Palaeogeography, Palaeoclimatology, Palaeoecology 190 (2003) 9–21

PALAEO

www.elsevier.com/locate/palaeo

Black Sea impact on the formation of eastern Mediterranean sapropel S1? Evidence from the Marmara Sea

M. Sperling[a,*], G. Schmiedl[a,1], Ch. Hemleben[a], K.C. Emeis[b], H. Erlenkeuser[c], P.M. Grootes[c]

[a] University of Tübingen, Sigwartstraße 10, D-72076 Tübingen, Germany
[b] IO-Warnemünde, Seestraße 15, D-18119 Rostock, Germany
[c] University of Kiel, Leibniz Laboratory, Max-Eyth-Strasse 11–13, D-24118 Kiel, Germany

Received 12 February 2002; received in revised form 11 June 2002; accepted 18 October 2002

Abstract

Water exchange between the Black Sea and the Mediterranean Sea has been a major focus of the paleohydrography of the eastern Mediterranean. Glacial melt water released from the Black Sea is a potential factor in the formation of sapropel S1, an organic-rich sediment layer that accumulated during the Early Holocene. A high-resolution study done on sediments from the Marmara Sea, the gateway between the Mediterranean and the Black Sea, sheds light on the Holocene exchange processes. Past sea surface temperature and sea surface salinity (SSS) were derived from stable oxygen isotope ratios ($\delta^{18}O$) of foraminiferal calcite and alkenone unsaturation ratios ($U^{k'}_{37}$). Heavy $\delta^{18}O$ values and high SSS in the Marmara Sea suggest absence of low salinity water from the Black Sea during S1. The comparison with data from the Levantine Basin and southern Aegean Sea outlines gradients of freshening in the eastern Mediterranean Sea, whereby the major sources of freshwater were closer to the Levantine Basin. It is thus concluded that the Black Sea was not a major freshwater source contributing to formation of S1. Given the absence of a low salinity layer, the deposition of organic-rich sediments corresponding to S1 in the Marmara Sea is likely the result of the global transgression and the concomitant re-organization of biogeochemical cycles, leading to enhanced productivity as shown by *Globigerina bulloides*.

Keywords: sapropel S1; Marmara Sea; planktic foraminifera; $\delta^{18}O$; alkenones

1. Introduction

Repeated layers of dark-colored sediments rich in organic carbon, termed 'sapropels', have been periodically deposited since at least Early Pliocene times in the otherwise oligotrophic eastern Mediterranean Sea. Various hypotheses have been proposed to explain the unusual accumulation of organic carbon in deep sea sediments, most of which suggest changes in the ratio of evaporation over precipitation in addition to river run-off, which was thought to decrease abyssal ventilation

[1] Present address: University of Leipzig, Talstraße 35, D-04103 Leipzig, Germany.
* Corresponding author.
E-mail address: michael.sperling@uni-tuebingen.de (M. Sperling).

0031-0182/02/$ – see front matter
PII: S0031-0182(02)00596-5

(overview in Cramp and O'Sullivan, 1999). The most recent sapropel (S1) accumulated during the Early Holocene, about 6000–9000 yr (uncorrected ^{14}C age; Rossignol-Strick, 1999) ago. Studies of isotope ratios on foraminiferal calcite confirmed that S1 was accompanied by dilution of the surface water by river run-off or meteoric water (e.g. Thunell and Williams, 1989).

The release of glacial melt water was originally perceived as the important factor leading to the deposition of S1 (e.g. Ryan, 1972). Freshwater derived from melting of northern European ice sheets, and released 7000–9500 yr BP (uncorrected ^{14}C age) through the Black Sea, was thought to contribute to the surface water freshening, at least in the Aegean Sea (Aksu et al., 1995a, 1999, 2002; Lane-Serff et al., 1997; Catagay et al., 2000). Alternative to this melt water hypothesis, enhanced freshwater flow from the southern catchment (i.e. Nile River), due to heavier African monsoon activity, may account for the low salinity layer (e.g. Fontugne et al., 1994; Rossignol-Strick, 1999). The purpose of this study is to evaluate the Black Sea contribution to the formation of S1 and to test both hypotheses by studying marine sediment cores close to the possible sources of freshwater. Proxy data of marine organisms from the Early Holocene of the Black Sea itself cannot be obtained, due to low salinities prior to 7500 yr BP (uncorrected ^{14}C age; Arthur and Dean, 1998). Studies have thus been performed on the adjacent Marmara Sea, a 210-km long and 75-km wide intercontinental basin, connected to the Mediterranean Sea via the Dardanelles Strait (Fig. 1). The oceanography of the Marmara Sea today is characterized by the outflow of brackish water from the Black Sea, whereas saline bottom water is flowing in from the Mediterranean Sea. The resulting sharp halocline leads to permanent stratification (Alavi, 1988). The low salinity outflow

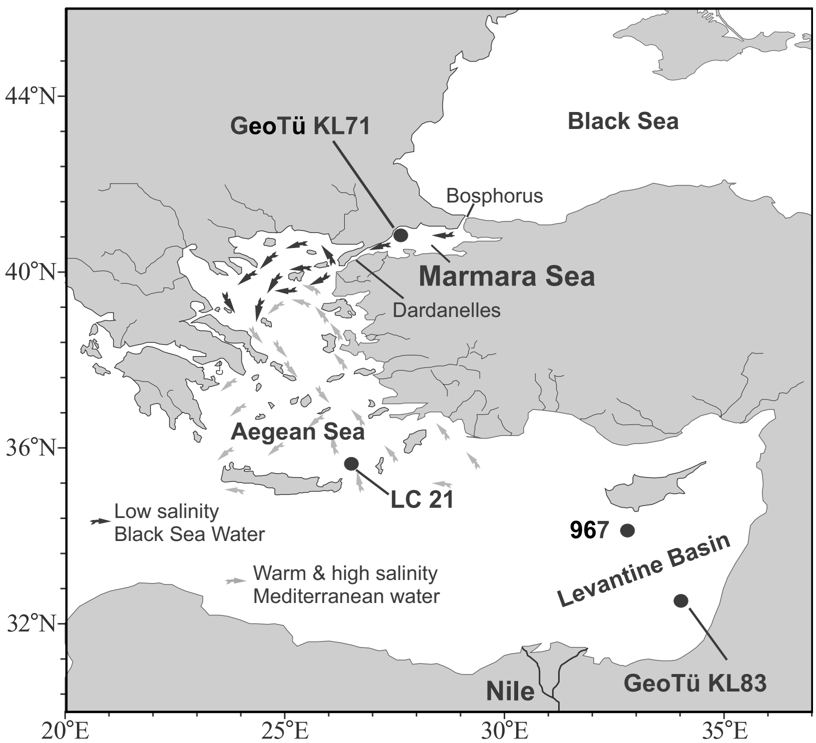


Fig. 1. Map of the eastern Mediterranean Sea showing the locations of sediment cores GeoTÜ KL71, GeoTÜ KL83, LC21 (Rohling et al., 2002), and 967 (Emeis et al., 2000). Arrows indicate modern surface water circulation in the Marmara Sea and the Aegean Sea (after Aksu et al., 1995a,b).

from the Black Sea can be traced throughout the northern Aegean Sea (Fig. 1; Aksu et al., 1995b). The sill depth of the Dardanelles is deeper (~65 m) than the Bosphorus (~35 m), and in consequence the marine intrusion of the Marmara Sea due to global sea-level rise occurred earlier than in the Black Sea (Catagay et al., 2000). The marine record of the Marmara Sea is thus longer, extending back to ~12 000 uncorrected yr BP ^{14}C (Catagay et al., 2000; Sperling et al., 2001). Here we present the first high-resolution record of sea surface temperature (SST) and sea surface salinity (SSS) of this important gateway. These data are compared with published records from the Aegean Sea (Rohling et al., 2002) and Levantine Basin (Emeis et al., 2000).

2. Materials and methods

Piston core GeoTü KL 71 was collected during the *Meteor* cruise M44/1 from the Marmara Sea (40°50.51′N, 27°45.79′E: 566 m water depth). Piston core GeoTü KL83 was collected in April 1999 during *Meteor* cruise M44/3 from the southeastern Levantine Basin (32°36.9′N, 34°08.9′E; 1433 m water depth) (see Fig. 1).

2.1. Chronology, total organic carbon, planktic foraminifera, and oxygen isotope records

The chronologies of cores GeoTü KL 71 (Marmara Sea) and GeoTü KL 83 (Levantine Basin) are based on accelerator mass spectrometry (AMS) ^{14}C dates performed at the Leibniz Laboratory for Radiometric Dating and Stable Isotope Research in Kiel with a precision of ±40 to ±60 years standard deviation (Table 1). The well-dated Cape Riva ash layer (Wulf et al., 2002) at 22 ka (calibrated calendar years) was used as a further time marker in core GeoTü KL 71. The paucity in foraminifera prevented reliable dating of the upper 90 cm of core GeoTü KL71. Total organic carbon (TOC) and bulk carbonate yielded anomalously old ages, probably due to the input of reworked material. The ^{14}C years were adapted by applying reservoir corrections (Siani et al., 2000) and calibrated to calendar years with the CALIB 4.3 program (Stuiver and Reimer, 1993). The age-model of GeoTü KL 71 was derived by linear interpolation between the calibrated time markers. GeoTü KL 83 from the Levantine Basin was dated by one ^{14}C age and correlation of the $\delta^{18}O$ curve to the isotope record of core ODP Site 967 (Emeis et al., 1998). If not stated otherwise, all ages are given as calibrated calendar years.

Core GeoTü KL 71 was sub-sampled at 1–2-cm intervals, and the sediment fraction larger than >63 µm was investigated for planktic foraminifera. TOC of core GeoTü KL71 was measured by the combustion technique using a VARIO elemental analyzer at the University of Tübingen. Oxygen isotopic measurements ($\delta^{18}O$) have been performed on the planktic foraminifera *Turborotalita quinqueloba* (GeoTü KL 71), and *Globigerinoides ruber* (GeoTü KL 83), following the standard procedures at the Leibniz Laboratory, Kiel. Efforts were made to use exceptionally

Table 1
Age control for the cores investigated based on AMS radiocarbon measurements

Core	Depth (cm)	Material	Laboratory number	^{14}C age (yr)	Reservoir age (yr)	Calibrated age (ka)
GeoTÜ KL 71	90–91	bulk carbonate	KIA-14788	15 610 ± 350	n.a.	n.a.
GeoTÜ KL 71	90–91	TOC (humic acid)	KIA-14788	8450 ± 70	n.a.	n.a.
GeoTÜ KL 71	95–98	benthic foraminifera	KIA-13931	8110 ± 43	346 ± 60	8.52
GeoTÜ KL 71	120–123	*Globigerina bulloides*	KIA-13410	9280 ± 50	346 ± 60	10.17
GeoTÜ KL 71	165–166	juvenile molluscs	KIA-13571	11 330 ± 60	346 ± 60	12.99
GeoTÜ KL 83	42.5–43.5	*Globigerinoides ruber*	KIA-15077	7370 ± 40	614 ± 40	7.6

The calibration was performed with the CALIB 4.3 program, using the MARINE98 ^{14}C calibration data set (Stuiver and Reimer, 1993).

well preserved specimens with a 'glassy' appearance, since tests of *T. quinqueloba* have been proven to be prone to artificial $\delta^{18}O$ depletion (Sperling et al., in press). The results are reported as per mil deviation with respect to the international PeeDee Belemnite standard, with a reproducibility better than 0.03 ‰.

2.2. Estimates of sea surface temperature and salinity

To date, past SSS cannot be determined directly from any of the available proxy data (Rohling, 2000). Paleosalinity is estimated by indirect approaches, using oxygen isotope records by subtracting temperature and global ice effect (e.g. Rostek et al., 1993; Thunell and Williams, 1989). The two most widespread methods to estimate past SST are based on the relative abundance of planktic foraminifera as indicators of particular environmental conditions, and the unsaturation ratios of alkenone $U^{k'}_{37}$ (e.g. Sbaffi et al., 2001). We consider the former method unsuitable in the Marmara Sea due to the unusually poor diversity of the planktic assemblages, which are mainly restricted to two small (<125 μm) species of *Turborotalita* spp. (Alavi, 1988; this study). The alkenone $U^{k'}_{37}$ method is based on the relative abundance of the di- and tri-unsaturated C^{37} alkenones synthesized by *Haptophyceae* algae (Brassell et al., 1986). Several studies have shown a linear relationship between $U^{k'}_{37}$ and ambient water temperature. Consequently, the $U^{k'}_{37}$ method has become a popular tool to estimate SST (Müller et al., 1998 and references therein). Error calculations of the $U^{k'}_{37}$ based SST estimates are discussed in Emeis et al. (in press) and found to be ±1.1°C in the Mediterranean during the Holocene. An evaluation of the confidence limits of SSS reconstructions was published by Rohling (2000), who calculated the uncertainty to be at least ±1.8 ‰ for the Mediterranean Sea. Given that, and further uncertainties considered below, trends rather than absolute values of SSS are discussed.

SST values were reconstructed from unsaturation ratios of long-chain ketones $U^{k'}_{37}$ (Brassell et al., 1986). Lyophilized and homogenized sediment samples were extracted with dichloromethane in a Dionex Accelerated Solvent Extractor 200 and analyzed using the gas chromatographic conditions as described in Emeis et al. (1998) with no prior clean-up. SST values were calculated from alkenone unsaturation ratios according to Müller et al. (1998):

$$\mathrm{SST}\ ^{\circ}\mathrm{C} = (U^{k'}_{37} - 0.044)/0.033$$

Salinity reconstructions were performed as described in Emeis et al. (1998) by using the expression given by Rostek et al. (1993):

$$S = \Delta S_o + S^* + (\Delta\delta^{18}O_F - a - b\Delta T)/c$$

In this equation, S stands for past local surface salinity and S* is the present-day local surface salinity. The difference between foraminiferal calcite $\delta^{18}O$ ratios at time T and the present is represented by the variable $\Delta\delta^{18}O_F$. ΔS_o and a express the global change of ocean salinity, and seawater $\delta^{18}O$, respectively, due to ice shield growth and decay. We used the Vogelsang (1990) data set for ice correction, which gives values in 1000-years intervals, and interpolated linearly between values. The maximum ice effect in our time-interval is $a = 0.59$ ‰ at 14 ka. We neglected the global change of ocean salinity in our current study, since the focus is on the Middle to Late Holocene, where the global ice-volume and thus the global ocean salinity did not change considerably. The constant b stands for the temperature effect of *Turborotalita quinqueloba* on $\delta^{18}O$, which is −0.17/K in the high latitude North Atlantic (Stangeew, 2001). Paleotemperature estimates were derived from $U^{k'}_{37}$, whereby the value from the core-top (1 cm core depth) was used as our modern end-member to calculate ΔT, the temperature change from modern to past. One drawback is that the core-top value may not be representative for modern conditions, which might bias all calculated past variations. On the other hand, the offset should be systematic in the paleoceanographic reconstructions and not of relevance, if relative changes, compared to modern, are considered. A further drawback is the possible and seasonal offset in the formation of the temperature and the isotopic signal. *Turborotalita quinqueloba* reproduces in a lunar cycle and builds its chamber in the upper 50-m water column (Stangeew, 2001). The depth habitat of this species is thus similar to the dominant alkenone producer *Emiliania huxleyi* (Winter and Siesser, 1994), but it is uncertain if peak abundances of both organisms occur simultaneously. Finally, the coefficient *c* relating salinity and $\delta^{18}O_{seawater}$ may be variable over time due to changing moisture sources of the Mediterranean (e.g. Rohling and Bigg, 1997). We used two ratios (0.25‰/p.s.u., Pierre, 1999; 0.45‰/p.s.u., Thunell and Williams, 1989) to bracket possible past relationships between salinity and $\delta^{18}O_{seawater}$.

The data presented are stored in the PANGAEA data base (www.pangaea.de).

3. Results

3.1. TOC and planktic foraminifera records

Core GeoTü KL 71 from the Marmara Sea exhibits a dark-colored layer deposited between 7 and 11 ka (Fig. 2A), thereby preceding sapropel S1 in the eastern Mediterranean Sea. TOC values are above 1.5 wt% within the dark-colored layer. A pale-colored layer displays reduced TOC values. The first planktic foraminifera occur at 13.7 ka (Fig. 2B). Planktic assemblages consist almost exclusively of *Turborotalita* spp., with only few other species occurring in any significant numbers. *Globigerina bulloides* is confined to the interval with high TOC contents, *Neogloboquadrina incompta* is abundant at the top of the pale-colored layer, and *Globigerinoides ruber* (red) is restricted to the post-sapropel interval.

3.2. Planktic oxygen isotope records, SST and SSS estimates

The $\delta^{18}O$ past-$\delta^{18}O$ present differences of planktic foraminifera from the Marmara Sea (*Turborotalita quinqueloba*, $\Delta\delta^{18}O_{Marmara}$), Levantine Basin (*Globigerinoides ruber*, $\Delta\delta^{18}O_{Levantine}$) are presented in Fig. 3A. For comparison, a published record from the southern Aegean Sea is also shown (*G. ruber*, $\Delta\delta^{18}O_{Aegean}$; Rohling et al., 2002). The $\Delta\delta^{18}O_{Marmara}$ curve varies little from 13.5 to 7 ka, except for slightly lighter values during the Bölling–Alleröd interstadial, and heavier values within the Younger Dryas. A prominent feature of the $\Delta\delta^{18}O_{Marmara}$ curve is the continuous trend toward lighter values after 7 ka, cumulating in the most depleted values around 5 ka. In contrast, $\Delta\delta^{18}O_{Levantine}$ and $\Delta\delta^{18}O_{Aegean}$ values decrease during the Early Holocene, with the most depleted values occurring within the sapropel interval. Trends in all three cores resemble each other closest since 5 ka.

To evaluate the influence of salinity on the $\Delta\delta^{18}O_{Marmara}$ signal, we used SST estimates based on $U^{k'}_{37}$ (Fig. 3B). The lowest SST in the Marmara Sea occurred shortly before the onset of the Younger Dryas, after which values increased steadily towards a thermal maximum at 8.7 ka. The remainder of the Holocene is characterized by a decreasing SST trend. To reconstruct SSS, the ice-effect due to global ice-shield growth and decay (data from Vogelsang, 1990) and the temperature effect (estimated from $U^{k'}_{37}$) were subtracted from the raw $\delta^{18}O$ Marmara data (for description see Emeis et al., 2000). Lower than modern SSS values occurred mainly prior to the Younger Dryas (Fig. 3C). Higher salinity prevailed during most of S1, and after 7.7 ka SSS decreased steadily towards modern conditions.

4. Discussion

4.1. Stable isotope records

The stable isotope data from the Levantine Basin and the southern Aegean Sea (Rohling et al., 2002) may be considered as representative for the eastern Mediterranean. The most depleted values occur during S1, mainly due to surface water freshening (Kallel et al., 1997; Rossignol-Strick, 1999; Emeis et al., 2000; Krishnamurthy et al., 2000). Since *Turborotalita quinqueloba* (Marmara Sea) and *Globigerinoides ruber* (Levantine Basin and Aegean Sea) are both shallow dwellers (Hemleben et al., 1989; Stangeew, 2001), it is likely that the isotope offset of the $\Delta\delta^{18}O_{Marmara}$ record is not

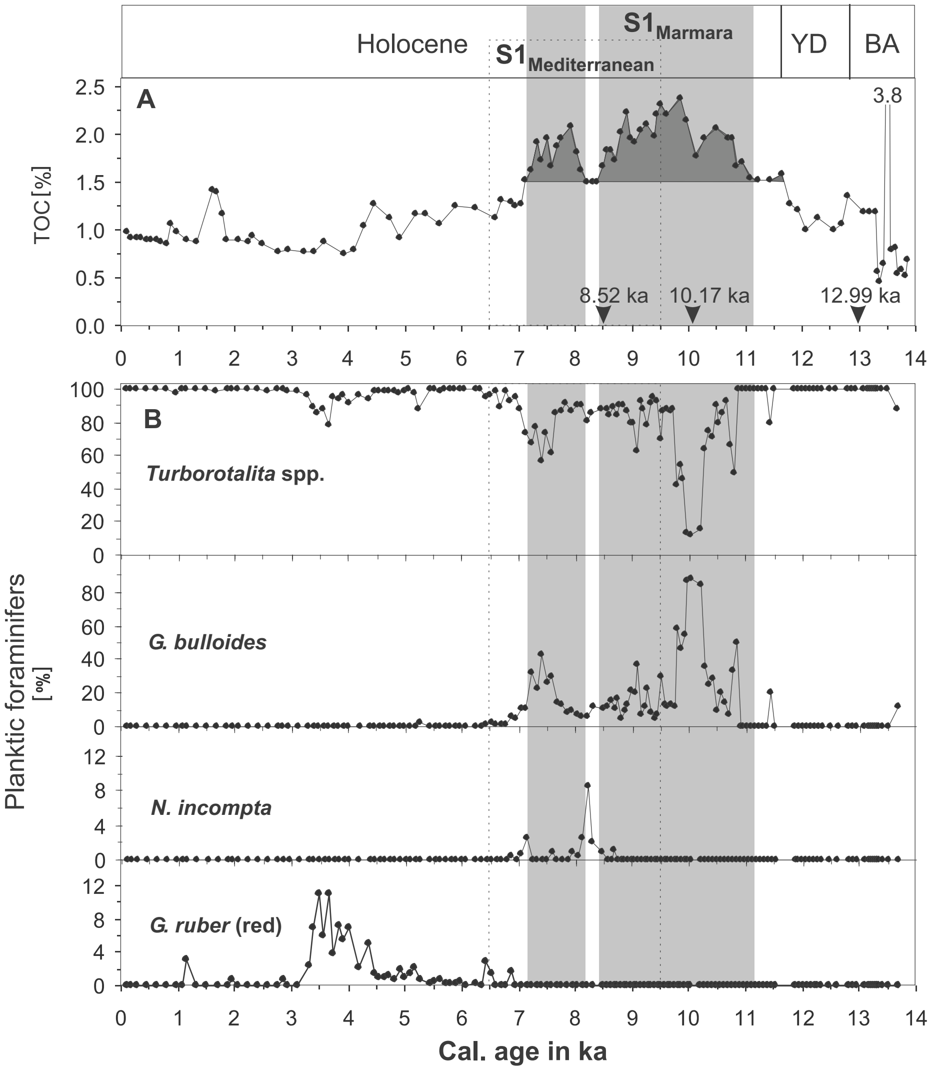


Fig. 2. Total organic carbon (TOC), planktic foraminifera counts (in percent), and ^{14}C ages (in calibrated calendar years) of core GeoTü KL71 from the Marmara Sea. Range of sapropel $S1_{Mediterranean}$ (dashed lines), $S1_{Marmara}$ (gray background), Younger Dryas (YD), and Bölling–Alleröd interstadial (BA) are indicated. Triangles show ^{14}C ages (A). Note the early onset of raised TOC values in the Marmara Sea, compared with the onset of S1 in the eastern Mediterranean. Planktic foraminifera counts (in percent) are shown in (B). The assemblages are strongly dominated by *Turborotalita quinqueloba* and *T. clarkei*. The adult stage of the latter is difficult to distinguish from the pre-adult stages of *T. quinqueloba* (Hemleben et al., 1989), both species were thus combined in *Turborotalita* spp.

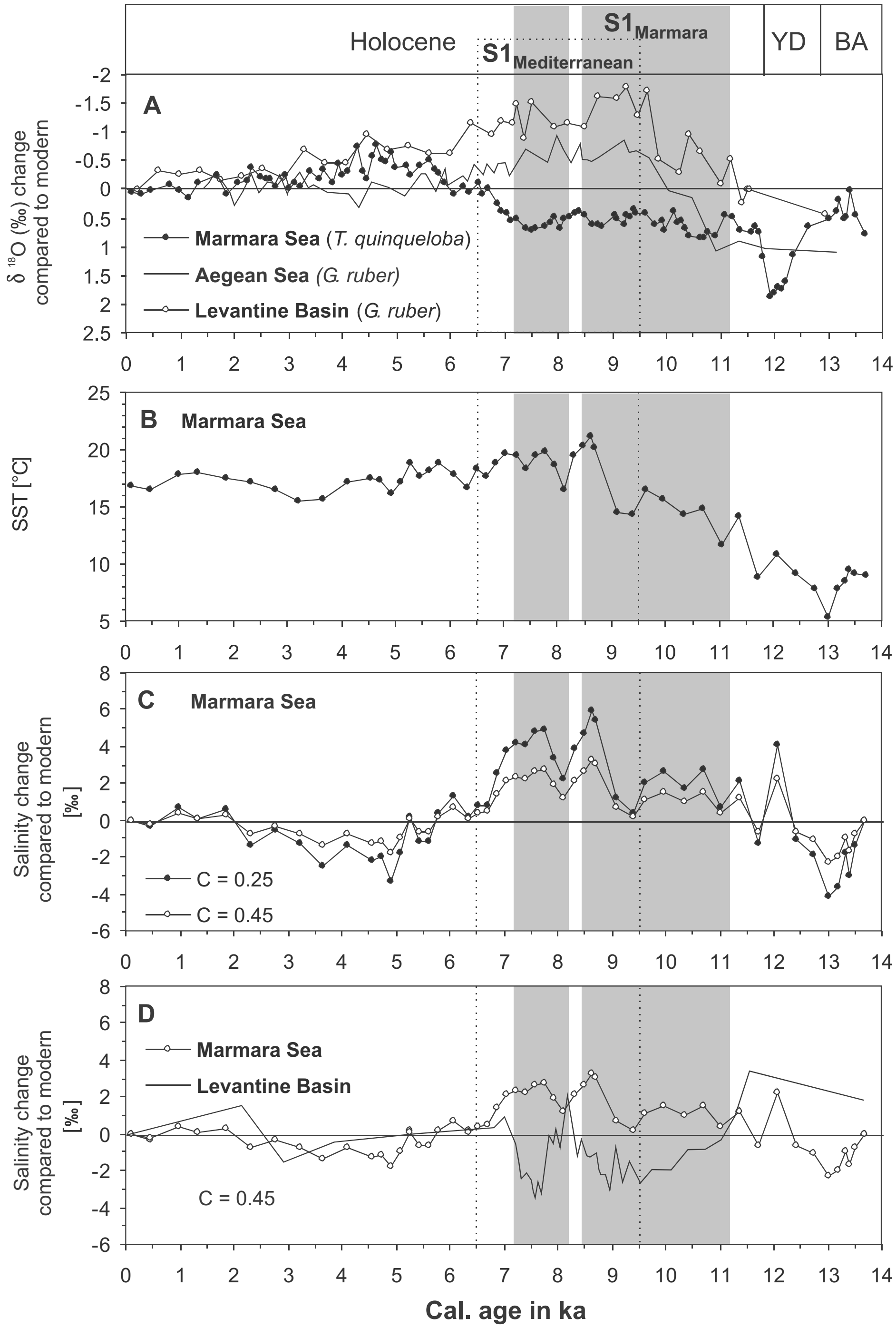
due to a habitat effect, but indicative of differences in SST and SSS. Within S1, the $\Delta\delta^{18}O_{Levantine}$ values are the most depleted (<-1.8‰). In comparison, $\Delta\delta^{18}O_{Aegean}$ are less negative, and $\Delta\delta^{18}O_{Marmara}$ heavier ($<+0.7$‰) than modern values. Consequently, our data indicate gradients of freshening, supporting earlier works (e.g. Rossignol-Strick, 1985). From the anomalously heavy $\Delta\delta^{18}O_{Marmara}$ values we infer that the major sources of surface water freshening were distal to the Marmara Sea, and the by comparison most depleted δ^{18}O Levantine values further support the hypothesis of the southern catchment as the main freshwater source during S1 (e.g. Rossignol-Strick, 1985; 1999; Krom et al., 2002).

4.2. SST and SSS estimates

The general trends of our SST estimates, showing a warm period between ~9 and 5.7 ka ('hypsithermal') and a cooling trend thereafter (Fig. 2B), agree well with other records from the Northern Hemisphere (e.g. Cacho et al., 2001a; Sbaffi et al., 2001; Marchal et al., 2002). A problem of our estimates is the slight warming during the cold Younger Dryas. Since the Younger Dryas was generally an arid phase in the area (Bottema, 1995), less melt water and increased influx of slightly warmer water originating from the Mediterranean Sea may account for this discrepancy. Alternatively, the incorporation of 'old' alkenones from the proceeding Bölling–Alleröd interstadial might have distorted the temperature signal. On the other hand, the major trends of SST in the Marmara Sea during the Holocene are roughly in phase with the Mediterranean Sea, consequently suggesting a synchronous climatic development. Therefore, an asynchronous SST pattern of the Marmara Sea and the Mediterranean cannot explain the anomalous heavy $\Delta\delta^{18}O_{Marmara}$ values occurring during deposition of S1. Given that, asynchronous SSS evolutions of both areas are the most likely explanation. However, a recent study yielded contradicting evidence (Aksu et al., 2002), the records of which from the Marmara Sea seem to indicate lower SSS during S1. Those reconstructions are based on transfer function analysis of planktic foraminifera assemblages. While this technique works well in open-marine environments with rather constant conditions and diverse assemblages, it may be unsuitable in small enclosed basins with large scale salinity, temperature, and productivity fluctuations such as the Marmara Sea (Sbaffi et al., 2001). Furthermore, our investigation of Core GeoTü KL 71 shows that the Holocene planktic assemblages in the Marmara Sea consist of unusually few species (Fig. 2B). Past diversity was probably not sufficient to permit statistically sound results by the transfer function technique.

4.3. Origin of organic-rich sediments in the Marmara Sea

Even after four decades of sapropel research, the precise mechanisms that lead to the formation of sapropels are still under debate because of the uncertainty on the relative roles of productivity and preservation of organic matter (overview in Cramp and O'Sullivan, 1999). The faunal assemblage variations of planktic foraminifera core GeoTü KL 71 indicate that the Holocene in the Marmara Sea was accompanied by marked changes in productivity. The occurrence of *Globigerina bulloides* within the organic-rich interval ($S1_{Marmara}$; Fig. 2A) indicates increased productivity in the surface waters (Rohling et al., 1997). The return to lower productivity in the post-sapropel is shown by the disappearance of *G. bulloides*. The stable isotope and SSS records suggest that deposition of $S1_{Marmara}$ was not accompanied by surface-water freshening, which was believed to be one of the main factors (Catagay et al., 2000; Aksu et al., 2002). However, despite intense stratification in the modern Marmara Sea due to Black Sea outflow, the sea floor is not anoxic and no sapropelic sediments are currently accumulating due to the short residence time of deep water (e.g. Alavi, 1988), proving that a low-salinity layer as the main trigger can be ruled out. Further evidence for a different origin of $S1_{Marmara}$ is our observation that deposition started about 1.5 ka earlier than S1 in the eastern Mediterranean Sea (Fig. 2A), supporting earlier works (Catagay et al., 2000). The key factor to $S1_{Marmara}$ is probably the low global sea-level prior to 9.5 ka (> 28 m below today; Fairbanks, 1989), restricting deep-water circulation and thus oxygenation of the sea floor. The following transgression over the shallow sill of the Dardanelles (~65 m) and the concomitant re-organization of biogeochemical cycles would explain the enhanced productivity as indicated by *G. bulloides*. $S1_{Marmara}$ is thus of different genesis and different time range than the well defined $S1_{Mediterranean}$.



4.4. Paleoceanographic implications

The $\delta^{18}O$ and SSS data suggest that $S1_{Marmara}$ was accompanied by higher salinity, which is in strong contrast to the freshening found elsewhere in the eastern Mediterranean Sea (Fig. 3D). In the modern Marmara Sea, the relatively low surface salinity is mainly caused by outflow from the

Black Sea, and to a lesser extent from local rivers (605 km^3/yr vs. 6 km^3/yr; Ünlüata et al., 1990). A decrease in precipitation during the Younger Dryas may have drawn the water-level of the Black Sea below its Bosphorus outlet (Ryan et al., 1997), thereby cutting off the Marmara Sea from its main freshwater source (Fig. 4A). High SSS during the Younger Dryas in the Marmara Sea may thus have been caused by the disconnection from the Black Sea. However, if the comparatively high SST during the Younger Dryas were an artifact due to reworking (see Section 4.3), the SSS may have been overestimated. Slightly lowered SSS values are recorded at the beginning of S1 around 9.3 ka, but not to an extent that would support the notion of a large inundation by freshwater moving through the Marmara Sea. At 8.7 ka SSS rose abruptly in the Marmara Sea. A rapid raising of the global sea-level, enhancing the exchange of the Mediterranean with the Marmara Sea, might explain this pattern although major melt water pulses occurred earlier (Fairbanks, 1989).

One possible explanation of the abrupt rise in SSS in the Marmara Sea involves the marine flooding of the Black Sea, which was either a gradual (e.g. Ross and Degens, 1974; Lane-Serff et al., 1997; Arthur and Dean, 1998) or a catastrophic event (Ryan et al., 1997; Ballard et al., 2001). Prior to 9.5 ka the Black Sea was a lake (Fig. 4A), but the height of the water level is under debate (Görür et al., 2001). Lane-Serff et al. (1997) argued on the base of model flux calculations that the water level was similar to the global sea-level, whereas an erosion surface in the Black Sea at a water depth of 123–156 m, interpreted as a submerged shore line, indicated a lower sea level (Ryan et al., 1997; Ballard et al., 2001). Reworked freshwater molluscs in the erosion layer are as young as $\sim$8.7 ka (8250 yr BP uncorrected ^{14}C age; Ryan et al., 1997). The temperature/salinity peak at 8.7 ka in the Marmara Sea coincides with the age of the erosion surface in the Black Sea, pointing to a causal connection. Our SSS estimates suggest higher values than today in the Marmara Sea ($<$30 p.s.u.; Ünlüata et al., 1990) at the onset of S1 (Fig. 4A). SSS values in the eastern Mediterranean Sea were relatively low (Emeis et al., 2000) due to the surface freshening accompanied with S1$_{\text{Mediterranean}}$, but still higher than in the Marmara Sea. Consequently, most likely a flooding with saline and presumably somewhat warmer water originating from the Mediterranean Sea led to increased SSS and SST in the Marmara Sea (Fig. 4B). In this scenario, the Black Sea would have filled up from the bottom, with low salinity surface water on top. We argue that after the filling of the Black Sea had been completed, the low salinity lid from the Black Sea intruded into the Marmara Sea and decreased surface salinity there (Fig. 4C). The flooding of the Black Sea may thus explain why the SST evolution of the Marmara Sea was in phase with that of the Mediterranean Sea, whereas the SSS evolution was not.

One may speculate about the impact of the proposed flooding on the paleoceanography of the region. During the initial stages freshwater-induced stratification may have been episodic and weak, thereby permitting occasional convection and oxygen supply to the sea floor in the Aegean Sea and adjacent areas. Frequently observed pale-colored sediments within S1$_{\text{Marmara}}$ (Fig. 2A) and S1$_{\text{Mediterranean}}$ (e.g. Mercone et al., 2001) may thus be connected to the flooding of the Black Sea. The 'interruption' of S1$_{\text{Mediterranean}}$

Fig. 3. Changes in δ^{18}O of planktic foraminifera from the Marmara Sea (core GeoTü KL 71), Levantine Basin (core Geo Tü KL 83), and Aegean Sea (core LC21; data from Rohling et al., 2002) are shown in (A). Ranges of sapropel S1$_{\text{Mediterranean}}$ (dashed lines) and S1$_{\text{Marmara}}$ (gray background) are indicated. Note the large isotopic offset between the Levantine Basin and Marmara Sea in the sapropel interval, and more synchronous fluctuations after 5.5 ka. (B) depicts the SST from the Marmara Sea, based on alkenone unsaturation ratios of core GeoTü KL 71. The SSS were calculated by applying two ratios, 0.25‰/p.s.u. and 0.45‰/p.s.u., whereby larger variations are being produced by the former (C). Note the salinity peak at 8.7 ka and the continuous decrease after 7.5 ka, which may be related to the flooding of the Black Sea shelf. (D) shows a comparison of the Marmara SSS record with a record from the Levantine Basin (core 967; Emeis et al., 2000). Note the discrepancy between both records prior to and during S1 $_{\text{Mediterranean}}$, depicting opposing trends.

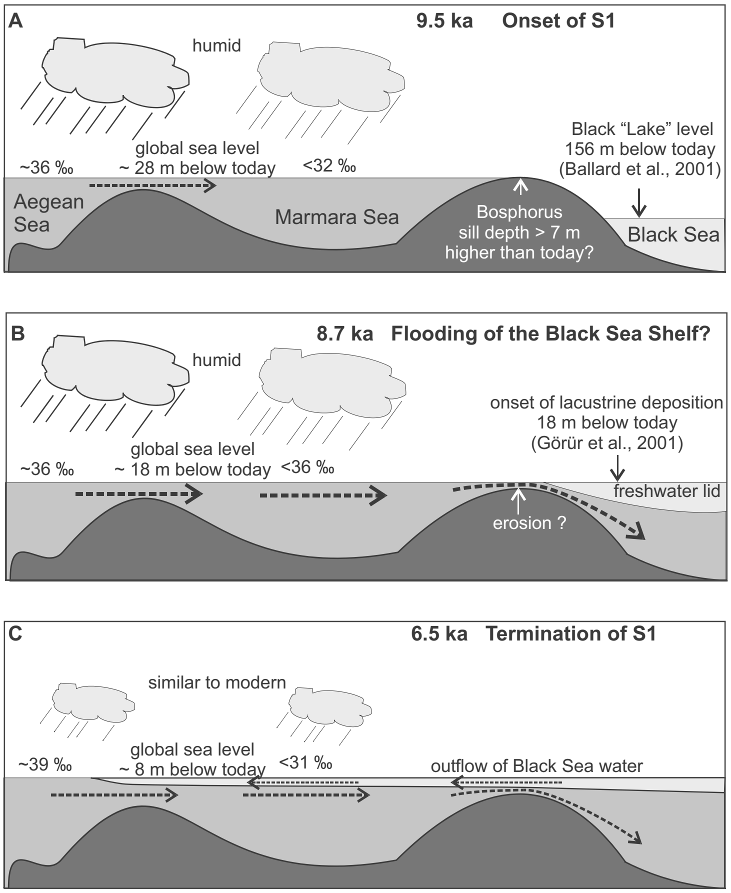


Fig. 4. Hypothetical model to explain the SSS development in the Marmara Sea. Global sea level fluctuations have been taken from Fairbanks (1989), SSS of the Marmara Sea are based on the $U^{k'}_{37}$ results from this study, the values from the eastern Mediterranean Sea are estimates based on Emeis et al. (2000). Arrows indicate currents originating from the Mediterranean Sea and the Black Sea. Today, the SSS gradient between the Marmara Sea and the eastern Mediterranean is more than 10‰ (Ünlüata et al., 1990), but was lower around 9.5 ka (∼4‰). However, the SSS values were still lower in the Marmara Sea compared with the Mediterranean Sea, possibly due to the small size of the former reservoir, which is more heavily influenced by increased precipitation or fluvial input of local rivers. The smaller SSS gradient may be caused by the disconnection to the Black Sea freshwater reservoir prior to 8.7 ka (A). This assumption requires that the sill depth of the Bosphorus was at least 7 m higher than today, since the modern depth of ∼35–40 m would have permitted marine inundation of the Black Sea at ∼10 ka (Lane-Serff et al., 1997). Erosion during the flooding could have removed sediments, and evidence for this may be a disconformity with a possible erosional lower boundary found in the Bosphorus (Catagay et al., 2000). At 8.7 ka the SSS values were comparable in both areas, presumably caused by the flooding of the Black Sea shelf (B). The modern SSS gradient between the Marmara Sea and the Mediterranean was achieved around 6.5 ka, indicating that the modern surface outflow of the Black Sea was fully established by this time (C).

was found be close to a global 8.2 ka cold event (Mercone et al., 2000; Geraga et al., 2000; Areztegui et al., 2000) and, consequently, it was suggested that thermohaline circulation and thus oxygenation of the sea floor was enhanced during cold events (e.g. Cacho et al., 2001b). We found no evidence of colder temperatures at the beginning of the 'interruption' in the Marmara Sea, but a peak occurrence (Fig. 2B) of the cooler water species *Neogloboquadrina incompta* (e.g. Rohling et al., 1997) at the top of the pale-colored layer of $S1_{Marmara}$, which coincides with a SST low (Fig.

2B), could be connected to the 8.2 ka cold event. However, it is unlikely that the cold event caused the 'interruption' of $S1_{Marmara}$, since the SST low and the *N. incompta* peak are clearly on top of the pale-colored layer. Theoretically increased bioturbation and 'burn-down' of TOC of the uppermost sediment layers may account for this discrepancy, but in this case one would expect that the climate signal of the cold event would be also 'smeared' down.

To confirm our hypotheses, ongoing research is focusing on the northern Aegean Sea. Today, the low salinity tongue originating from the Black Sea can be traced throughout the northern Aegean Sea (Fig. 1), which is therefore a promising study area for combined high-resolution studies of $U^{k'}_{37}$ and $\delta^{18}O$ to clarify nature and timing of the Black Sea outflow.

5. Summary

A high-resolution record of SSS and SST from the Marmara Sea unravels the timing of the outflow of Black Sea water during the Holocene. Heavy $\delta^{18}O$ Marmara values and high SSS are in strong contrast to the isotopic depletion found in the Levantine Basin during S1. This indicates that the Black Sea was not likely a major contributor to the surface water freshening accompanied with S1 in the eastern Mediterranean Sea. The comparison with data from the southern Aegean Sea suggests gradients of freshening, and that the major source of freshwater was closer to the Levantine Basin. Our data support the hypothesis of a southern Mediterranean source as the origin of the freshening. Furthermore, the paleoclimatic evolution of the Mediterranean Sea was synchronous to that of the Marmara Sea in terms of SST with a thermal maximum occurring during deposition of S1, but asynchronous with respect to the SSS evolution. This pattern is possibly due to the marine flooding of the Black Sea Shelf at 8.7 ka, which drew saline water from the Mediterranean into the Marmara Sea. The deposition of organic-rich sediments in the Marmara Sea preceding S1 in the eastern Mediterranean Sea is likely the result of the transgression and the concomitant reorganization of biogeochemical cycles, leading to enhanced productivity as indicated by *Globigerina bulloides*.

Acknowledgements

We thank the *Meteor* M44/1 and M44/3 crews and scientific parties for recovery of the core material, and Sven Eidel (Tübingen), Hans Cordt (Kiel) and Heinz Heckt (Kiel) for laboratory assistance. The reviews of Ali Aksu, Fred Prahl, Petra Heinz and one anonymous reviewer are gratefully acknowledged. This research was funded by the Deutsche Forschungsgemeinschaft (DFG-grants He 697/40 and Em 37/8).

References

Aksu, A.E., Hiscott, R.N., Mudie, P.T., Rochon, A., Kaminski, M.A., Abrajano, T., Yasar, D., 2002. Persistent Holocene outflow from the Black Sea to the eastern Mediterranean contradicts Noah's flood hypothesis. GSA Today 12, 4–10.

Aksu, A.E., Hiscott, R.N., Yasar, D., 1999. Oscillating Quaternary water levels of the Marmara Sea and vigorous outflow into the Aegean Sea from the Marmara Sea–Black Sea drainage corridor. Mar. Geol. 153, 275–302.

Aksu, A.E., Yasar, D., Mudie, P.J., 1995a. Paleoclimatic and paleoceanographic conditions leading to development of sapropel layer S1 in the Aegean Sea. Palaeogeogr. Palaeoclimatol. Palaeoecol. 116, 71–101.

Aksu, A.E., Yasar, D., Mudie, P.J., Gillespie, H., 1995b. Late glacial–Holocene paleoclimatic and paleoceanographic evolution of the Aegean Sea; micropaleontological and stable isotopic evidence. Mar. Micropaleontol. 25, 1–28.

Alavi, S.n., 1988. Late Holocene deep-sea benthic foraminifera from the Sea of Marmara. Mar. Micropaleontol. 13, 213–237.

Areztegui, D., Asioli, 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.

Arthur, M.A., Dean, W.E, 1998. Organic-matter production and preservation and evolution of anoxia in the Holocene Black Sea. Paleoceanography 13, 395–411.

Ballard, R.D., Coleman, D.F., Rosenberg, G.D., 2001. Further evidence of abrupt Holocene drowning of the Black Sea shelf. Mar. Geol. 170, 253–261.

Bottema, S., 1995. The Younger Dryas in the eastern Mediterranean. In: Global Younger Dryas, vol. 2. Quaternary Science Reviews 14, pp. 883–891.

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., Sarnthein, M., 1986. Molecular stratigraphy: a new tool for climatic assessment. Nature 320, 129–133.

Cacho, I., Grimalt, J.0., Canals, M., Sbaffi, L., Shackleton, N.J., Schönfeld, J., Zahn, R., 2001a. Variability of the western Mediterranean Sea surface temperature during the last 25,000 years and its connection with the Northern Hemisphere climatic changes. Paleoceanography 16, 40–52.

Cacho, I., Grimalt, J.O., Sierro, F.J, Shackleton, N., Canals, M., 2001b. Evidence for enhanced Mediterranean thermohaline circulation during rapid climatic coolings. Earth Planet. Sci. Lett. 183, 417–429.

Catagay, M.N., Gorur, N., Algan, O., Eastoe, C., Tchapalyga, A., Ongan, D., Kuhn, T., Kuscu, L., 2000. Late glacial–Holocene palaeoceanography of the Sea of Marmara; timing of connections with the Mediterranean and the Black seas. Mar. Geol. 167, 191–206.

Cramp, A., O'Sullivan, G., 1999. Neogene sapropels in the Mediterranean; a review. Mar. Geol. 153, 11–28.

Emeis, K.-C., Schulz, H., Struck, U., Rossignol-Strick, M., Erlenkeuser, H., Howell, M.W., Kroon, D., Mackensen, H., Ishizuka, S., Oba, T., Sakamoto, T., Koizumi, I., in press. Eastern Mediterranean surface water temperatures and $\delta^{18}O$ composition during deposition of sapropels in the late Quaternary. Paleoceanography.

Emeis, K.-C., Schulz, H.-M., Struck, U., Sakamoto, T., Doose, H., Erlenkeuser, H., Howell, M., Kroon, D., Paterne, M., 1998. Stable isotope and temperature records of sapropels from ODP Sites 964 and 967: Constraining the physical environment of sapropel formation in the Eastern Mediterranean Sea. In: Robertson, A.H.F., Emeis, K.-C., Richter, C., Camerlenghi, A. (Eds.), Proc. ODP, Sci. Res., 160. Ocean Drilling Program, College Station, TX, pp. 309–331.

Emeis, K.Ch., Struck, U., Schulz, H.M., Rosenberg, R., Bernasconi, S.M., Erlenkeuser, H., Sakamoto, T., Martinez, R.F., 2000. Temperature and salinity variations of Mediterranean Sea surface waters over the last 16,000 years from records of planktic stable oxygen isotopes and alkenone unsaturation ratios. Palaeogeogr. Palaeoclimatol. Palaeoecol. 158, 259–280.

Fairbanks, R.G., 1989. 17,000-year glacio–eustatic sea level record; influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. Nature 342, 637–642.

Fontugne, M., Arnold, L., Labeyrie, M., Paterne, M., Calvert, S.E., Duplessy, J.C., 1994. Paleoenvironment, sapropel chronology and Nile River discharge during the last 20,000 years as indicated by deep-sea sediments. Radiocarbon 34, 75–88.

Geraga, M., Tsaila, M.S., Ioakim, C., Papatheodorou, G., Ferentinos, G., 2000. Evaluation of palaeoenvironmental changes during the last 18,000 years in the Myrtoon Basin, SW Aegean Sea. Palaeogeogr. Palaeoclimatol. Palaeoecol. 156, 1–17.

Görür, N., Catagay, M.N., Emre, Ö., Bedri, A., Sakinc, M., Islamoglu, Y., Oya, A., Erkal, T., Kecer, M., Akkök, R., Harlik, G., 2001. Is the abrupt drowning of the Black Sea shelf at 7150 yr BP a myth? Mar. Geol. 176, 65–73.

Hemleben, Ch., Spindler, M., Anderson, O.P., 1989. Modern Planktic Foraminifera. Springer, New York, 363 pp.

Kallel, N., Paterne, M., Labeyrie, L., Duplessy, J.C., Arnold, M., 1997. Temperature and salinity records of the Tyrrhenian Sea during the last 18,000 years. Paleogeogr. Paleoclimatol. Paleoecol. 135, 97–108.

Krishnamurthy, R.V., Meyers, P.A., Lovan, N.A., 2000. Isotopic evidence of sea-surface freshening, enhanced productivity, and improved organic matter preservation during sapropel deposition in the Tyrrhenian Sea. Geology 28, 263–266.

Krom, M.D., Stanley, J.D., Cliff, R.A., Woodward, J.C., 2002. Nile River sediment fluctuations over the past 7000 yr and their key role in sapropel development. Geology 30, 71–74.

Lane-Serff, G.F., Rohling, E.J., Bryden, H.L., Charnock, H., 1997. Postglacial connection of the Black Sea to the Mediterranean and its relation to the timing of sapropel formation. Paleoceanography 12, 169–174.

Marchal, O., Cacho, I., Stocker, T.F., Grimalt, J.O., Calvo, E., Martrat, B., Shackleton, N., Vautravers, M., Cortijo, E., van Kreveld, S., Andersson, C., Koc, N., Chapman, M., Sbaffi, L., Duplessy, J.C., Sarnthein, M., Turon, J.L., Duprat, J., Jansen, E., 2002. Apparent long-term cooling of the sea surface in the northeast Atlantic and Mediterranean during the Holocene. Quat. Sci. Rev. 21, 455–483.

Mercone, D., Thompson, J., Abu-Zied, R.H., Croudace, I.W., Rohling, E.J., 2001. High-resolution geochemical and micropaleontological profiling of the most recent eastern Mediterranean sapropel. Mar. Geol. 177, 25–44.

Mercone, D., Thompson, J., Croudace, I.W., 2000. Duration of S1, the most recent sapropel in the eastern Mediterranean Sea, as indicated by accelerator mass spectrometry radiocarbon and geochemical evidence. Paleoceanography 15, 336–347.

Müller, P.J., Kirst, G., Ruhland, G., von Storch, I., Rosell-Mélé, A., 1998. Calibration of the alkenone paleotemperature index UK'37 based on core tops from the eastern South Atlantic and the global ocean (60°N–60°S). Geochim. Cosmochim. Acta 62, 1757–1772.

Pierre, C., 1999. The oxygen and carbon isotope distribution in the Mediterranean water masses. Mar. Geol. 153, 41–55.

Rohling, E.J., 2000. Paleosalinity: confidence limits and future applications. Mar. Geol. 162, 1–11.

Rohling, E.J., Bigg, G.R., 1997. Paleosalinity and $\delta^{18}O$; a critical assessment. J. Geophys. Res. C 103, 1307–1318.

Rohling, E.J., Jorissen, F.J., de-Stigter, H.C., 1997. 200 year interruption of Holocene sapropel formation in the Adriatic Sea. J. Micropalaeontol. 16, 97–108.

Rohling, E.J., Mayewski, P.A., Ramadan, H.A., Casford, J.S.L., Hayes, A., 2002. Holocene atmosphere–ocean interactions; records from Greenland and the Aegean Sea. Clim. Dyn. 18, 587–593.

Rossignol-Strick, M., 1985. Mediterranean Quaternary sapropels, and immediate response of the African monsoon to variation of insolation. Palaeogeogr. Palaeoclimatol. Palaeoecol. 49, 237–263.

Rossignol-Strick, M., 1999. The Holocene climatic optimum and pollen records of sapropel 1 in the eastern Mediterranean, 9000–6000 BP. In: Roberts, N., Kuzucuoglu, C., Karabiyikoglu, M. (Eds.), The Late Quaternary in the Eastern Mediterranean Region. Quaternary Science Reviews 18, pp. 515–530.

Ross, D.A., Degens, E.T., 1974. Recent sediments of Black Sea. In: The Black Sea; Geology, Chemistry, and Biology; Sediments. Memoir American Association of Petroleum Geologists 20, pp. 183–199.

Rostek, F., Ruhland, G., Bassinot, F., Mueller, P.J., Labeyrie, L.D., Lancelot, Y., Bard, E., 1993. Reconstructing sea surface temperature and salinity using $\delta^{18}O$ and alkenone records. Nature 364, 319–321.

Ryan, W.B.F., Pitman, W.C., III, Major, C.O., Shimkus, K., Moskalenko, V., Jones, G.A., Dimitrov, P., Gorur, N., Sakinc, M., Yuce, H., 1997. An abrupt drowning of the Black Sea shelf. Mar. Geol. 138, 119–126.

Ryan, W.B.F., 1972. The stratigraphy of late Quaternary sediments in the eastern Mediterranean. In: Stanley, D.J. (Ed.), The Mediterranean Sea: A Natural Laboratory. Dowden, Hutchinson, Ross, Stroudsbourg, PA, pp. 149–169.

Sbaffi, L., Wezel, F.C., Kallel, N., Paterne, M., Cacho, I., Ziveri, P., Shackleton, N., 2001. Response of the pelagic environment to palaeoclimatic changes in the central Mediterranean Sea during the Late Quaternary. Mar. Geol. 178, 39–62.

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.

Sperling, M., Schmiedl, G., Hemleben, Ch., 2001. Termination 1, Younger Dryas, and Noah's flood: 18,000 years of climate change in the Sea of Marmara. ICPVII, program and abstracts, p. 189.

Sperling, M., Weldeab, S., Schmiedl, G., in press. Drying of samples may alter foraminiferal isotopic ratios and faunistic composition. Micropaleontology 48.

Stangeew, E., 2001. Distribution and Isotopic Composition of Living Planktic Foraminifera *N. pachyderma* (sinistral) and *T. quinqueloba* in the High Latitude North Atlantic. Ph.D. Thesis, Universität Kiel.

Stuiver, M., Reimer, P.J., 1993. Extended ^{14}C database and revised CALIB radiocarbon calibration program. Radiocarbon 35, 215–230.

Thunell, R.C., Williams, D.F., 1989. Glacial–Holocene salinity changes in the Mediterranean Sea; hydrographic and depositional effects. Nature 338, 493–496.

Ünlüata, Ü., Oguz, T., Özsoy, E., 1990. On the physical oceanography of the Turkish Straits. In: The Physical Oceanography of Sea Straits, NATO/ASI Series, Kluwer, pp. 25–60.

Vogelsang, E., 1990. Paläo-Ozeanographie des europäischen Nordmeeres an Hand stabiler Kohlenstoff- und Sauerstoffisotope. Ph.D. Thesis, Universität Kiel.

Winter, A., Siesser, W.G. (Eds.), 1994. Coccolithophores. University Press, Cambridge.

Wulf, S., Kraml, M., Kuhn, T., Schwarz, M., Inthorn, M., Keller, J., Halbach, P., 2002. Marine tephra from the Cape Riva Eruption (22 ka) of Santorini in the Sea of Marmara. Mar. Geol. 183, 131–141.