2000]. Lower surface-water salinity and relatively warm winter conditions are thought to have led to the restriction of deep-water formation [Aksu et al., 1995; Emeis et al., 1998; Rohling et al., 2015]. In addition, the enhanced pluvial conditions have promoted nutrient input by the borderlands' rivers [Rossignol-Strick, 1985; Rohling and Hilgen, 1991; Mélières et al., 1997], and may thus have resulted in elevated primary productivity and organic matter fluxes to the sea floor. The higher oxygen demand for the decomposition of surplus organic matter and the restricted circulation are considered to have further sustained lower oxygen levels in the deep water column and at the sediment/water interface. This must have contributed to the enhanced preservation of organic matter [e.g. Reed et al., 2011].

Despite the numerous multi-disciplinary studies, the exact mechanism for sapropel formation is still debated. There is, however, a widely accepted consensus that elevated primary productivity and reduced oxygen conditions must both have been prerequisites for sapropel formation and preservation [e.g. De Lange and Ten Haven, 1983; Rohling and Gieskes, 1989; Emeis et al., 1991; De Rijk et al., 1999; Calvert and Fontugne, 2001; Moodley et al., 2005]. The latter is related to the intensity of deep-water formation, i.e. redox conditions.

1.3. Trace metals and redox conditions

The sapropelic layers exhibit a distinct geochemical composition that reflects the redox sedimentary conditions as well as the increased levels of primary productivity. The characteristic enrichments of S, Fe and redox-sensitive elements such as V, Mo and Cu in sapropelic layers imply that low oxygen or even anoxic conditions must have been established at the sediment/water interface [e.g. Calvert, 1983; Pruysers et al., 1991; Passier et al., 1997; Jilbert et al., 2010]. Conversely, manganese appears to be commonly depleted in the sapropel sediments. This is due to its mobilization, under suboxic to anoxic conditions [Mangini et al., 2001]. This is thought to have resulted in enhanced fluxes of dissolved Mn^{2+} to the bottom waters and to its re-precipitation as solid phase manganese-oxides under oxygenated conditions [De Lange et al., 1989; Pruysers et al., 1993; Van Santvoort et al., 1996; Thomson et al., 1999; Reitz et al., 2006a; Ni Fhlaitherta et al., 2010].

The elevated Ba concentrations in sapropel layers have been linked to the excess amount of organic matter exported from the surface water and hence are considered as a reliable paleoproductivity proxy for this environment [Van Santvoort et al., 1996; Thomson et al., 1999; Martinez-Ruiz et al., 2000; Paytan et al., 2004; Jilbert et al., 2010]. Furthermore, in the Mediterranean, Ba preservation is usually not affected by diagenetic mobilization, thus Ba/Al can be used to determine the initial sapropel extent [Van Santvoort et al., 1996; Reitz et al., 2006a; De Lange et al., 2008].

Another well-described feature of the most-recent S1 sapropel in particular, is the distinct dark-brown layer, "marker bed", often present above it [Murat and Got, 1987; De Lange et al., 1989; Pruysers et al., 1993; Thomson et al., 1995; Van Santvoort et al., 1996; Reitz et al., 2006a]. This manganese-rich layer depicts the re-oxygenation event of the water column and sediments at the end of sapropel formation, i.e. the onset of regular deep-water ventilation [Van Santvoort et al., 1996; De Lange et al., 1999; Reitz et al., 2006a; De Lange et al., 2008]. Depending on bioturbation and sedimentation rates, it is possible that after the re-oxygenation of the bottom-water, excess oxygen may have diffused downward into the sapropelic sediments and has degraded the organic matter from the upper part of the sapropel. This so-called post-depositional oxidation front is commonly observed for sapropel S1 [De Lange et al., 1989; Pruysers et al., 1993; Higgs et al., 1994; Van Santvoort et al., 1996; Passier et al., 1996].

1.4. Deep-water formation

Present-day eastern Mediterranean deep-water formation is determined by low- and mid-latitude induced enhanced evaporation and surface-water cooling [Theocharis and Georgopoulos, 1993; Pinardi and Masetti, 2000]. In addition, local, internal thermohaline variability may play a role [Krokos et al., 2014]. This may be modulated by the inflow of riverine water from northern borderlands, e.g. Po river to Adriatic Sea [Artegiani et al., 1997], Axios river and Black-Sea to N. Aegean Sea [Poulos et al., 1997; Velaoras et al., 2013]. Enhanced evaporation leads to Levantine Intermediate Water (LIW) formation; the latter flowing also into the Adriatic and Aegean basins, may upon sustained northern-borderland winter-cooling lead to enhanced densification, ultimately resulting in deep-water formation. The onset of the Holocene and subsequently the humid climate period resulted in sea surface water with enhanced temperature and reduced salinity, both of which contributed to the formation of reduced-density LIW. At the same time, for the northern borderlands, increased precipitation and possibly deglaciation resulted in enhanced river run-off to the Adriatic and Aegean Seas, lowering the density of surface water even more. In combination with the more general absence of persistent cooling periods in the northern borderlands, i.e. Bora in Adriatic Sea, and Vardar in Aegean, densification was mostly insufficient for deep-water formation. However, a few distinct but brief, cold episodes have occurred (see below). Sapropels have been deposited during humid climate conditions alone. Evidently, during periods of sapropel deposition, deep-water formation has been ceased and anoxic conditions have been established in the deep waters and at the sediment/water interface. However, the enhanced regeneration of sedimentary phosphate [Slomp et al., 2002, 2004] and the high accumulation of trace metals [Nijenhuis et al., 1999] indicate that the Mediterranean circulation, albeit diminished, must have persisted during this period.

The occurrence of short episodes of climate deterioration coincident with the temporal re-ventilation of bottom waters has been reported for land [e.g. Bar-Matthews et al., 2000, 2003; Pross et al., 2009; Peyron et al., 2011] and for marine records [e.g. Rohling et al., 1997; De Rijk et al., 1999; Ariztegui et al., 2000; Mercone et al., 2001; Casford et al., 2003; Gogou et al., 2007; Piva et al., 2008; Siani et al., 2013; Triantaphyllou et al., 2016]. During sapropel S1 formation such an event has been identified at 8.2 ka BP. It is thought to have resulted in the temporary resumption of bottom-water formation and cessation of sapropel formation. Its occurrence has been linked to a cool outbreak from the Siberia High [Rohling and Palike, 2005] in response to a northern Hemisphere widespread cooling [Alley et al., 1997; Mayewski et al., 2004]. This underlines the impact of the northern climate system to deep-water formation and ventilation of the Mediterranean [Rohling et al., 2002].

In view of this eminent importance of deep-water formation for the basin-wide ventilation, and for the preservation of sedimentary components, two intermediate-depth cores were retrieved from two sites under the direct influence of the two deep-water formation areas, i.e. Adriatic and Aegean Seas (Fig. 1). These cores have been studied in high resolution, so as to detect relationships and mechanisms that lead to onset and interruption of deep-water ventilation. We focus in particular on the sapropel S1 stagnation period, its onset, interruptions, and ending, and link these to global climate records.

2. Material & methods

2.1. Material

Two high-sedimentation-rate cores were used in this study; a 3.18 m long gravity core (KN3) from south of Kos island (27°12.03′E, 36°40.60′N, water depth 607 m) collected in 2008 by R/V Aegaeo, and a 4.73 m piston core (MP50PC) recovered during the Macchiato cruise in 2009 from immediately south of the western Otranto Strait sill (South Adriatic Sea). (39N29′, 18E31′, water depth 775 m) (Fig. 1). Both cores were sampled and analyzed at 0.5 cm resolution. Distinctly dark layers were recognized in both cores, representing sapropel S1, at depth 155–198 cm in KN3 core and 19–55 cm in MP50PC core.

2.2. Methods

All samples were split in two aliquots, one for micropaleontological and one for geochemical analyses. The former set of samples was washed and sieved and the samples from the latter were freeze-dried and ground in an agate mortar. For the construction of the age model, nine accelerator mass spectrometry (AMS) radiocarbon ^{14}C were performed at Poznan Radiocarbon Laboratory, Poland, and one at Beta Analytic Radiocarbon Dating, Florida USA using clean planktonic foraminifera hand-picked from the >63 μm size fraction. All other analyses were performed at Utrecht University laboratory facilities.

2.2.1. TOC

Organic C was determined using a Fisons NA 1500 CNS elemental analyzer. Inorganic C was removed prior to the analysis by reacting samples with 1 M HCl twice (4 and 12 h). The samples were then rinsed two times with demineralized water, dried at ~60 °C, and ground in an agate mortar. In-house and international standards were used and the average standard deviation of all measurements was <1%.

2.2.2. Elemental concentrations

An average of 125 mg of sediment was dissolved using 2.5 ml of HF (40%) and a pre-mixed acid ($HClO_4$ 45.5% and HNO_3 16.25%) in closed teflon vessels and heated at 90 °C for 12 h. Subsequently, the lid was removed and samples were evaporated at 160 °C and subsequently dissolved in 25 ml 1 M HNO_3 (Reitz et al., 2006a). Major and minor element concentrations were determined using an Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) using radial view measurements. The accuracy of the measurements was monitored by including international and in-house standards and several samples in duplicate. The standard deviation for all measurements was less than 3%. The elemental concentrations are normalized to Al in order to minimize carbonate-dilution effects.

3. Results

3.1. Age model and sedimentation rates

Conventional ^{14}C ages were calibrated using the program CALIB 6.0 (Marine 09) [Stuiver and Reimer, 1993; Stuiver et al., 1998] with a regional reservoir age correction (ΔR) for Aegean Sea core of 149 ± 30 yrs for the sapropel interval [Facorellis et al., 1998] and 58 ± 85 outside the sapropel [Reimer and McCormac, 2002], and 118 ± 60 yrs for the Adriatic Sea core (Table 1) [Reimer and McCormac, 2002]. Due to high amounts of tephra present in the 46.5–48.0 cm interval in the Adriatic site (MP50PC), the age model was constructed by interpolation between dated points (Fig. 2). The tephra components, in the 46.5–48.0 cm interval, belong to two different sources; the lower and most abundant one originated from Mercato eruption [Cioni et al., 1999, 2008] of Somma- Vesuvius and the upper one from E1/Fiumebianco-Gabellotto eruption from Lipari island (D. Insinga pers. commun.). The interpolated age assessment of our tephra layer falls within the age range suggested, i.e. 9680 ± 480 cal. BP [Wulf et al., 2004, 2008] and 8500 ± 100 cal ka BP [Zanchetta et al., 2011], but due to the large uncertainty of the exact age of the events, these can only be used to confirm the age model. Tephra is the dominant fraction in these samples, therefore all other sediment components are "diluted". This leads to low concentrations for C_{org}, $CaCO_3$ and trace metals and to enhanced elemental concentrations for tephra-related elements, e.g. Ti, Zr. In this core the dark-coloured organic-rich layer spans between 10.2 ± 0.3 to 6.6 ± 0.3 cal ka BP (Fig. 2).

In the Aegean Sea core (KN3), the ash layer from the precisely dated Santorini eruption (Z2; 1601–1625 B.C. Friedrich et al., 2006) was recognized by its geochemical signal [Reitz et al., 2006b] and used as an additional age marker at depth 75.8 cm. In this core, the interval below 200 cm (~8.2 cal ka BP) is thought to be related to a slump (i.e. deviating elemental concentrations and poor preservation of planktonic foraminifera). Thus the sapropel interval recovered in this core, extends from 8.2 to 6.3 ± 0.5 cal ka BP. The multiple radiocarbon dating points and the consistent fit to a steady sedimentation rate as well as visual and texture-related observations ensure that no other slumps or hiatuses have affected the sedimentary record in the reported S1 interval. The ^{14}C data indicate a nearly linear relation between age and depth of the sediment (Fig. 3).

Sedimentation rates were calculated for the South Adriatic site during S1 to be ~10.2 cm/kyr and for the South Aegean Sea site ~27.3 cm/kyr. The resulting sample resolution is 50 and 18 yrs for the S. Adriatic and S. Aegean sediments, respectively. Hereafter all ages are discussed in cal. ka BP.

3.2. Geochemical data

In both cores, during the sapropel interval TOC (%) is up to 3 times higher than in the adjacent marls. At the end of the sapropel layer organic carbon content returns to low values that are characteristic for Eastern-Mediterranean sediments.

In core MP50PC, the shape of the Ba/Al profile is identical to that of TOC (%). Two distinctly depleted intervals in both profiles can be distinguished at 9.2 and 8.3 cal ka BP. The disruption of the record at 9.2 cal ka BP coincides with the tephra interval and is rather short

Fig. 1. Central Mediterranean with the two cores used in this study. MP50PC and KN3 are located under the direct influence of the two Deep-water formation areas, resp. the Adriatic and Aegean Sea.

and abrupt. The overall trend is towards lower values at ~8.3 cal ka BP. Almost the same high values are observed before and after the 8.3 cal ka BP interruption. The TOC and Ba/Al values both start to decline at 7.4 cal ka BP and progressively return to background values at 6.6 cal ka BP (Fig. 4).

Redox-sensitive elements, such as V, Mo, and Cu, as well as Fe and S, exhibit variations similar to those of TOC and Ba/Al profiles. These elements respond also to the 8.3 cal ka BP interrupt and start to reduce gradually (e.g. V) or rapidly (e.g. Mo), shortly after 7.4 cal ka BP (Fig. 4).

During the sapropel interval, the Mn/Al profile appears slightly depleted but exhibits two peaks, a more prominent one at 8.2 cal ka BP and a smaller one at 7.4 cal ka BP. In addition, the end of the sapropel is marked by a pronounced enrichment in the Mn/Al values.

For the S. Aegean core KN3, the recovered part of sapropel S1 corresponds to the so called S1b, upper sapropel interval [Rohling et al., 1997; De Rijk et al., 1999]. During this interval, Ba/Al and TOC profiles are enhanced and exhibit distinct, short-term variability, with identical patterns (Fig. 5). Likewise, redox-sensitive elements such as V and Mo, although not considerably enriched, co-vary with Ba/Al and TOC within the sapropel, while Fe and S exhibit slightly higher concentrations, and return simultaneously to background values, at ~6.3 cal ka BP. Furthermore, the Mn/Al content is somewhat depleted during the sapropel interval and a prominent two-lobe high peak is observed between 7.4 and 7.2 cal ka BP reaching values up to 10 times the background value (Fig. 5).

4. Discussion

The two cores of this study have been retrieved from intermediate water depths (i.e. typical LIW water depths), from locations known to be under the direct influence of the Eastern Mediterranean deep-water formation areas. MP50PC was collected immediately south from the western-part of Otranto Strait. Thus site MP50PC belongs geographically to the N.Ionian Sea, but is situated under the direct influence of the Adriatic Deep Water outflow. Consequently, from hereon we will refer to this site as ‘Adriatic site’, whereas KN3, recovered from the South Aegean Sea, will be referred to as ‘Aegean site’. Their high-sedimentation rates are expected to record and preserve even small repulses of deep-water formation. In this study we focus on sapropel S1 deposits alone.

4.1. Paleoproductivity and preservation of organic matter

For non-sapropel sediments, the low organic-carbon contents observed in the studied cores are consistent with the oligotrophic state of the basin [Bethoux, 1989]. For both cores, Ba/Al ratio and C_{org} content are noticeably elevated within the sapropel S1 interval, as a result of enhanced accumulation and preservation of organic carbon fluxes at the sea floor, i.e. sapropel-like conditions. The close co-variation of Ba/Al ratio and TOC (%) and the concomitant return to background values at the end of S1 denote that no appreciable post-depositional oxidation front has affected the upper part of the organic-rich layer. Thus, the enhanced organic carbon interval represents the full initial sapropel extent for these cores [e.g. De Lange et al., 1989; Thomson et al., 1995, 1999; Van Santvoort et al., 1996; Martinez-Ruiz et al., 2000]. Presumably rapid burial of organic matter due to the high-sedimentation rates has enhanced preservation and prevented potential post-depositional oxidation.

In the following sections, we will first evaluate the general sapropel vs. non-sapropel conditions. Subsequently, we will focus on the rapid changes of the upper boundary, and then on the variability within the sapropel period.

4.2. Sedimentary redox conditions (sapropel vs. non-sapropel)

Although there are several definitions used in the literature to describe environmental redox-conditions, in this paper we use the following: ‘Anoxic’ conditions are largely used to describe the

Table 1
Samples in cores MP50PC and KN3 with 14C ages and reservoir age corrections; Used reservoir age corrections for all dating point is ~400 years (included in calibration program Marine 09); a-f: additional regional reservoir age correction for Adriatic Sea ΔR = 118 ± 60 (Reimer and McCormac, 2002), and h-k: for Aegean core KN3 core ΔR = 149 ± 30 years for sapropel interval (Facorellis et al., 1998) and 58 ± 85 outside the sapropel (Reimer and McCormac, 2002). g:* Santorini ash layer (Friedrich et al., 2006).

	Sample	av. depth (cm)	14C age (BP) ±1σ error (yr)	ΔR (yr)	1σ age cal BP (yr)
a	MP50PC#5 5.0–5.5	5.2	3700 ± 30	118 ± 60	3394–3554
b	MP50PC#5 19.5–20.0	19.7	6265 ± 35	118 ± 60	6488–6658
c	MP50PC#5 39.0–39.5	39.2	8020 ± 40	118 ± 60	8291–8440
d	MP50PC#5 48.5–49.0	48.7	8670 ± 50	118 ± 60	9074–9295
e	MP50PC#5 57.0–57.5	57.2	9540 ± 50	118 ± 60	10 181–10 3633
f	MP50PC#4 36.5–37.0	111.7	17 930 ± 90	118 ± 60	20 836–21 1822
g	KN3 75.5	75.7*			3563
h	KN3 118-121	119.5	4980 ± 40	58 ± 85	5072–5349
i	KN3 149-152	150.5	6070 ± 40	149 ± 30	6284–6384
j	KN3 163-165	164	6760 ± 40	149 ± 30	7078–7218
k	KN3 181-184	182.5	7040 ± 50	149 ± 30	7342–7460

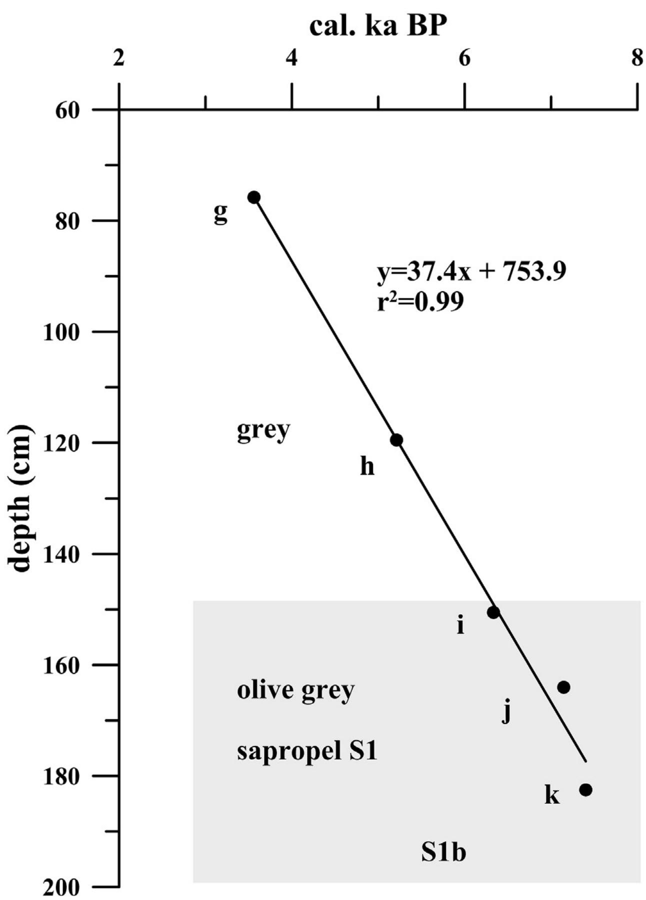

Fig. 2. General sediment description and age model for Adriatic-influenced core MP50PC (for a-f, see Table 1).

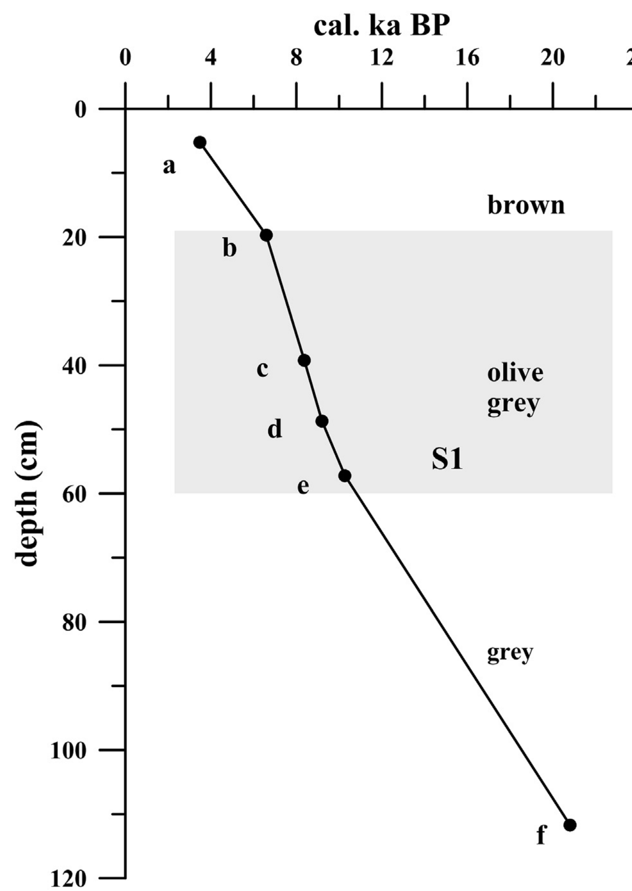

Fig. 3. General sediment description and age model for Aegean KN3 core (For g-k, see Table 1).

complete lack of dissolved oxygen and the presence of sulphide in the water. 'Suboxic' conditions are usually referring to reducing conditions but without the necessary complete lack of dissolved oxygen, but require the presence of additional electron acceptors (such as Mn(IV) and Fe(III)) [e.g. Yakushev and Newton, 2013 and references therein]. 'Intermittently oxic' conditions signify the sporadic oxygenation of the bottom waters, whereas 'oxic' conditions suggest the more continuous presence of dissolved oxygen in the water.

In the absence of considerable diagenetic alteration in the sediments of this study, enrichments observed in redox-sensitive elements are considered to represent initial depositional conditions. Redox-sensitive elements follow diverse pathways of precipitation that are mostly associated with different redox conditions. Vanadium is known to precipitate under suboxic conditions and is associated with the accumulation of organic matter, and thus elevated V/Al ratio is commonly used to describe suboxic conditions. Molybdenum is usually enriched in sediments at anoxic conditions, i.e. in the presence of free sulfides in the bottom and/or pore waters [Emerson and Huested, 1991; Calvert and Pedersen, 1993; Crusius et al., 1996; Crusius and Thomson, 2000; Zheng et al., 2000; Nameroff et al., 2002; Tribovillard et al., 2006; Jilbert et al., 2010]. Sulphur and Fe enrichments within the sapropels have been attributed to pyrite formation which points to sulphate-

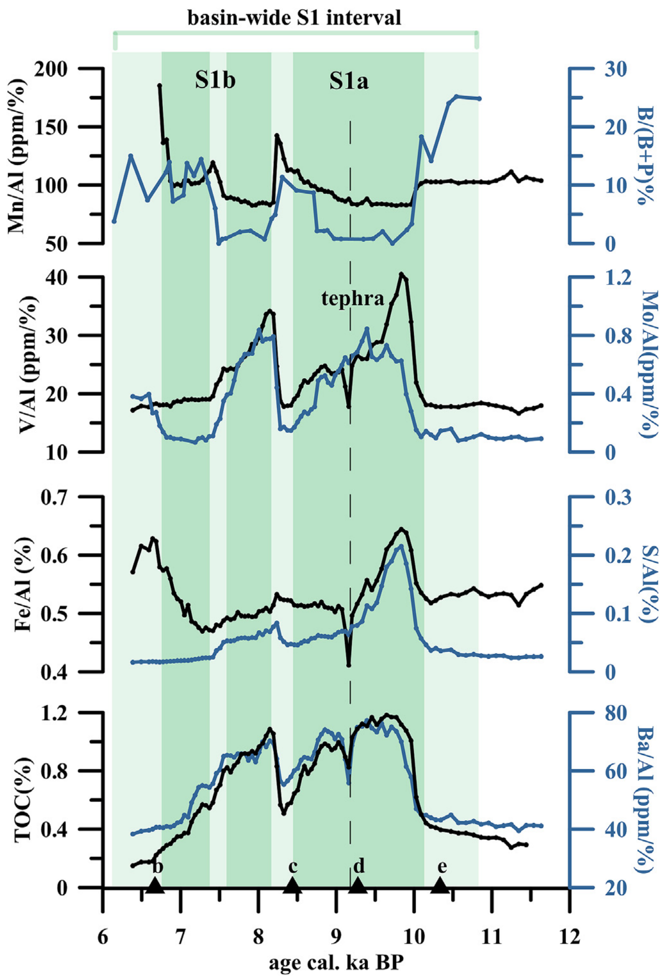

Fig. 4. TOC(%), major and minor elements distribution during S1 in MP50PC core, South Adriatic site core. Indicated above is the basin-wide S1 interval (De Lange et al., 2008). Triangulars indicate the dating points (for b-e, see Table 1); dashed line is distinct tephra horizon.

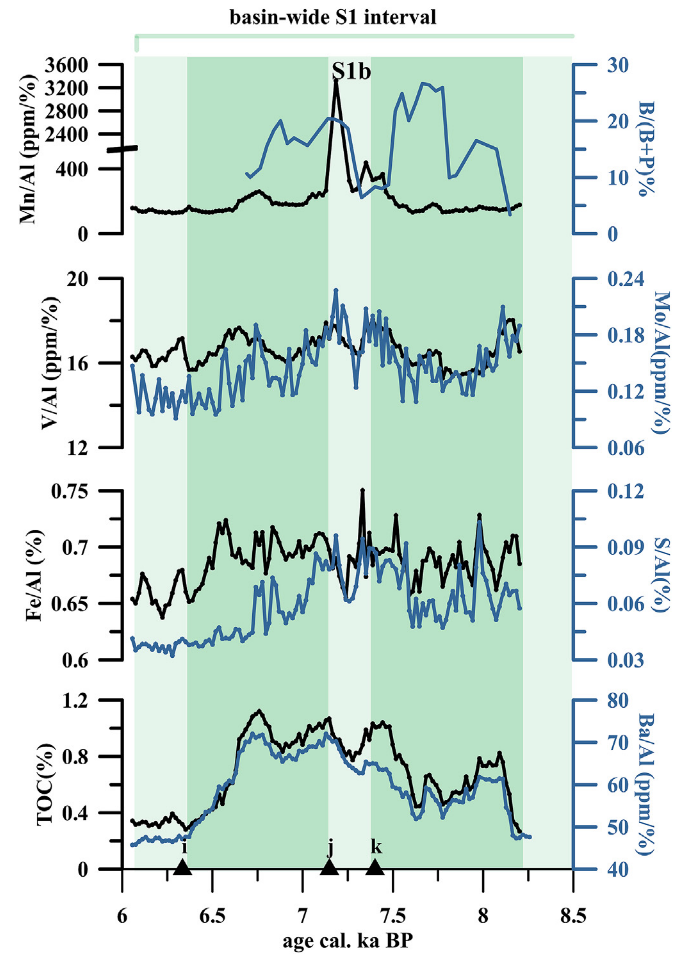

Fig. 5. TOC(%), major and minor elements distribution the last 8.2 cal ka BP in the KN3 core, South Aegean Sea. Indicated above is the basin-wide S1 interval (De Lange et al., 2008). Triangulars indicate the dating points (for i-k, see Table 1).

reducing conditions in the sediment and in the bottom-water during sapropel formation [Thomson et al., 1995; Passier et al., 1996; Reed et al., 2011]. Hence its enrichment expressed in Mo/Al values indicates anoxic conditions. Manganese oxides, which are the dominant fraction of the total Mn in oxic sediments, exhibit the opposite behavior compared to the other trace elements due to microbial mobilization under low-oxygen conditions [Burdige and Kepkay, 1983]. Consequently, manganese-oxides are present under oxic conditions, start to decline under dysoxic conditions (very low oxygen conditions), and may be slightly reduced or enriched under intermittently oxic conditions (depending on bottom-water redox state and associated dissolved Mn^{2+} content). This can be depicted by a lower Mn/Al ratio under suboxic sedimentary conditions. Other factors such as provenance of the detrital fraction, diagenetic formation of pyrite or adsorption to Mn- and Fe-oxyhydroxides could also lead to enhancements of some of these elements in the sediments (e.g. Mo, Co, Cu, and Cr) [Pruysers et al., 1991; Nameroff et al., 2002]. Therefore, these elements should be used with caution for determining redox conditions, taking into account differences in their (im)mobilization pathways [e.g. Nameroff et al., 2002; Tribovillard et al., 2006].

For the Adriatic site, fully oxic bottom-water and sedimentary conditions appear to have been prevailing prior to and post sapropel formation. In contrast, during most of the sapropel period lower levels of Mn/Al, which are thought to represent distinctly suboxic to anoxic conditions, are distinguishable. However, enhanced Mn contents are noticeable during short episodes (this will be discussed in section 4.4). From our record it derives that strictly anoxic conditions have been developed rapidly after the onset of sapropel deposition in the Adriatic Sea. Accordingly, V, Mo, Fe and S, all are elevated at the bottom of S1 concomitant to a major increase in Ba/Al ratio and organic matter content, whereas thereafter these fluctuate tightly coupled (Fig. 4). This suggests that sustained anoxic conditions with enhanced deposition of organic matter lasted for approximately 1500 years (ca. 10.1–8.6 cal ka BP). After a short interruption at ~8.3 cal ka BP (see section 4.4), redox-sensitive elements diagnostic for anoxic conditions, as well as the Ba/Al ratio and TOC content, all increase rapidly and remain enriched until around 6.6 cal ka BP, indicating that low-oxygen conditions have been established for another ~1400 years. However, after 7.4 cal ka BP, bottom-water conditions change into more suboxic to possibly intermittently oxic.

For the S. Aegean site, the sedimentary record shows a great variability during deposition of the recovered S1b unit. Similarly to the Adriatic site, high amounts of organic carbon tightly coupled with the enhanced Ba/Al ratio, compared to the post-S1 values, indicate that increased primary production has persisted during this interval from 8.2 to approximately 6.3 cal ka BP. The Mn/Al ratio at the Aegean site is distinctly higher than for the Adriatic site. This denotes that deposition of the organic-rich unit in the Aegean has taken place under suboxic to nearly oxic conditions, which is consistent with the regular recurrence of benthic foraminifera (Fig. 5). Redox-sensitive elements, such as V and Mo, even though only slightly enriched over their crustal abundances, probably due to high sedimentation-rate-related dilution, co-vary with TOC content and Ba/Al ratio (Fig. 5). This underlines that some level of oxygen depletion occurs in the bottom water/surface sediment, contributing to enhanced preservation of organic matter. Repeated oscillations of major and minor elements advocate that there has been a recurring alternation between oxic and suboxic conditions. This means that bottom waters were probably not continuously oxygen-depleted. The high manganese peak, at 7.4 cal ka BP, connotes the resumption of more-continuous oxygenation thus deep-water formation from that time onward.

4.3. Ending of sapropel S1

In the Adriatic site record, the end of sapropel deposition, as defined from the ending of enhanced C_{org} and Ba fluxes, has occurred at approximately 6.6 cal ka BP. However, already from ca. 7.4 cal ka BP onward, redox-sensitive elements move to lower concentrations abruptly (e.g. Mo, S) or more progressively (e.g. V, Fe). In addition, Mn/Al remains at a moderately depleted level. This means that environmental redox conditions abruptly changed from anoxic to suboxic, and gradually from suboxic to oxic, being intermittently oxic (the latter on basis of Mn/Al). Thus from 7.4 cal ka BP onwards the end of anoxic/suboxic (oxygen-devoid) environmental conditions is clearly decoupled from continuing enhanced organic-fluxes, i.e. sapropel-like conditions. In other words, enhanced organic fluxes continued but bottom-water conditions were no longer anoxic but rather suboxic or even intermittently oxic. The latter observation suggests also that enhanced primary productivity without fully anoxic bottom-water conditions may still lead to sapropel formation under the sedimentary conditions encountered for our sites. The onset of benthic foraminiferal assemblages [e.g. Jorissen et al., 1993], indicating the partial re-oxygenation of bottom-water, has evoked the idea that sapropel deposition may have ended earlier in the Adriatic Sea than in the deep Mediterranean. From our data this appears to be the case for the level of oxygenation, thus for the bottom-water ventilation, but not for surface-waters related bottom-arriving organic-fluxes.

In the Aegean, sedimentary conditions favoring sapropel deposition seem to have persisted until approximately 6.3 cal ka BP. Similarly to the Adriatic site core, the restoration of more continuously oxic conditions at this site, may not have been simultaneous with the reported basin-wide termination of sapropel formation [De Lange et al., 2008]. Furthermore, the premature oxic conditions in the Aegean Sea, as deduced from previous mostly benthic foraminifera-based studies, have led to the conclusion that sapropel formation terminated earlier than elsewhere, i.e. at 7.1 cal ka BP [Kuhnt et al., 2007; Kotthoff et al., 2008a; Schmiedl et al., 2010; Tachikawa et al., 2015]. From our record it is clear that indeed the resumption of deep-water formation has occurred at ca 7.4 cal ka BP, as inferred from the Mn/Al ratio and the benthic foraminifera record (Fig. 5). However, our record also evidently demonstrates that high amounts of organic carbon continued to be exported from the surface waters. Thus shallow-water ‘sapropelic’ conditions continued until 6.3 cal ka BP. Apparently, and despite the more oxic bottom-water conditions, the continued bottom-arriving enhanced organic fluxes have been preserved at this high-sedimentation-rate site.

In summary, for both intermediate water-depth sites near the deep-water formation areas, it appears that the bottom-water oxygenation has resumed earlier (at ca 7.4 cal ka BP) than the final ending of sapropelic conditions as indicated by organic-fluxes proxies (at ca 6.6 and 6.3 cal ka BP in Adriatic site and Aegean Sea, respectively). The high sedimentation rates encountered in these cores and the applied high-resolution sampling have contributed to the detection and preservation of these processes and mechanisms.

4.4. Variability within sapropel S1

Distinct fluctuations in the geochemical records of both cores indicate that during sapropel S1 deposition, bottom-water conditions must have been somewhat variable. In the Adriatic site, productivity- and anoxia-related elemental profiles are almost identical from the onset of sapropel formation until 7.4 cal ka BP. The first interruption, at ca 9.2 cal ka BP is related to the deposition of high amounts of tephra (see section 3.1). Immediately after this event, elemental concentration profiles return rapidly to their previous, enhanced levels. Subsequently these follow the overall trend towards lower values, indicating that the strictly anoxic conditions have started to weaken for the sediments of the Adriatic site. A gradual drop can be observed for Mo, which is the only measured element whose sedimentary origin is predominantly by uptake from the water column under anoxic conditions. Its stepwise decline implies that sedimentary conditions have started to become less sulphidic, culminating at ~8.3 cal ka BP. In accordance, the gradual increase in Mn levels represents increasingly (sub)oxic conditions (Fig. 4). At this 8.2 cal ka. BP event, sapropel formation has been diminished or even ceased during ~200 years, as deduced from TOC and Ba/Al profiles (Fig. 4). At the same time, the sediment redox conditions have been suboxic or even intermittently oxic (e.g. low S/Al, Mo/Al and increased Mn/Al). All observations concord with the temporary resumption of deep-water ventilation, i.e. the moderation of redox conditions in the bottom-waters. This is consistent with the repopulation of the sea-floor by benthic foraminifera, as observed in the same samples (Fig. 4) and reported for other Adriatic Sea sites [e.g. Jorissen et al., 1993; Rohling et al., 1997; De Rijk et al., 1999].

The end of this event is marked by the restoration of elevated V, Mo and Cu concentrations and moderate enrichments in S, as well as the rapid decline in Mn content. All these observations consistently point to the rapid re-establishment of conditions favorable for sapropel preservation, i.e. high accumulation of organic matter and suboxic to anoxic conditions.

In the Adriatic site record at 7.4 cal ka BP, a short enrichment in Mn content and re-appearance of benthic foraminifera concur with a significant reduction in the concentration of redox-sensitive elements, reflecting an oxygenation event. In fact some of them (Mo,Al, Fe/Al, S/Al) are as low as their present values, thus pointing to oxic depositional conditions. This integrated evidence indicates the occurrence of a re-ventilation event during the S1b interval that interrupted the accumulation of high amounts of organic matter. However, elemental profiles of V/Al and Mn/Al denote that sedimentary conditions remained suboxic to at least intermittently oxic. after this 7.4 cal ka BP event and until the end of the organic-rich interval.

This re-ventilation of bottom-water is detectable also in our Aegean sedimentary record as demonstrated by the concurrent increase in Mn/Al, the decrease in anoxia-related elements, and in Ba/Al, and TOC. The high enrichment in the manganese profile at approximately 7.4–7.2 cal ka BP indicates in fact, that regular bottom-water ventilation, thus full oxygenation, must have occurred from this time onward. The clear expression of a 7.4 cal ka BP oxygenation event at both sites underlines that this is not a local, but rather a more general, climate-related event.

4.5. Correspondences and differences between Adriatic and Aegean Seas

The records of the present study demonstrate that sapropel S1 deposition has taken place under largely similar but in detail noticeably different depositional settings at the two study areas and at these water depths. Explicitly, the trace-metal distribution illustrates that relatively stable conditions with periods of anoxic to recurrently sulphidic conditions have occurred in the S. Adriatic site. However, for the Aegean area it is clear that sapropel S1 deposition has taken place under suboxic to intermittently oxic conditions. Such less oxygen-restricted conditions at shallower depths in the Aegean Sea are consistent with previous studies [e.g. Abu-Zied et al., 2008; Marino et al., 2009; Triantaphyllou et al., 2009, 2016]. This is not only evident from the presence of benthic foraminifera, but also from the relatively constant manganese contents well above its crustal Mn/Al value (Fig. 5). This value is substantially higher in Aegean than in Adriatic site sediments for the same time interval, suggesting the former was more often oxygenated. The dynamic relationship between deep-water formation and oxygenation of bottom-waters in the Aegean Sea, has been suggested previously on the basis of benthic foraminifera data [Casford et al., 2003], and is associated with significant climatic instability as implied by alkenone SST variations and microfossils, particularly within the S1b interval [e.g., Gogou et al., 2007; Triantaphyllou et al., 2009, 2016].

The 7.4 cal ka BP oxygenation event is prominent in both records. In the Adriatic site record, this is expressed as a temporary restoration of oxic conditions followed by more intermittently oxic/suboxic conditions until 6.6 cal ka BP (Fig. 6c). In the Aegean this event is expressed as a distinct drop in the enhanced Ba/Al and TOC content concomitant with a large manganese peak at 7.4 cal ka BP corroborating that sediments have been oxic (Fig. 6d). Here, the 7.4 cal ka BP event seems to have been the triggering factor for the final re-oxygenation of the deep-waters in the Aegean Sea. This may be due to the greater response of this sub-basin to Northern-Hemispheric cold spells, attributable to its relatively small size and shallow water depth [Rohling et al., 2002, Rohling and Palike, 2005].

The change in conditions that have resulted in the final cessation of accumulation of high amounts of organic matter and associated proxies at the sea-floor has taken place almost simultaneously in the two Eastern Mediterranean Sea deep-water formation areas at 6.6 and 6.3 cal ka BP, in Adriatic and Aegean Seas respectively. This observation is in accordance with the time and duration of sapropel S1 suggested by De Lange et al., (2008), considering all age and sampling uncertainties.

4.6. Variability and relation to paleoclimate

During sapropel formation, the precession-related prevailing warm and humid conditions with enhanced winter and summer precipitation dominate in the low-latitude southern borderlands. Furthermore, the related northward migration of the ITCZ (Intertropical Convergence Zone) and associated higher riverine influx have contributed to the restriction of Mediterranean circulation. Nonetheless, two episodes of climate deterioration during the last sapropel S1 formation have been profoundly expressed in our records, at ca. 8.2 and 7.4 cal ka BP.

4.6.1. The 8.2 cal ka BP event

The ~8.2 cal ka BP interruption of sapropel S1 deposition observed in our Adriatic site sediment record has also been reported in other studies for Adriatic and Aegean Seas, as the so-called “8.2 ka event” [De Rijk et al., 1999; Rohling et al., 2002]. Its origin has been linked to a rapid cooling due to the intensification of the Siberian High and the subsequent cold winds blowing over the Eastern Mediterranean [Rohling et al., 2002; Rohling and Palike, 2005]. This has resulted in the severe cooling of the surface water and subsequently the resumption of deep-water formation. The slight offset in timing of this event observed between our 8.3 cal ka BP and the reported 8.2 can be attributed to limitations of radiocarbon dating [Rohling et al., 2002]. After this northern borderland ‘cold event’, deep-water formation ceased again due to sustained southern and northern borderland related enhanced precipitation and run-off. The former resulted in low-density LIW, whereas the latter, even enhanced by ongoing deglaciation, resulted via rivers in reduced density surface waters in Adriatic and Aegean Seas.

4.6.2. The 7.4 cal ka BP event

The nature and intensity of the second event at 7.4 cal ka BP in our Adriatic site record, resembling the 8.2 ka event, points also to a climate origin and hence is thought to be the result of a cold episode. However, reducing bottom-water conditions do not return subsequently after this event. This interpretation is confirmed by the concomitant restoration of deep-water formation in the South Aegean Sea. The geochemical profiles and the re-population of benthic foraminifera indicate that fully oxic seafloor conditions have been established at 7.4 cal ka BP for this site. This conforms with a suggested re-oxygenation of bottom waters in the central and South Adriatic Sea for this period [e.g. Artizegui et al., 2000; Piva et al., 2008; Vigliotti et al., 2011; Siani et al., 2013; Combourieu-Nebout et al., 2013; Goudeau et al., 2014]. However, from our detailed record it is clear that this does not mark the end of sapropel deposition but rather the partial re-oxygenation of the bottom waters. Subsequently, improved oxygen conditions prevail from that time until the end of sapropel-like conditions. This distinct, cool and arid episode at ~7.4 cal ka BP has been detected in a number of high-resolution studies based on lake deposits, marine sediments and speleothems ranging from the Italian Alps to the middle East, such as in Northern Sicily [Frisia et al., 2006], in Corchia Cave [Spötl et al., 2010], lake Preola [Magny et al., 2011], in Renela cave [Zhornyak et al., 2011], in Poleva Cave in Romania [Constantin et al., 2007], Soreq Cave in Levant [Bar-Matthews et al., 2000], North and South Aegean Sea [Kuhnt et al., 2007; Kotthoff et al., 2008b; Triantaphyllou, 2014; Triantaphyllou et al., 2016], lakes in Eastern Africa [Gasse 2000], Stymphalia lake in Peloponessus [Heymann et al., 2013], Ohrid lake in Albania [Vogel et al., 2010] and Tunisia Strait [Desprat et al., 2013]. This cold episode largely expressed in climate records, expanding from polar to tropical regions, has been attributed to a weakening in North Hemisphere summer insolation [Bond et al., 2001]. It becomes now explicit from our records that this cold and arid spell, has caused the temporary enhanced deep-water ventilation and consequently the restoration of intermittently to more continuously oxic conditions in the Adriatic and Aegean, respectively.

This event has been followed by a transitional phase, at ~7.5–7.1 cal ka. BP, with progressively less pluvial/more arid conditions in the Eastern Mediterranean region [e.g. Jalut et al., 2009; Davis et al., 2003; Dormoy et al., 2009; Cheddadi and Bar-Hen, 2008; Triantaphyllou et al., 2009; Schmiedl et al., 2010; Magny et al., 2011; Peyron et al., 2011; Joannin et al., 2012; Magny et al., 2013; Peyron et al., 2013]. Decreased humid conditions between 7.9 and 7.3 cal ka BP have been reported and attributed to a cold and arid spell for the North Aegean Sea [Triantaphyllou et al., 2009, 2016; Triantaphyllou 2014] and to a lowering of humidity entrained from low latitudes to the South Aegean [Kouli et al., 2012]. Additionally, the southward retreat of ITCZ and a shortening in summer monsoonal periods have been reported from speleothem in Qunf cave (Southern Omman) to have occurred after

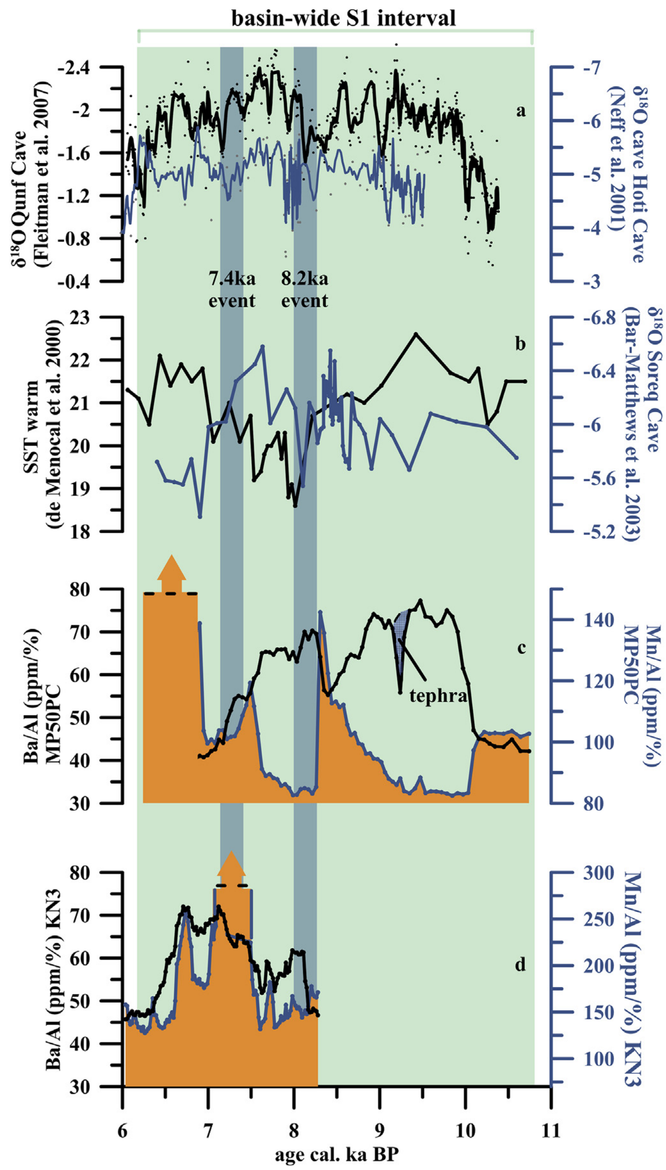

Fig. 6. a) d[18]O from stalagmites (black line) in Qunf Cave, Southern Oman (Fleitmann et al., 2007) and d[18]O from stalagmites (blue line) in Hoti Cave in Northern Oman (Neff et al., 2001), b) SST warm months (black line) from West Africa (De Menocal et al., 2000) and d[18]O records from stalagmite (blue line) from Soreq Cave Israel (Bar Matthews et al., 2003), c) Ba/Al (black line) and Mn/Al (blue line) profile from South Adriatic site core, d) Ba/Al (black line) and Mn/Al (blue line) profile from South Aegean Sea core. Indicated above is the basin-wide S1 interval (De Lange et al., 2008). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

7.5 cal ka BP (Fig. 6a) in response to reduced solar activity [Fleitmann et al., 2003, 2007; Marriner et al., 2012]. This conforms with the reconstruction of Nile hydrological activity [Weldeab et al., 2014] and the southward migration of vegetation [Hély et al., 2014]. This transition to more cool and arid conditions concurs with the onset of deep-water formation in the Adriatic and Aegean areas, expressed as an increased oxygenation event in our sediments from these two regions. The impact of this event seems stronger in our Aegean than in the Adriatic site. At this stage, it would be speculative to attribute this to a more severe climatic imprint for the Aegean. Clearly, more sites need to be studied before such conclusion may be confirmed.

4.7. Consequences for deep-basin ventilation

The reduced Mediterranean deep-water ventilation during sapropel S1 formation is related to the reduced surface water salinity concurring with the last African Humid phase. The Adriatic site record indicates a swift increase of primary productivity and depletion of oxygen of benthic waters. It seems, hence, that the ocean had a rapid response to the progressive increase of insolation [De Menocal et al., 2000] and reducing conditions have been established at the bottom-water at the onset of sapropel S1 deposition. The pronounced interruption of sapropel deposition in our Adriatic site sedimentary record at 8.2 cal ka BP and in published Aegean records [e.g. De Rijk et al., 1999; Gogou et al., 2007; Kotthoff et al., 2008a; Ní Fhlaithearta et al., 2010; Geraga et al., 2010; Katsouras et al., 2010] connotes the widespread climate deterioration that, despite its short duration, has caused the resumption of Mediterranean deep-water formation.

The second event that disrupted deposition of sapropel sediments at 7.4 cal ka BP for our Aegean and Adriatic sites also points to the resumption of deep-water formation and the overall improvement of oxygen conditions in the deep water. The improvement of deep-water oxygenation, i.e. deep-water formation is similar to that observed for the 8.2 cal ka BP event. The clear registration of both events indicates that this temporarily resumed deep-water formation resulted in the ventilation down to at least ~700 m, and possibly for some areas even to ~2800 m [Ariztegui et al., 2000].

5. Conclusions

The high-resolution sampling of high-sedimentation rate cores from sites under the direct influence of the deep-water formation areas, has allowed the systematic investigation of climate-related paleoceanographic variations during sapropel S1 formation. During deposition of most of this organic-rich unit, sedimentary conditions were oxygen-depleted and reflect enhanced primary productivity for the two studied, Adriatic and Aegean sites. However, the integrated results suggest that there are also subtle differences in the depositional settings between the two areas. Bottom-water conditions at intermediate water depths, in the Adriatic site have been mostly anoxic during sapropel S1 deposition, whereas those in the Aegean Sea have been mainly suboxic to intermittently oxic. Furthermore, distinct events were observed in our Adriatic site core at 8.2 and 7.4 cal ka BP. During these events the deposition of organic-rich sediments was interrupted and deep-water oxygen conditions improved. In our Aegean core where sediments younger than 8.2 cal ka BP were recovered, only the latter event was detected.

Both events were associated with northern borderland climate-related cold spells. The 8.2 cal ka BP event was accompanied by the temporary resumption of deep-water formation and the concomitant cessation of elevated primary productivity. The 7.4 cal ka BP cooling event resulted in the temporary halt of enhanced organic carbon fluxes to the seafloor along with the final resumption of deep-water formation in the Aegean Sea and the improvement of bottom-water oxygen conditions in the Adriatic site.

After the 7.4 cal ka BP event, deposition of sapropel S1 continued under suboxic conditions in the Adriatic site, and under nearly oxic conditions in the Aegean. This important observation could only be preserved and detected due to the relatively high sedimentation rates in our cores (resp. 10.2 and 27.3 cm/ka) and the high sampling resolution. The last period of sapropel S1 deposition (from 7.4 cal ka BP onwards) coincides with the gradual decrease of pluvial conditions and the progressive recovery of the Eastern Mediterranean circulation. Final termination of sapropel formation, as defined by its organic matter content, has occurred almost simultaneously for the two areas, at ca. 6.6 ± 0.3 and 6.3 ± 0.5 cal ka BP, in Adriatic and Aegean Seas respectively, in accordance with reported ages.

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