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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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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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ABSTRACT

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.

Keywords: sapropel S1, eastern Mediterranean, deep-water ventilation, interruptions, sediment geochemistry

1. Introduction

1.1 Circulation in the Mediterranean Sea

The present-day Eastern Mediterranean is a well-ventilated and oligotrophic system [Béthoux 1989; Wu & Haines, 1996] following a density-driven, anti-estuarine circulation pattern. The 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 et al., 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 et al., 1996; 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 & Hilgen, 1991; Melieres 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 & Gieskes, 1989; Emeis et al., 1991; De Rijk et al., 1999; Calvert & Fontugne, 2001; Moodley et al., 2005]. The latter is related to the intensity of deep-water formation, i.e. redox conditions.

74 1.3 Trace metals and redox conditions

75 The sapropelic layers exhibit a distinct geochemical composition that reflects the redox
76 sedimentary conditions as well as the increased levels of primary productivity. The characteristic
77 enrichments of S, Fe and redox-sensitive elements such as V, Mo and Cu in sapropelic layers imply
78 that low oxygen or even anoxic conditions must have been established at the sediment/water
79 interface [e.g. Calvert, 1983; Pruysers et al., 1991; Passier et al., 1997; Jilbert et al., 2010].
80 Conversely, manganese appears to be commonly depleted in the sapropel sediments. This is due to
81 its mobilization, under suboxic to anoxic conditions [Mangini et al., 2001]. This is thought to have
82 resulted in enhanced fluxes of dissolved Mn^{2+} to the bottom waters and to its re-precipitation as solid
83 phase manganese-oxides under oxygenated conditions [De Lange et al., 1989; Pruysers et al.,
84 1993; Van Santvoort et al., 1996; Thomson et al., 1999; Reitz et al., 2006a; Ni Fhlaithearta et al.,
85 2010].

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

93 Another well-described feature of the most-recent S1 sapropel in particular, is the distinct
94 dark-brown layer, “marker bed”, often present above it [Murat & Got, 1987; De Lange et al., 1989;
95 Pruysers et al., 1993; Thomson et al., 1995; Van Santvoort et al., 1996; Reitz et al., 2006a]. This
96 manganese-rich layer depicts the re-oxygenation event of the water column and sediments at the end
97 of sapropel formation, i.e. the onset of regular deep-water ventilation [van Santvoort et al., 1996; De
98 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; Pruyssers 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 & Georgopoulos, 1993; Pinardi & 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

123 sediment/water interface. However, the enhanced regeneration of sedimentary phosphate [Slomp et
124 al., 2002; 2004] and the high accumulation of trace metals [Nijenhuis, et al., 1999] indicate that the
125 Mediterranean circulation, albeit diminished, must have persisted during this period.

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

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

143

144 **2. Material & Methods**

145 **2.1 Material**

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

153 **2.2 Methods**

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

161 *TOC*

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

167 *Elemental concentrations*

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

177

178 **3. Results**

179 3.1 Age model and sedimentation rates

180 Conventional ^{14}C ages were calibrated using the program CALIB 6.0 (Marine 09) [Stuiver &
181 Reimer, 1993; Stuiver et al., 1998] with a regional reservoir age correction (ΔR) for Aegean Sea core
182 of 149 ± 30 yrs for the sapropel interval [Facorellis et al., 1998] and 58 ± 85 outside the sapropel
183 [Reimer & McCormac, 2002], and 118 ± 60 yrs for the Adriatic Sea core (table 1) [Reimer &
184 McCormac, 2002]. Due to high amounts of tephra present in the 46.5 - 48.0 cm interval in the
185 Adriatic site (MP50PC), the age model was constructed by interpolation between dated points (fig.2).
186 The tephra components, in the 46.5 – 48.0 cm interval, belong to two different sources; the lower and
187 most abundant one originated from Mercato eruption [Cioni et al., 1999; 2008] of Somma- Vesuvius
188 and the upper one from E1/Fiumebianco-Gabellotto eruption from Lipari island (D. Insinga pers.
189 commun.). The interpolated age assessment of our tephra layer falls within the age range suggested,
190 i.e. 9680 ± 480 cal. BP [Wulf et al., 2004; 2008] and 8500 ± 100 cal. ka BP [Zanchetta et al., 2011], but

191 due to the large uncertainty of the exact age of the events, these can only be used to confirm the age
192 model. Tephra is the dominant fraction in these samples, therefore all other sediment components are
193 “diluted”. This leads to low concentrations for C_{org} , $CaCO_3$ and trace metals and to enhanced
194 elemental concentrations for tephra-related elements, e.g. Ti, Zr. In this core the dark-coloured
195 organic-rich layer spans between 10.2 ± 0.3 to 6.6 ± 0.3 cal. ka BP (fig. 2).

196 In the Aegean Sea core (KN3), the ash layer from the precisely dated Santorini eruption (Z2;
197 1601-1625 B.C. Friedrich et al., 2006) was recognized by its geochemical signal [Reitz et al., 2006b]
198 and used as an additional age marker at depth 75.8 cm. In this core, the interval below 200 cm (~8.2
199 cal. ka BP) is thought to be related to a slump (i.e. deviating elemental concentrations and poor
200 preservation of planktonic foraminifera). Thus the sapropel interval recovered in this core, extends
201 from 8.2 to 6.3 ± 0.5 cal. ka BP. The multiple radiocarbon dating points and the consistent fit to a
202 steady sedimentation rate as well as visual and texture-related observations ensure that no other
203 slumps or hiatuses have affected the sedimentary record in the reported S1 interval. The ^{14}C data
204 indicate a nearly linear relation between age and depth of the sediment (fig. 3).

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

208 209 3.2 Geochemical data

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

213 In core MP50PC, the shape of the Ba/Al profile is identical to that of TOC (%). Two
214 distinctly depleted intervals in both profiles can be distinguished at 9.2 and 8.3 cal. ka BP. The

215 disruption of the record at 9.2 cal. ka BP coincides with the tephra interval and is rather short and
216 abrupt. The overall trend is towards lower values at ~8.3 cal. ka BP. Almost the same high values are
217 observed before and after the 8.3 cal. ka BP interruption. The TOC and Ba/Al values both start to
218 decline at 7.4 cal. ka BP and progressively return to background values at 6.6 cal. ka BP (fig. 4).

219 Redox-sensitive elements, such as V, Mo, and Cu, as well as Fe and S, exhibit variations
220 similar to those of TOC and Ba/Al profiles. These elements respond also to the 8.3 cal. ka BP
221 interrupt and start to reduce gradually (e.g. V) or rapidly (e.g. Mo), shortly after 7.4 cal. ka BP (fig.
222 4).

223 During the sapropel interval, the Mn/Al profile appears slightly depleted but exhibits two
224 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
225 of the sapropel is marked by a pronounced enrichment in the Mn/Al values.

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

235

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 [Béthoux, 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 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 & Newton 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 & Huested, 1991; Calvert & Pedersen, 1993; Crusius et al., 1996; Crusius & 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-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; Namerroff et al., 2002]. Therefore, these elements should be used with caution for determining redox conditions, taking into account differences in their (im)mobilisation pathways [e.g. Namerroff 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

310 production has persisted during this interval from 8.2 to approximately 6.3 cal. ka BP. The Mn/Al
311 ratio at the Aegean site is distinctly higher than for the Adriatic site. This denotes that deposition of
312 the organic-rich unit in the Aegean has taken place under suboxic to nearly oxic conditions, which is
313 consistent with the regular recurrence of benthic foraminifera (fig.5). Redox-sensitive elements, such
314 as V and Mo, even though only slightly enriched over their crustal abundances, probably due to high
315 sedimentation-rate-related dilution, co-vary with TOC content and Ba/Al ratio (fig.5). This
316 underlines that some level of oxygen depletion occurs in the bottom water/surface sediment,
317 contributing to enhanced preservation of organic matter. Repeated oscillations of major and minor
318 elements advocate that there has been a recurring alternation between oxic and suboxic conditions.
319 This means that bottom waters were probably not continuously oxygen-depleted. The high
320 manganese peak, at 7.4 cal. ka BP, connotes the resumption of more-continuous oxygenation thus
321 deep-water formation from that time onward.

322 4.3 Ending of sapropel S1

323 In the Adriatic site record, the end of sapropel deposition, as defined from the ending of
324 enhanced C_{org} and Ba fluxes, has occurred at approximately 6.6 cal. ka BP. However, already from
325 ca. 7.4 cal. ka BP onward, redox-sensitive elements move to lower concentrations abruptly (e.g. Mo,
326 S) or more progressively (e.g. V, Fe) . In addition, Mn/Al remains at a moderately depleted level.
327 This means that environmental redox conditions abruptly changed from anoxic to suboxic, and
328 gradually from suboxic to oxic, being intermittently oxic (the latter on basis of Mn/Al). Thus from
329 7.4 cal. ka BP onwards the end of anoxic/suboxic (oxygen-devoid) environmental conditions is
330 clearly decoupled from continuing enhanced organic- fluxes, i.e. sapropel-like conditions. In other
331 words, enhanced organic fluxes continued but bottom-water conditions were no longer anoxic but
332 rather suboxic or even intermittently oxic. The latter observation suggests also that enhanced primary
333 productivity without fully anoxic bottom-water conditions may still lead to sapropel formation under

334 the sedimentary conditions encountered for our sites. The onset of benthic foraminiferal assemblages
335 [e.g. Jorissen et al., 1993], indicating the partial re-oxygenation of bottom-water, has evoked the idea
336 that sapropel deposition may have ended earlier in the Adriatic Sea than in the deep Mediterranean.
337 From our data this appears to be the case for the level of oxygenation, thus for the bottom-water
338 ventilation, but not for surface-waters related bottom-arriving organic-fluxes.

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

352 In summary, for both intermediate water-depth sites near **the** deep-water formation areas, it
353 appears that the bottom-water oxygenation has resumed earlier (at ca 7.4 cal. ka BP) than the final
354 ending of sapropelic conditions as indicated by organic-fluxes proxies (at ca 6.6 and 6.3 cal. ka BP in
355 Adriatic **site** and Aegean Sea, respectively). The high sedimentation rates encountered in these cores
356 and the applied high-resolution sampling have contributed to the detection and preservation of these
357 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.

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

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

396 4.5 Correspondences and differences between Adriatic and Aegean Seas

397 The records of the present study demonstrate that sapropel S1 deposition has taken place
398 under largely similar but in detail noticeably different depositional settings at the two study areas **and**
399 **at these water depths.** Explicitly, the trace-metal distribution illustrates that relatively stable
400 conditions with periods of anoxic to recurrently sulphidic conditions have occurred in the S. Adriatic
401 **site.** However, for the Aegean area it is clear that sapropel S1 deposition has taken place under
402 suboxic to intermittently oxic conditions. Such **less oxygen-restricted conditions at shallower depths**
403 **in the Aegean Sea are consistent with previous studies [e.g. Abu-Zied et al 2008; Marino et al., 2009;**
404 **Triantaphyllou et al. 2009, 2016].** This is not only evident from the presence of benthic foraminifera,
405 but also from the relatively constant manganese contents well above its crustal Mn/Al value (fig.5).

406 This value is substantially higher in Aegean than in Adriatic **site** sediments for the same time
407 interval, suggesting the former was more often oxygenated. The dynamic relationship between deep-
408 water formation and oxygenation of bottom-waters in the Aegean Sea, has been suggested previously
409 on the basis of benthic foraminifera data [Casford et al., 2003], and is associated with significant
410 climatic instability as implied by alkenone SST variations and microfossils, particularly within the
411 S1b interval [e.g., Gogou et al., 2007; Triantaphyllou et al., 2009, **2016**].

412 The **7.4 cal. ka BP oxygenation event** is prominent in both records. In the Adriatic **site** record,
413 this is expressed as a temporary restoration of oxic conditions followed by more intermittently
414 oxic/suboxic conditions until 6.6 cal. ka BP (fig. **6c**). In the Aegean this event is expressed as a
415 distinct drop in the enhanced Ba/Al and TOC content concomitant with a large manganese peak at
416 7.4 cal. ka BP corroborating that sediments have been oxic (fig. **6d**). Here, the 7.4 cal. ka BP event
417 seems to have been the triggering factor for the final re-oxygenation of the deep-waters in the
418 Aegean Sea. This may be due to the greater response of this sub-basin to Northern-Hemispheric cold
419 spells, attributable to its relatively small size and shallow water depth [Rohling et al., 2002, Rohling
420 & Palike 2005].

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

427 4.6 Variability and relation to paleoclimate

428 During sapropel formation, the precession-related prevailing warm and humid conditions with
429 enhanced winter and summer precipitation dominate in the low-latitude southern borderlands.

430 Furthermore, the related northward migration of the ITCZ (Intertropical Convergence Zone) and
431 associated higher riverine influx have contributed to the restriction of Mediterranean circulation.
432 Nonetheless, two episodes of climate deterioration during the last sapropel S1 formation have been
433 profoundly expressed in our records, at ca. 8.2 and 7.4 cal. ka BP.

434 4.6.1 The 8.2 cal. ka BP event

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

447 4.6.2 The 7.4 cal. ka BP event

448 The nature and intensity of the second **event** at 7.4 cal ka BP in our Adriatic **site** record,
449 resembling the 8.2 ka event, points also to a climate origin and hence is thought to be the result of a
450 cold episode. However, **reducing bottom-water conditions do not return subsequently after this event.**
451 This interpretation is confirmed by the concomitant restoration of deep-water formation in the South
452 Aegean Sea. The geochemical profiles and the re-population of benthic foraminifera indicate that
453 fully oxic seafloor conditions have been established at 7.4 cal. ka BP for this site. This conforms with
454 a suggested re-oxygenation of bottom waters in the central and South Adriatic Sea for this period

455 [e.g. Artizegui et al., 2000; Piva et al., 2008; Viglioti et al., 2011; Siani et al., 2013; Combourieu-
456 Neboutbet al 2013; Goudeau et al., 2014]. However, from our detailed record it is clear that this does
457 not mark the end of sapropel deposition but rather the partial re-oxygenation of the bottom waters.
458 Subsequently, improved oxygen conditions prevail from that time until the end of sapropel-like
459 conditions. This distinct, cool and arid episode at ~7.4 cal. ka BP has been detected in a number of
460 high-resolution studies based on lake deposits, marine sediments and speleothems ranging from the
461 Italian Alps to the middle East, such as in Northern Sicily [Frisia et al., 2006], in Corchia Cave
462 [Spotl et al., 2010], lake Preola [Magny et al., 2011], in Renela cave [Zhornyak et al., 2011], in
463 Poleva Cave in Romania [Constantin et al., 2007], Soreq Cave in Levant [Bar-Matthews et al.,
464 2000], North and South Aegean Sea [Kuhnt et al., 2007; Kotthof et al., 2008b; Triantaphyllou, 2014;
465 Triantaphyllou et al., 2016], lakes in Eastern Africa [Gasse 2000], Stymphalia lake in Peloponessus
466 [Heymann et al., 2013], Ohrid lake in Albania [Vogel et al., 2010] and Tunisia Strait [Desprat et al.,
467 2013]. This cold episode largely expressed in climate records, expanding from polar to tropical
468 regions, has been attributed to a weakening in North Hemisphere summer insolation [Bond et al.,
469 2001]. It becomes now explicit from our records that this cold and arid spell, has caused the
470 temporary enhanced deep-water ventilation and consequently the restoration of intermittently to
471 more continuously oxic conditions in the Adriatic and Aegean, respectively.

472 This event has been followed by a transitional phase, at ~7.5-7.1 cal. ka. BP, with
473 progressively less pluvial / more arid conditions in the Eastern Mediterranean region [e.g. Jalut et al.,
474 2000; Davis et al., 2003; Dormoy et al., 2007; Cheddadi & Bar-Hen, 2008; Triantaphyllou et al.,
475 2009; Schmiedl et al., 2010; Magny et al., 2011; Peyron et al., 2011; Joannin et al., 2012; Magny et
476 al., 2013; Peyron et al., 2013]. Decreased humid conditions between 7.9 and 7.3 cal. ka BP have
477 been reported and attributed to a cold and arid spell for the North Aegean Sea [Triantaphyllou et al.,
478 2009, 2016; Triantaphyllou 2014] and to a lowering of humidity entrained from low latitudes to the
479 South Aegean [Kouli et al., 2010]. Additionally, the southward retreat of ITCZ and a shortening in

480 summer monsoonal periods have been reported from speleothem in Qunf cave (Southern Oman) to
481 have occurred after 7.5 cal ka BP (fig. 6a) in response to reduced solar activity [Fleitmann et al.,
482 2003, 2007; Marriner et al., 2012]. This conforms with the reconstruction of Nile hydrological
483 activity [Weldeab et al., 2014] and the southward migration of vegetation [Hély et al., 2014]. This
484 transition to more cool and arid conditions concurs with the onset of deep-water formation in the
485 Adriatic and Aegean areas, expressed as an increased oxygenation event in our sediments from these
486 two regions. The impact of this event seems stronger in our Aegean than in the Adriatic site. At this
487 stage, it would be speculative to attribute this to a more severe climatic imprint for the Aegean.
488 Clearly, more sites need to be studied before such conclusion may be confirmed.

489

490 4.7 Consequences for deep-basin ventilation

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

501 The second event that disrupted deposition of sapropel sediments at 7.4 cal. ka BP for our
502 Aegean and Adriatic sites also points to the resumption of deep-water formation and the overall
503 improvement of oxygen conditions in the deep water. The improvement of deep-water oxygenation,

504 i.e. deep-water formation is similar to that observed for the 8.2 cal. ka BP event. The clear
505 registration of both events indicates that this temporarily resumed deep-water formation resulted in
506 the ventilation down to at least ~700 m, and possibly for some areas even to ~2800 m [Ariztegui et
507 al., 2000].

508 **5. Conclusions**

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

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

527 After the 7.4 cal. ka BP event, deposition of sapropel S1 continued under suboxic conditions
528 in the Adriatic site, and under nearly oxic conditions in the Aegean. This important observation
529 could only be preserved and detected due to the relatively high sedimentation rates in our cores (resp.
530 10.2 and 27.3 cm/ka) and the high sampling resolution. The last period of sapropel S1 deposition
531 (from 7.4 cal. ka BP onwards) coincides with the gradual decrease of pluvial conditions and the
532 progressive recovery of the Eastern Mediterranean circulation. Final termination of sapropel
533 formation, as defined by its organic matter content, has occurred almost simultaneously for the two
534 areas, at ca. 6.6 ± 0.3 and 6.3 ± 0.5 cal. ka BP, in Adriatic and Aegean Seas respectively, in accordance
535 with reported ages.

536

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546

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. *Mar. Micropaleontol.* 67, 46–68. doi:10.1016/j.marmicro.2007.08.006
- Aksu, A.E., Yaşar, D., Mudie, 1995. Paleoclimatic and paleoceanographic conditions leading to development of sapropel layer S1 in the Aegean Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 116, 71–101.
- Alley, R.B., Mayewski, P.A., Sowers, T., Stuiver, M., Taylor, K.C., Clark, P.U., 1997. Holocene climatic instability: A prominent, widespread event 8200 yr ago. *Geology* 25, 483–486. doi:10.1130/0091-7613(1997)025<0483
- Ariztegui, D., Ascoli, A., Lowe, J.J., Trincardi, F., Vigliotti, L., Tamburini, F., Chondrogianni, C., Accorsi, C.A., Bandini Mazzanti, M., Mercuri, A.M., Van der Kaars, S., McKenzie, J. A., Oldfield, F., 2000. Palaeoclimate and the formation of sapropel S1: inferences from Late Quaternary lacustrine and marine sequences in the central Mediterranean region. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 215–240. doi:10.1016/S0031-0182(00)00051-1
- Bar-Matthews, M., Ayalon, A., Kaufman, A., 2000. Timing and hydrological conditions of Sapropel events in the Eastern Mediterranean, as evident from speleothems, Soreq cave, Israel. *Chem. Geol.* 169, 145–156. doi:10.1016/S0009-2541(99)00232-6
- Bar-Matthews, M., Ayalon, A., Gilmour, M., Matthews, A., Hawkesworth, C.J., 2003. Sea – land oxygen isotopic relationships from planktonic foraminifera and speleothems in the Eastern Mediterranean region and their implication for paleorainfall during interglacial intervals. *Geochim. Cosmochim. Acta* 67, 3181–3199.
- Bethoux, J.P., 1989. Oxygen consumption, new production, vertical advection and environmental evolution in the Mediterranean Sea. *Deep - Sea Res.* 36, 769–781.
- Bond, G., Kromer, B., Beer, J., Muscheler, R., Evans, M.N., Showers, W., Hoffmann, S., Lotti-Bond, R., Hajdas, I., Bonani, G., 2001. Persistent solar influence on North Atlantic climate during the Holocene. *Science*. 294, 2130–6. doi:10.1126/science.1065680
- Burdige, D.J., Kepkay, P.E., 1983. Determination of bacterial manganese oxidation rates in sediments using an in-situ dialysis technique I. Laboratory studies. *Geochim. Cosmochim. Acta* 47, 1907–1916. doi:10.1016/0016-7037(83)90207-7
- 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, 78–94.

- Calvert, S.E., Pedersen, T.F., 1993. Geochemistry of Recent oxic and anoxic marine sediments: Implications for the geological record. *Mar. Geol.* 113, 67–88. doi:10.1016/0025-3227(93)90150-T
- Calvert, S.E., 1983. Geochemistry of Pleistocene sapropels and associated sediments from the Eastern Mediterranean. *Oceanol. Acta* 6, 255–267.
- Casford, J.S.L., Rohling, E.J., Abu-Zied, R.H., Fontanier, C., Jorissen, F.J., Leng, M.J., Schmiedl, G., Thomson, J., 2003. A dynamic concept for eastern Mediterranean circulation and oxygenation during sapropel formation. *Palaeogeogr. Palaeoclim. Palaeoecol.* 190, 103–119. doi:10.1016/S0031-0182(02)00601-6
- Cheddadi, R., Bar-Hen, A., 2008. Spatial gradient of temperature and potential vegetation feedback across Europe during the late Quaternary. *Clim. Dyn.* 32, 371–379. doi:10.1007/s00382-008-0405-7
- Cioni, R., Santacroce, R., Sbrana, A., 1999. Pyroclastic deposits as a guide for reconstructing the multi-stage evolution of the Somma-Vesuvius Caldera. *Bull. Volcanol.* 61, 207–222. doi:10.1007/s004450050272
- Cioni, R., Bertagnini, A., Santacroce, R., Andronico, D., 2008. Explosive activity and eruption scenarios at Somma-Vesuvius (Italy): Towards a new classification scheme. *J. Volcanol. Geotherm. Res.* 178, 331–346. doi:10.1016/j.jvolgeores.2008.04.024
- Combourieu-Nebout, N., Peyron, O., Bout-Roumazielles, V., Goring, S., Dormoy, I., Joannin, S., Sadori, L., Siani, G., Magny, M., 2013. Holocene vegetation and climate changes in the central Mediterranean inferred from a high-resolution marine pollen record (Adriatic Sea). *Clim. Past* 9, 2023–2042. doi:10.5194/cp-9-2023-2013
- Constantin, S., Bojar, A.-V., Lauritzen, S.-E., Lundberg, J., 2007. Holocene and Late Pleistocene climate in the sub-Mediterranean continental environment: A speleothem record from Poleva Cave (Southern Carpathians, Romania). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 243, 322–338. doi:10.1016/j.palaeo.2006.08.001
- Crusius, J., Thomson, J., 2000. Comparative behavior of authigenic Re, U, and Mo during reoxidation and subsequent long-term burial in marine sediments. *Geochim. Cosmochim. Acta* 64, 2233–2242.
- Crusius, J., Calvert, S., Pedersen, T., Sage, D., 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth Planet. Sci. Lett.* 145, 65–78.
- Davis, B.A.S., Brewer, S., Stevenson, A.C., Guiot, J., Data contributors 2003. The temperature of Europe during the Holocene reconstructed from pollen data. *Quat. Sci. Rev.* 22, 1701–1716. doi:10.1016/S0277-3791(03)00173-2
- De Lange G.J., Ten Haven, L. 1983. Recent sapropel formation in the eastern Mediterranean. *Nature* 305, 797 - 798 (27 October 1983); doi:10.1038/305797a0

- De Lange, G.J., Middleburg, J.J., Pruyssers, P.A., 1989. Discussion: Middle and Late Quaternary depositional sequences and cycles in the eastern Mediterranean. *Sedimentology* 36, 151–158.
- De Lange, G.J., Van Santvoort, P.J.M., Langereis, C., Thomson, J., Corselli, C., Michard, A., Rossignol-Strick, M., Paterne, M., Anastasakis, G., 1999. Palaeo-environmental variations in eastern Mediterranean sediments: a multidisciplinary approach in a prehistoric setting. *Prog. Oceanogr.* 44, 369–386. doi:10.1016/S0079-6611(99)00037-3
- 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* 1, 606–610. doi:10.1038/ngeo283
- De Menocal, P., Ortiz, J., Guilderson, T., Adkins, J., Sarnthein, M., Baker, L., Yarusinsky, M., 2000. Abrupt onset and termination of the African Humid Period: rapid climate responses to gradual insolation forcing. *Quat. Sci. Rev.* 19, 347–361.
- De Rijk, S., Hayes, A., Rohling, E.J., 1999. Eastern Mediterranean sapropel S1 interruption: an expression of the onset of climatic deterioration around 7 ka BP. *Mar. Geol.* 153, 337–343.
- Desprat, S., Combourieu-Nebout, N., Essallami, L., Sicre, M. A., Dormoy, I., Peyron, O., Siani, G., Bout Roumazeilles, V., Turon, J.L., 2013. Deglacial and Holocene vegetation and climatic changes in the southern Central Mediterranean from a direct land–sea correlation. *Clim. Past* 9, 767–787. doi:10.5194/cp-9-767-2013
- Dormoy, I., Peyron, O., Combourieu Nebout, N., Goring, S., Kotthoff, U., Magny, M., Pross, J., 2009. Terrestrial climate variability and seasonality changes in the Mediterranean region between 15000 and 4000 years BP deduced from marine pollen records. *Clim. Past* 5, 615–632. doi:10.5194/cp-5-615-2009
- Emeis, K.-C., Camerlenghi, A., McKenzie, J.A., Rio, D., Sprovieri, R., 1991. The occurrence and significance of Pleistocene and Upper Pliocene sapropels in the Tyrrhenian Sea. *Mar. Geol.* 100, 155–182.
- Emeis, K.-C. and Shipboard Scientific Party 1996. 2. Paleoceanography and sapropel introduction. *Proc. Ocean Drill. Program, Initial Reports* 160, 21–28.
- Emeis, K.-C., Schulz, H.-M., Struck, U., Sakamoto, T., Dooe, H., Erlenkeuser, H., Howell, M., Kroon, D., Paterne, M., 1998. Stable isotope and alkenone temperature records of sapropels from sites 964 and 967: constraining the physical environment of sapropel formation in the Eastern Mediterranean Sea. *Proc. Ocean Drill. Program, Sci. Results* 160, 309–331.
- Emerson, S.R., Huested, S.S., 1991. Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. *Mar. Chem.* 34, 177–196. doi:10.1016/0304-4203(91)90002-E

- Facorellis, Y., Maniatis, Y., 1998. Apparent ^{14}C ages of marine mollusk shells from a Greek island: calculation of the marine reservoir effect in the Aegean Sea. *Radiocarbon* 40, 963–973.
- Fleitmann, D., Burns, S.J., Mudelsee, M., Neff, U., Kramers, J., Mangini, A., Matter, A., 2003. Holocene forcing of the Indian monsoon recorded in a stalagmite from southern Oman. *Science* 300, 1737–9. doi:10.1126/science.1083130
- Fleitmann, D., Burns, S.J., Mangini, A., Mudelsee, M., Kramers, J., Villa, I., Neff, U., Al-Subbary, A.A., Buettner, A., Hippler, D., Matter, A., 2007. Holocene ITCZ and Indian monsoon dynamics recorded in stalagmites from Oman and Yemen (Socotra). *Quat. Sci. Rev.* 26, 170–188. doi:10.1016/j.quascirev.2006.04.012
- Friedrich, W.L., Kromer, B., Friedrich, M., Heinemeier, J., Pfeiffer, T., Talamo, S., 2006. Santorini eruption radiocarbon dated to 1627-1600 B.C. *Science*. 312, 548. doi:10.1126/science.1125087
- Frisia, S., Borsato, A., Mangini, A., Spötl, C., Madonia, G., Sauro, U., 2006. Holocene climate variability in Sicily from a discontinuous stalagmite record and the Mesolithic to Neolithic transition. *Quat. Res.* 66, 388–400. doi:10.1016/j.yqres.2006.05.003
- Gasse, F., 2000. Hydrological changes in the African tropics since the Last Glacial Maximum. *Quat. Sci. Rev.* 19, 189–211. doi:10.1016/S0277-3791(99)00061-X
- Geraga, M., Ioakim, C., Lykousis, V., Tsaila-Monopolis, S., Mylona, G., 2010. The high-resolution palaeoclimatic and palaeoceanographic history of the last 24,000 years in the central Aegean Sea, Greece. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 287, 101–115. doi:10.1016/j.palaeo.2010.01.023
- Gogou, A., Bouloubassi, I., Lykousis, V., Arnaboldi, M., Gaitani, P., Meyers, P.A., 2007. Organic geochemical evidence of Late Glacial – Holocene climate instability in the North Aegean Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 256, 1–20. doi:10.1016/j.palaeo.2007.08.002
- Gogou, A., Bouloubassi, I., Lykousis, V., Arnaboldi, M., Gaitani, P., Meyers, P.A., 2007. Organic geochemical evidence of Late Glacial-Holocene climate instability in the North Aegean Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 256, 1-20.
- Goudeau, M.-L.S., Grauel, A.-L., Tessarolo, C., Leider, A., Chen, L., Bernasconi, S.M., Versteegh, G.J.M., Zonneveld, K.A.F., Boer, W., Alonso-Hernandez, C.M., De Lange, G.J., 2014. The Glacial–Interglacial transition and Holocene environmental changes in sediments from the Gulf of Taranto, central Mediterranean. *Mar. Geol.* 348, 88–102. doi:10.1016/j.margeo.2013.12.003
- Hély, C., Lézine, A.-M., APD Contributors, 2014. Holocene changes in African vegetation: tradeoff between climate and water availability. *Clim. Past* 10, 681–686. doi:10.5194/cp-10-681-2014

- Heymann, C., Nelle, O., Dörfler, W., Zagana, H., Nowaczyk, N., Xue, J., Unkel, I., 2013. Late Glacial to mid-Holocene palaeoclimate development of Southern Greece inferred from the sediment sequence of Lake Stymphalia (NE-Peloponnese). *Quat. Int.* doi:10.1016/j.quaint.2013.02.014
- Higgs, N.C., Thomson, J., Wilson, T.R.S., Croudace, I.W., 1994. Modification and complete removal of eastern Mediterranean sapropels by postdepositional oxidation. *Geology* 22, 423–426. doi:10.1130/0091-7613(1994)022<0423:MACROE>2.3.CO;2
- Hilgen, F.J., 1991. Astronomical calibration of Gauss to Matuyama sapropels in the Mediterranean and implication for the Geomagnetic Polarity Time Scale. *Earth Planet. Sci. Lett.* 104, 226–244. doi:10.1016/0012-821X(91)90206-W
- Jalut, G., Dedoubat, J.J., Fontugne, M., Otto, T., 2009. Holocene circum-Mediterranean vegetation changes: Climate forcing and human impact. *Quat. Int.* 200, 4–18. doi:10.1016/j.quaint.2008.03.012
- Jilbert, T., Reichert, G.-J., Aeschlimann, B., Günther, D., Boer, W., De Lange, G.J., 2010. Climate-controlled multidecadal variability in North African dust transport to the Mediterranean. *Geology* 38, 19–22. doi:10.1130/G25287.1
- Joannin, S., Brugiapaglia, E., de Beaulieu, J.-L., Bernardo, L., Magny, M., Peyron, O., Goring, S., Vannire, B., 2012. Pollen-based reconstruction of Holocene vegetation and climate in southern Italy: the case of Lago Trifoglietti. *Clim. Past* 8, 1973–1996. doi:10.5194/cp-8-1973-2012
- Jorissen, F.J., Asoli, A., Borsetti, A.M., Capotondi, L., de Visser, J.P., Hilgen, F.J., Rohling, E.J., van der Borg, K., Vergnaud Grazzini, C., Zachariasse, W.J., 1993. Late Quaternary central Mediterranean biochronology. *Mar. Micropaleontol.* 21, 169–189.
- Katsouras, G., Gogou, A., Bouloubassi, I., Emeis, K.-C., Triantaphyllou, M., Roussakis, G., Lykousis, V., 2010. Organic carbon distribution and isotopic composition in three records from the eastern Mediterranean Sea during the Holocene. *Org. Geochem.* 41, 935–939. doi:10.1016/j.orggeochem.2010.04.008
- Kidd, R.B., Cita, M.B., Ryan, W.B.F., 1978. 13.1 Stratigraphy of eastern Mediterranean sapropel sequences recovered during DSDP Leg 42A and their paleoenvironmental significance, in: Hsu, K., Montadert, L. et al. (Eds.), *Initial Reports DSDP vol.42A*. Washington, pp. 421–443.
- Kotthoff, U., Pross, J., Mller, U.C., Peyron, O., Schmiedl, G., Schulz, H., Bordon, A., 2008a. Climate dynamics in the borderlands of the Aegean Sea during formation of sapropel S1 deduced from a marine pollen record. *Quat. Sci. Rev.* 27, 832–845. doi:10.1016/j.quascirev.2007.12.001
- Kotthoff, U., Mller, U.C., Pross, J., Schmiedl, G., Lawson, I.T., van de Schootbrugge, B., Schulz, H., 2008b. Lateglacial and Holocene vegetation dynamics in the Aegean region: an integrated view based on pollen data from marine and terrestrial archives. *The Holocene* 18, 1019–1032. doi:10.1177/0959683608095573

- Kouli, K., Gogou, A., Bouloubassi, I., Triantaphyllou, M.V., Ioakim, Chr., Katsouras, G., Roussakis, G., Lykousis, V., 2012. Late postglacial paleoenvironmental change in the northeastern Mediterranean region: Combined palynological and molecular biomarker evidence. *Quat. Int.* 261, 118–127. doi:10.1016/j.quaint.2011.10.036
- Krokos, G., Velaoras, D., Korres, G., Perivoliotis, L., Theocharis, A., 2014. On the continuous functioning of an internal mechanism that drives the Eastern Mediterranean thermohaline circulation: The recent activation of the Aegean Sea as a dense water source area. *Journal of Marine Systems*, 129:484–489
- 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. *Mar. Micropaleontol.* 64, 141–162. doi:10.1016/j.marmicro.2007.04.003
- Magny, M., Vannière, B., Calo, C., Millet, L., Leroux, A., Peyron, O., Zanchetta, G., La Mantia, T., Tinner, W., 2011. Holocene hydrological changes in south-western Mediterranean as recorded by lake-level fluctuations at Lago Preola, a coastal lake in southern Sicily, Italy. *Quat. Sci. Rev.* 30, 2459–2475. doi:10.1016/j.quascirev.2011.05.018
- Magny, M., Combourieu-Nebout, N., de Beaulieu, J.L., Bout-Roumazielles, V., Colombaroli, D., Desprat, S., Francke, A., Joannin, S., Ortu, E., Peyron, O., Revel, M., Sadori, L., Siani, G., Sicre, M.A., Samartin, S., Simonneau, A., Tinner, W., Vannière, B., Wagner, B., Zanchetta, G., Anselmetti, F., Brugiapaglia, E., Chapron, E., Debret, M., Desmet, M., Didier, J., Essallami, L., Galop, D., Gilli, A., Haas, J.N., Kallel, N., Millet, L., Stock, A., Turon, J.L., Wirth, S., 2013. North–south palaeohydrological contrasts in the central Mediterranean during the Holocene: tentative synthesis and working hypotheses. *Clim. Past* 9, 2043–2071. doi:10.5194/cp-9-2043-2013
- Mangini, A., Jung, M., Laukenmann, S., 2001. What do we learn from peaks of uranium and of manganese in deep sea sediments? *Mar. Geol.* 177, 63. doi:10.1016/S0025-3227(01)00124-4
- Marriner, N., Flaux, C., Kaniewski, D., Morhange, C., Leduc, G., Moron, V., Chen, Z., Gasse, F., Empereur, J.-Y., Stanley, J.-D., 2012. ITCZ and ENSO-like pacing of Nile delta hydro-geomorphology during the Holocene. *Quat. Sci. Rev.* 45, 73–84. doi:10.1016/j.quascirev.2012.04.022
- Marino, G., Rohling, E.J., Sangiorgi, F., Hayes, A., Casford, J.L., Lotter, A.F., Kucera, M., Brinkhuis, H., 2009. Early and middle Holocene in the Aegean Sea: interplay between high and low latitude climate variability. *Quat. Sci. Rev.* 28, 3246–3262. doi:10.1016/j.quascirev.2009.08.011
- Martinez-Ruiz, F., Kastner, M., Paytan, A., Ortega-Huertas, M., Bernasconi, S.M., 2000. Geochemical evidence for enhanced productivity during S1 sapropel deposition in the eastern Mediterranean. *Paleoceanography* 15, 200–209.
- Mayewski, P.A., Rohling, E.J., Curt Stager, J., Karlén, W., Maasch, K.A., Meeker, L.D., Meyerson, E.A., Gasse, F., van Kreveld, S., Holmgren, K., Lee-Thorp, J., Rosqvist, G.,

- Rack, F., Staubwasser, M., Schneider, R.R., Steig, E.J., 2004. Holocene climate variability. *Quat. Res.* 62, 243–255. doi:10.1016/j.yqres.2004.07.001
- Ménières, M.-A., Rossignol-Strick, M., Malaizé, B., 1997. Relation between low latitude insolation and $\delta^{18}\text{O}$ change of atmospheric oxygen for the last 200kyrs, as revealed by Mediterranean sapropels. *Geophysical Res. Lett.* 24, 1235–1238.
- 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. *Mar. Geol.* 177, 25–44.
- Moodley, L., Middelburg, J.J., Herman, P.M.J., Soetaert, K., De Lange, G.J., 2005. Oxygenation and organic-matter preservation in marine sediments: Direct experimental evidence from ancient organic carbon-rich deposits. *Geology* 33, 889. doi:10.1130/G21731.1
- Murat, A., Got, H., 1987. Middle and Late Quaternary depositional sequences and cycles in the eastern Mediterranean. *Sedimentology* 34: 885–899. doi: 10.1111/j.1365-3091.1987.tb00810.x
- Nameroff, T.J., Balistrieri, L.S., Murray, J.W., 2002. Suboxic trace metal geochemistry in the eastern tropical North Pacific. *Geochim. Cosmochim. Acta* 66, 1139–1158.
- Neff, U., Burns, S.J., Mangini, A., Mudelsee, M., Fleitmann, D., Matter, A., 2001. Strong coherence between solar variability and the monsoon in Oman between 9 and 6 kyr ago. *Nature* 411, 290–3. doi:10.1038/35077048
- Ní Fhlaithearta, S., Reichert, G.-J., Jorissen, F.J., Fontanier, C., Rohling, E.J., Thomson, J., De Lange, G.J., 2010. Reconstructing the seafloor environment during sapropel formation using benthic foraminiferal trace metals, stable isotopes, and sediment composition. *Paleoceanography* 25, PA4225. doi:10.1029/2009PA001869
- Nijenhuis, I.A., Bosch, H.-J., Sinninghe Damsté, J.S., Brumsack, H.-J., De Lange, G.J., 1999. Organic matter and trace element rich sapropels and black shales: a geochemical comparison. *Earth Planet. Sci. Lett.* 169, 277–290.
- Olausson, E. 1961. Studies in deep-sea cores. *Red. Swed. Deep-Sea Exped 1947-1948.* 8, 337-391.
- Passier, H.F., Middelburg, J.J., van Os, B.J.H., De Lange, G.J., 1996. Diagenetic pyritisation under eastern Mediterranean caused by downward sulphide diffusion sapropels. *Geochim. Cosmochim. Acta* 60, 751–763.
- Passier, H.F., Middelburg, J.J., De Lange, G.J., Böttcher, M.E., 1997. Pyrite contents, microtextures, and sulfur isotopes in relation to formation of the youngest eastern Mediterranean sapropel. *Geology* 25, 519–522. doi:10.1130/0091-7613(1997)025<0519:PCMASI>2.3.CO

- Paytan, A., Martinez-Ruiz, F., Eagle, M., Ivy, A., Wankel, S.D., 2004. Using sulfur isotope to elucidate the origin of barite associated with high organic matter accumulation events in marine sediments. *Geol. Soc. Am. Bull.* 379, 151–160. doi:10.1130/0-8137-2379-5.151
- Peyron, O., Goring, S., Dormoy, I., Kotthoff, U., Pross, J., de Beaulieu, J.-L., Drescher-Schneider, R., Vannière, B., Magny, M., 2011. Holocene seasonality changes in the central Mediterranean region reconstructed from the pollen sequences of Lake Accesa (Italy) and Tenaghi Philippon (Greece). *The Holocene* 21, 131–146. doi:10.1177/0959683610384162
- Peyron, O., Magny, M., Goring, S., Joannin, S., de Beaulieu, J.-L., Brugiapaglia, E., Sadori, L., Garfi, G., Kouli, K., Ioakim, C., Combourieu-Nebout, N., 2013. Contrasting patterns of climatic changes during the Holocene across the Italian Peninsula reconstructed from pollen data. *Clim. Past* 9, 1233–1252. doi:10.5194/cp-9-1233-2013
- Piva, A., Ascoli, A., Trincardi, F., Schneider, R.R., Vigliotti, L., 2008. Late Holocene climate variability in the Adriatic Sea (Central Mediterranean). *The Holocene* 18, 153–167. doi:10.1177/0959683607085606
- Pross, J., Kotthoff, U., Müller, U.C., Peyron, O., Dormoy, I., Schmiedl, G., Kalaitzidis, S., Smith, A.M., 2009. Massive perturbation in terrestrial ecosystems of the Eastern Mediterranean region associated with the 8.2 kyr B.P. climatic event. *Geology* 37, 887–890. doi:10.1130/G25739A.1
- Pruysers, P.A., De Lange, G.J., Middelburg, J.J., 1991. Geochemistry of eastern Mediterranean sediments: Primary sediment composition and diagenetic alterations. *Mar. Geol.* 100, 137–154.
- Pruysers, P.A., De Lange, G.J., Middelburg, J.J., Hydes, D.J., 1993. The diagenetic formation of metal-rich layers in sapropel-containing sediments in the eastern Mediterranean. *Geochim. Cosmochim. Acta* 57, 527–536. doi:10.1016/0016-7037(93)90365-4
- Reed, D.C., Slomp, C.P., De Lange, G.J., 2011. A quantitative reconstruction of organic matter and nutrient diagenesis in Mediterranean Sea sediments over the Holocene. *Geochim. Cosmochim. Acta* 75, 5540–5558. doi:10.1016/j.gca.2011.07.002
- Reimer, P.J., McCormac, F.G., 2002. Marine Radiocarbon reservoir correction for the Mediterranean and aegean Seas. *Radiocarbon* 44, 159–166.
- Reitz, A., Thomson, J., De Lange, G.J., Hensen, C., 2006a. Source and development of large manganese enrichments above eastern Mediterranean sapropel S1. *Paleoceanography* 21, n/a–n/a. doi:10.1029/2005PA001169
- Reitz, A., Thomson, J., De Lange, G.J., Green, D.R.H., Slomp, C.P., Gebhardt, A.C., 2006b. Effects of the Santorini (Thera) eruption on manganese behavior in Holocene sediments of the eastern Mediterranean. *Earth Planet. Sci. Lett.* 241, 188–201. doi:10.1016/j.epsl.2005.10.027

- Rohling, E.J., Gieskes, W.W.C., 1989. Late Quaternary changes in Mediterranean Intermediate Water density and formation rate. *Paleoceanography* 4(5), 531–545.
- Rohling, E.J., Hilgen, F.J., 1991. The eastern Mediterranean climate at times of sapropel formation : a review. *Geol. en Mijnb.* 70, 253–264.
- Rohling, E.J., Pälike, H., 2005. Centennial-scale climate cooling with a sudden cold event around 8.200 years ago. *Nature* 434, 975–979.
- Rohling, E.J., Jorissen, F.J., De Stigter, H.C., 1997. 200 Year Interruption of Holocene sapropel formation in the Adriatic Sea. *J. Micropalaeontology* 16, 97–108.
- Rohling, E.J., Mayewski, P., Abu-Zied, R., Casford, J., Hayes, A., 2002. Holocene atmosphere-ocean interactions: records from Greenland and the Aegean Sea. *Clim. Dyn.* 18, 587–593. doi:10.1007/s00382-001-0194-8
- Rohling, E.J., Marino, G., Grant, K.M., 2015. Mediterranean climate and oceanography, and the periodic development of anoxic events (sapropels). *Earth-Science Rev.* 143, 62–97. doi:10.1016/j.earscirev.2015.01.008
- Rosignol-Strick, M., 1985. Mediterranean quaternary sapropels, an immediate response of the african monsoon to variation of insolation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 49, 237–263.
- Schlitzer, R., Roether, W., Oster, H., Junghans, H.-G., Hausmann, M., Johannsen, H., Michelato, A., 1991. Chlorofluoromethane and oxygen in the Eastern Mediterranean. *Deep Sea Res. Part A. Oceanogr. Res. Pap.* 38, 1531–1551. doi:10.1016/0198-0149(91)90088-W
- Schmiedl, G., Kuhnt, T., Ehrmann, W., Emeis, K.-C., Hamann, Y., Kotthoff, U., Dulski, P., Pross, J., 2010. Climatic forcing of eastern Mediterranean deep-water formation and benthic ecosystems during the past 22 000 years. *Quat. Sci. Rev.* 29, 3006–3020. doi:10.1016/j.quascirev.2010.07.002
- Siani, G., Paterne, M., Arnold, M., Bard, E., Métivier, B., Tisnerat, N., Bassinot, F., 2000. Radiocarbon reservoir ages in the mediterranean sea and black sea. *Radiocarbon* 42, 271–280.
- Siani, G., Magny, M., Paterne, M., Debret, M., Fontugne, M., 2013. Paleohydrology reconstruction and Holocene climate variability in the South Adriatic Sea. *Clim. Past* 9, 499–515. doi:10.5194/cp-9-499-2013
- Slomp, C.P., Thomson, J., De Lange, G., 2002. Enhanced regeneration of phosphorus during formation of the most recent eastern Mediterranean sapropel (S1). *Geochim. Cosmochim. Acta* 66, 1171–1184.
- Slomp, C.P., Thomson, J., De Lange, G.J., 2004. Controls on phosphorus regeneration and burial during formation of eastern Mediterranean sapropels. *Mar. Geol.* 203, 141–159. doi:10.1016/S0025-3227(03)00335-9

- Spötl, C., Nicolussi, K., Patzelt, G., Boch, R., 2010. Humid climate during deposition of sapropel 1 in the Mediterranean Sea: Assessing the influence on the Alps. *Glob. Planet. Change* 71, 242–248. doi:10.1016/j.gloplacha.2009.10.003
- Stuiver, M., Reimer, P.J., 1993. Extended ^{14}C data base and revised calib 3.0 ^{14}C age calibration program. *Radiocarbon* 35, 215–230.
- Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hughen, K.A., Kromer, B., McCormac, G., van der Plicht, J., Spurk, M., 1998. INTCAL98 Radiocarbon age calibration, 24,000-0 cal BP. *Radiocarbon* 40, 1041–1083.
- Tachikawa, K., Vidal, L., Cornuault, M., Garcia, M., Pothin, A., Sonzogni, C., Bard, E., Menot, G., Revel, M., 2015. Eastern Mediterranean Sea circulation inferred from the conditions of S1 sapropel deposition. *Clim. Past* 11, 855–867. doi:10.5194/cp-11-855-2015
- Thomson, J., Higgs, N.C., Wilson, T.R.S., Croudace, I.W., De Lange, G.J., Van Santvoort, P.J.M., 1995. Redistribution and geochemical behaviour of redox-sensitive elements around S1, the most recent eastern Mediterranean sapropel. *Geochim. Cosmochim. Acta* 59, 3487–3501.
- 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. *Mar. Geol.* 153, 77–89. doi:10.1016/S0025-3227(98)00089-9
- Triantaphyllou, M. V., 2014. Coccolithophore assemblages during the Holocene Climatic Optimum in the NE Mediterranean (Aegean and northern Levantine Seas, Greece): Paleoceanographic and paleoclimatic implications. *Quat. Int.* doi:10.1016/j.quaint.2014.01.033
- Triantaphyllou, M.V., Ziveri, P., Gogou, A., Marino, G., Lykousis, V., Bouloubassi, I., Emeis, K.-C., Kouli, K., Dimiza, M., Rosell-Melé, A., Papanikolaou, M., Katsouras, G., Nunez, N., 2009. Late Glacial–Holocene climate variability at the south-eastern margin of the Aegean Sea. *Mar. Geol.* 266, 182–197. doi:10.1016/j.margeo.2009.08.005
- Triantaphyllou, M.V., Gogou, A., Dimiza, M.D., Kostopoulou, S., Parinos, C., Roussakis, G., Geraga, M., Bouloubassi, I., Fleitmann, D., Zervakis, V., Velaoras, D., Diamantopoulou, A., Sampatakaki, A., Lykousis, V., 2016. Holocene climatic optimum centennial-scale paleoceanography in the NE Aegean (Mediterranean Sea). *Geo-Mar. Lett.* 36, 51–66.
- Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.* 232, 12–32. doi:10.1016/j.chemgeo.2006.02.012
- 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. *Geochim. Cosmochim. Acta* 60, 4007–4024.

Velaoras, D., Kassis, D., Perivoliotis, L., Pagonis, P., Hondronasios, A., Nittis, K., 2013. Temperature and salinity variability in the Greek Seas based on POSEIDON stations time series: preliminary results. *Med. Mar. Sci.* 14, 5–18

Vigliotti, L., Asioli, A., Bergami, C., Capotondi, L., Piva, A., 2011. Magnetic properties of the youngest sapropel S1 in the Ionian and Adriatic Sea: inference for the timing and mechanism of sapropel formation. *Ital. J. Geosci.* 130, 106–118. doi:10.3301/IJG.2010.29

Vogel, H., Wagner, B., Zanchetta, G., Sulpizio, R., Rosén, P., 2010. A paleoclimate record with tephrochronological age control for the last glacial-interglacial cycle from Lake Ohrid, Albania and Macedonia. *J. Paleolimnol.* 44, 295–310. doi:10.1007/s10933-009-9404-x

Weldeab, S., Menke, V., Schmiedl, G., 2014. The pace of East African monsoon evolution during the Holocene. *Geophys. Res. Lett.* 41, 1724–1731. doi:10.1002/2014GL059361

Wu, P., Haines, K., 1996. Modeling the dispersal of Levantine Intermediate Water and its role in Mediterranean deep water formation. *J. Geophys. Res.* 101, 6591–6607.

Wulf, S., Kraml, M., Brauer, A., Keller, J., Negendank, J.F.W., 2004. Tephrochronology of the 100ka lacustrine sediment record of Lago Grande di Monticchio (southern Italy). *Quat. Int.* 122, 7–30. doi:10.1016/j.quaint.2004.01.028

Wulf, S., Kraml, M., Keller, J., 2008. Towards a detailed distal tephrostratigraphy in the Central Mediterranean: The last 20,000 yrs record of Lago Grande di Monticchio. *J. Volcanol. Geotherm. Res.* 177, 118–132. doi:10.1016/j.jvolgeores.2007.10.009

Yakushev, E. V., 2013. Chemical Structure of Pelagic Redox Interfaces. doi:10.1007/978-3-642-32125-2

Zanchetta, G., Sulpizio, R., Roberts, N., Cioni, R., Eastwood, W.J., Siani, G., Caron, B., Paterne, M., Santacroce, R., 2011. Tephrostratigraphy, chronology and climatic events of the Mediterranean basin during the Holocene: An overview. *The Holocene* 21, 33–52. doi:10.1177/0959683610377531

Zheng, Y., Anderson, R.F., van Geen, A., Kuwabara, J., 2000. Authigenic molybdenum formation in marine sediments: A link to pore water sulfide in the Santa Barbara Basin. *Geochim. Cosmochim. Acta* 64, 4165–4178.

Zhornyak, L.V., Zanchetta, G., Drysdale, R.N., Hellstrom, J.C., Isola, I., Regattieri, E., Piccini, L., Baneschi, I., Couchoud, I., 2011. Stratigraphic evidence for a “pluvial phase” between ca 8200–7100 ka from Renella cave (Central Italy). *Quat. Sci. Rev.* 30, 409–417. doi:10.1016/j.quascirev.2010.12.003

			<i>14C age (BP) $\pm 1\sigma$</i>		<i>1σ age cal BP</i>
	<i>sample</i>	<i>av. Depth (cm)</i>	<i>error (yr)</i>	<i>ΔR (yr)</i>	<i>(yr)</i>
<i>a</i>	MP50PC#5 5,0-5,5	5,2	3700 $\pm$ 30	118 $\pm$ 60	3394-3554
<i>b</i>	MP50PC#5 19,5-20,0	19,7	6265 $\pm$ 35	118 $\pm$ 60	6488-6658
<i>c</i>	MP50PC#5 39,0-39,5	39,2	8020 $\pm$ 40	118 $\pm$ 60	8291-8440
<i>d</i>	MP50PC#5 48,5-49,0	48,7	8670 $\pm$ 50	118 $\pm$ 60	9074-9295
<i>e</i>	MP50PC#5 57,0-57,5	57,2	9540 $\pm$ 50	118 $\pm$ 60	10181-10363
<i>f</i>	MP50PC#4 36,5-37,0	111,7	17930 $\pm$ 90	118 $\pm$ 60	20836-21182
<i>g</i>	KN3 75,5	75,7*			3563
<i>h</i>	KN3 118-121	119,5	4980 $\pm$ 40	58 $\pm$ 85	5072-5349
<i>i</i>	KN3 149-152	150,5	6070 $\pm$ 40	149 $\pm$ 30	6284-6384
<i>j</i>	KN3 163-165	164	6760 $\pm$ 40	149 $\pm$ 30	7078-7218
<i>k</i>	KN3 181-184	182,5	7040 $\pm$ 50	149 $\pm$ 30	7342-7460

Table 1. Samples in cores MP50PC and KN3 with ^{14}C 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 $\Delta R=118\pm 60$ (Reimer & McCormac, 2002), and h-k: for Aegean core KN3 core $\Delta R=149\pm 30$ 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).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 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.

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

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

Figure 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.

Figure 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)

Figure 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., 2010), 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).