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Hydrogen isotopic compositions of long-chain alkenones record freshwater flooding of the Eastern Mediterranean at the onset of sapropel deposition

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Abstract

Sapropels are organic-rich sediment layers that were intermittently deposited in the Mediterranean Sea, especially in its eastern basin, during the last 10Myr. The associated anoxic events that gave rise to sapropel formation resulted indirectly from the impact of African monsoon maxima on the basin's hydrography. Sharp shifts in oxygen isotopes (δ^{18}O) to values more depleted in the heavy isotope (^{18}O) in carbonates from surface dwelling planktonic foraminifera, slightly preceding sapropel deposition, suggest that the Mediterranean was flooded by large amounts of freshwater leading to the development of a low salinity of the surface water and a strong density stratification of the water column. However, the degree of freshwater flooding and concomitant drop in sea surface salinity (SSS) remain elusive. Recent work has shown that the hydrogen isotope (δD) values of long-chain alkenones produced by haptophyte algae depend mainly on the δD of the water and on salinity, and may therefore offer a new tool for salinity reconstructions. Our analysis of the δD of alkenones from last interglacial sapropel S5 from the Aegean Sea shows a large decrease in δD of 25‰ at the onset of sapropel formation, suggesting a drop in SSS of 6, from 39 to 33. Although the absolute SSS estimates should be interpreted with care as they are subject to relatively large uncertainties, the estimated SSS values appear quite reasonable as they, for example, yield SSS before sapropel deposition similar to that of the present day Aegean Sea. To reduce uncertainties in SSS estimates, the δD-salinity relationship has to be better constrained with cultures and also tested in field studies. However, our results do illustrate the promise of a combined use of δD of alkenones, $U^{k'}_{37}$ of alkenones, and δ^{18}O of surface dwelling planktonic foraminifera, for SSS reconstructions.

Keywords: S5 sapropel; paleosalinity; hydrogen isotopes; alkenones

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1. Introduction

Sapropels are organic-rich sediment layers that were deposited in the Mediterranean (especially in the eastern Mediterranean; i.e., east of the Strait of Sicily) at times of orbitally induced insolation maxima (Rossignol-Strick et al., 1982; Rossignol-Strick, 1983, 1985). These sapropels are often readily visually recognizable by their distinctly dark color and are associated with times of anoxia in the water column, even extending towards the photic zone (Passier et al., 1999; Menzel et al., 2002; Rohling et al., 2006). The anoxic events that gave rise to sapropel formation reflect an indirect impact of African monsoon maxima on the basin's hydrography. This impact concerns the routing of African monsoon precipitation into the Mediterranean via the Nile River (Rossignol-Strick et al., 1982; Rossignol-Strick, 1983, 1985) and other, currently dry, systems along the wider North African margin (Rohling et al., 2002). It has also been suggested based on metal signatures that significant amounts of freshwater arrived in the eastern Mediterranean Sea from the Southern European continent (Rinna et al., 2002). At the onset of sapropel deposition the Mediterranean was flooded by large amounts of freshwater leading to the development of low salinity surface water and inducing a strong density stratification of the water column.

Sapropel S5 formed during one of the insolation/monsoon maxima of the last interglacial period (124–119ka). This monsoon maximum was interrupted by a dry interlude of several centuries, with concomitant cooling over the north of the basin (Rohling et al., 2002, 2004; Scrivner et al., 2004). The S5 sapropel is intensely developed, characterized by high organic carbon accumulation rates (e.g., Fontugne and Calvert, 1992), a lack of benthic fossils that suggests persistent anoxia below 300m water depth (Rohling and Gieskes, 1989; Rohling et al., 1993), and the presence of the carotenoid isorenieratene which indicates euxinia at the base of the photic layer (Rohling et al., 2006; Marino et al., 2007). Previous studies have attempted to quantify the freshwater flooding that promoted the development of stratification and collapse of deep-sea ventilation that caused sapropel formation (Rohling, 1999; Rohling et al., 2004), particularly with respect to the strong δ^{18}O-depletion in surface dwelling planktonic foraminifera (up to 3.5‰) at the onset of sapropel formation. However, the degree of freshwater flooding and concomitant drop in sea surface salinity (SSS) is uncertain due to several factors which affect the isotopic composition of water/foraminifera (e.g., evaporation, isotopic composition of precipitation and runoff, sea water temperature, etc.) and previous studies have, therefore, used modeling (Rohling et al., 2004) and simplified S: δ^{18}O relationships to arrive at estimates of past salinity changes during sapropel formation.

Krishnamurthy et al. (2000) used an alternative approach to estimate the amount of freshwater flooding, by analyzing the δD of bulk organic matter in sapropels. They found a substantially depleted δD signal within sapropels compared to the adjacent marls in the Tyrrhenian Sea, also suggesting a substantially enhanced flux of freshwater and drop in SSS during sapropel deposition. However, bulk organic matter represents different types of organic matter from all kind of different sources, including organic compounds that may have exchanged hydrogen atoms with their environment (e.g. Schimmelmann et al., 2004).

A potentially new tool for salinity reconstructions considers δD values of long-chain alkenones produced by haptophyte algae, since they only possess covalently bound hydrogen atoms, which are not likely to be exchanged during diagenesis (Sessions et al., 2004). Paul (2002) found that the fractionation between δD of the culture medium water and the C_{37} alkenones produced by *Emiliania huxleyi* was relatively constant at ~ 232‰ when varying the δD value of the culture medium. Englebrecht and Sachs (2005) reported a similar fractionation of ~ 225‰. However, recent work on *E. huxleyi* and another common oceanic haptophyte algae, *Gephyrocapsa oceanica*, cultured at different salinities and temperatures, suggests that hydrogen isotope fractionation by these algae depends both on the δD of the water and on salinity, and to some degree growth rate (Schouten et al., 2006). Thus, the δD of C_{37} alkenones of *E. huxleyi* largely depends on salinity and the δD of water, which itself is again strongly correlated with salinity (Mook, 2001). Salinity changes, therefore, form a key aspect of changes in the δD of C_{37} alkenones, suggesting it could be useful as a paleosalinity proxy.

In this study we analyzed the δD of alkenones in the S5 sapropel from the Aegean Sea (cf. Marino et al., 2007) and compared that with the δ^{18}O of carbonates from surface dwelling foraminifera. In addition, we estimated SSS based on our δD record and the δ^{18}O of carbonates from surface dwelling foraminifera in combination with $U^{k'}_{37}$ SST.

2. Materials and methods

Samples analyzed are from the S5 sapropel retrieved from southeastern Aegean Sea core LC21, recovered in 1995 during the EC-MAST2 PALEOFLUX program (35°40′N; 26°35′E; 1522m water depth; Marino et al., 2007). For this core, stable oxygen and carbon isotope records of the carbonate tests of shallow and sub-thermocline dwelling foraminifera, total organic carbon (TOC), $U^{k'}_{37}$ temperatures, and isorenieratene concentrations have been previously reported (Marino et al., 2007).

For determination of δD of alkenones core slices were extracted ultrasonically using methanol, methanol: dichloromethane (1:1, v:v) and dichloromethane. The total lipid extract was separated using column chromatography with aluminium oxide as stationary phase and a mixture of hexane and dichloromethane (9:1, v:v) to elute the apolar fraction and a mixture of hexane and dichloromethane (1:1, v:v) to elute the alkenone fraction.

Alkenone fractions were analyzed by gas chromatography (GC) using an Agilent 6890 gas chromatograph with a flame ionization detector using a fused silica capillary column (25m × 0.32mm) coated with CP Sil-5 (film thickness = 0.12μm) with helium as carrier gas. The fractions (in ethyl acetate) were injected on-column at 70°C. The oven was programmed to subsequently increase the temperature to 130°C with 20°C min^{-1}, and then with 4°C min^{-1} to 320°C at which it was held isothermal for 10min.

Compound-specific hydrogen isotopic compositions of the alkenones were determined by GC/thermal conversion/isotope ratio monitoring mass spectrometer using a Thermo Electron DELTA^{Plus} XL mass spectrometer. GC conditions were similar to conditions for GC analysis except that the film thickness of the CPSil 5 column was 0.4μm and that a constant flow of He was used at 1.5ml min^{-1}. Compounds were pyrolyzed at 1450°C in an empty ceramic tube, which was pre-activated by a methane flow of 0.5ml min^{-1} for 5min. H_3^+-factors were determined daily on the isotope mass spectrometer and varied between 2 and 3. H_2 gas with known isotopic composition was used as reference and a mixture of C_{16}–C_{32} *n*-alkanes of known isotopic composition (ranging from − 42‰ to − 256‰ vs. VSMOW) was used to monitor the performance of the system. The average offsets between the measured hydrogen isotopic composition of the C_{16}–C_{32} *n*-alkanes and their values determined off-line were generally 5‰ or less. Analyses were done at least in duplicate and the reproducibility was always better than 7‰. A squalane standard was co-injected with every sample and its average value was − 171 ± 5‰ which compared favorably with its off-line determined value of − 170‰.

3. Results and discussion

3.1. Stable hydrogen isotopic composition of C_{37} alkenones

The onset of S5 sapropel deposition occurs at ~ 1005cm sediment depth as indicated by TOC values rising from ~ 0.3% below the sapropel to an initial maximum of ~ 13% within the sapropel at ~ 985cm depth. After a decrease to ~ 9% at 970cm depth a maximum TOC content of ~ 14% is reached at ~ 965cm depth.

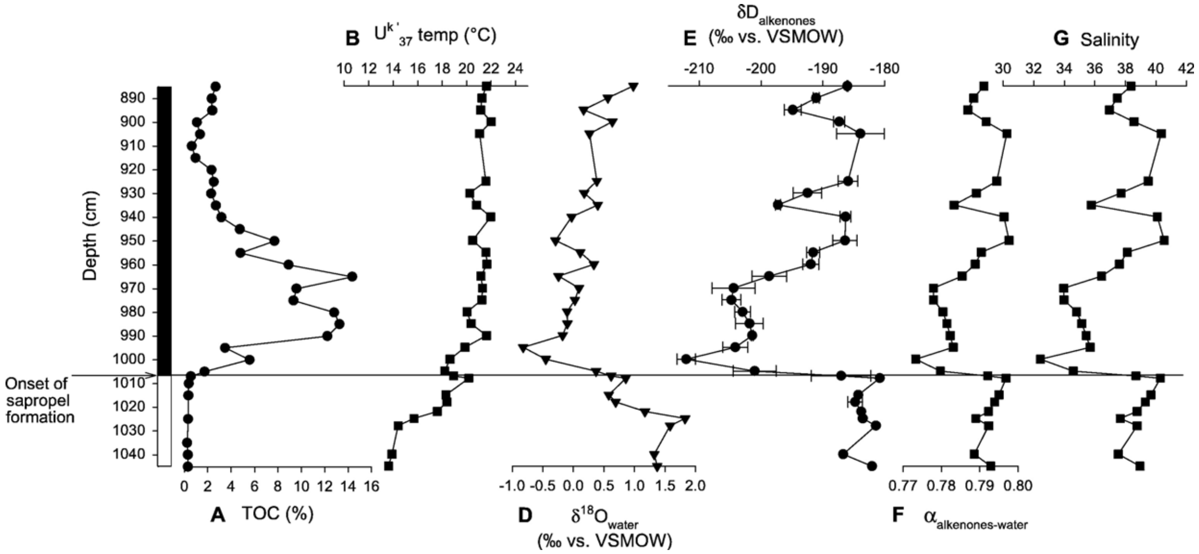

Fig. 1. Stratigraphic record of south eastern Aegean Sea core LC21 from the Mediterranean Sea of (A) TOC in % (from Marino et al., 2007), (B), $U^{k'}_{37}$ temperature in °C (from Marino et al., 2007, (C) $\delta^{18}O_{water}$ in ‰ vs. VSMOW (from Marino et al., 2007), (D) $\delta D_{alkenones}$ in ‰ vs. VSMOW, (E) $\alpha_{alkenones-water}$ and (F) estimated sea surface salinities. Solid line indicates onset of sapropel deposition as indicated by elevated TOC contents. The bar next to the depth scale indicates the pre-sapropel layer (white) and sapropel layer (black).

Above 965cm sediment depth TOC values slowly drop to ~ 0.3% at ~ 875cm depth (Marino et al., 2007) indicating that sapropel deposition has ended.

The hydrogen isotope composition of the C_{37} alkenones is ~ − 185‰ below the S5 sapropel. It then rapidly decreases to ~ − 210‰ at the base of the S5 sapropel before it slowly returns to ~ − 190‰, close to the pre-sapropel value, before sapropel deposition ended and then remained more or less constant (Fig. 1D). Based on the culture studies by Schouten et al. (2006) for alkenone-producing algae, the large shift in δD can be explained by three factors: salinity, growth rate and δD of water. Growth rate is likely to have had a minor effect as extremely large increases in growth rate would be needed to cause a 25‰ depletion in δD (Schouten et al., 2006). Furthermore, analysis of Pliocene (5.3 to 1.8Ma) eastern Mediterranean sapropels showed that C_{37} alkenones within sapropels are slightly depleted in ^{13}C relative to values below the sapropel (Menzel et al., 2003). As $\delta^{13}C$ of alkenones strongly depends on growth rate (Laws et al., 1995; Popp et al., 1998) this depletion suggests a slight decrease in haptophyte growth rates. Likely, the increase in bulk primary production during deposition of the S5 sapropel is mainly due to enhanced diatom production, rather than increased haptophyte production (Kemp et al., 1999; Giunta et al., 2006). Thus, the large depletion in δD of C_{37} alkenones during the onset of sapropel deposition was caused by either a large depletion in δD of the water, a substantial lowering in SSS, or both.

Further clues on the cause of the depletion in δD of C_{37} alkenones can be obtained by examining the $\delta^{18}O$ of foraminiferal carbonate shells which depends on both $\delta^{18}O$ of the sea water ($\delta^{18}O_{water}$) and temperature (e.g. Erez and Luz, 1983; Bemis et al., 1998) whereby the ^{18}O of the sea water co-varies with salinity. By combining the $\delta^{18}O$ record of the planktonic foraminifer *Globerigerinoides ruber* with SST estimates from long-chain alkenones (the $U^{k'}_{37}$ index, with SST (°C) = ($U^{k'}_{37}$ − 0.044) / 0.033, Müller et al., 1998; Fig. 1B) we obtain estimates of $\delta^{18}O_{water}$ using the temperature-^{18}O fractionation equation of Bemis et al. (1998):

$$T(°C) = 16.5 - 4.80\left(\delta^{18}O_{\text{carbonate shell}} - \delta^{18}O_{water}\right) \tag{1}$$

The results suggest that $\delta^{18}O_{water}$ was around 1.5‰ and shifted, prior to sapropel deposition, to lighter values of about 1.0‰ (Fig. 1C). At the onset of sapropel deposition there was a large shift of about 1.5‰ towards even lighter values (Fig. 1C). During sapropel deposition, $\delta^{18}O_{water}$ values slowly returned to just below pre-sapropel values. After sapropel deposition has ended the $\delta^{18}O_{water}$ values finally return to pre-sapropel values (Marino et al., 2007). The timing and direction of these shifts in $\delta^{18}O_{water}$ coincide in general with those in δD of alkenones, i.e. large shifts towards light values during the onset of sapropel deposition and gradual return to pre-sapropel values during sapropel deposition. This confirms that the alkenone δD record reflects changes in the δD of water and/or SSS. The two-step shift in $\delta^{18}O$ to lighter values is not evident in the δD record. We note that the initial $\delta^{18}O$ shift coincides with the start of an increase in the $U^{k'}_{37}$-derived temperatures. It is, therefore, unclear whether the decrease in $\delta^{18}O_{ruber}$ reflects an actual decrease in $\delta^{18}O_{water}$ or an even larger temperature shift for *G. ruber* compared to that experienced by haptophyte algae.

The δD of eastern Mediterranean surface water (δD_{water}) can be estimated from the $\delta^{18}O$ of the water using the eastern Mediterranean meteoric water line (MMWL; Gat and Carmi, 1987; Bar-Matthews et al., 2003):

$$\delta D_{water} \approx 8 \times \delta^{18}O_{water} + d \tag{2}$$

with d = deuterium excess. For the MMWL d is 22‰ rather than the global average of 10‰ due to local circumstances (e.g. evaporation, water source, prevailing winds etc.). The deuterium excess (d) during the last interglacial has been shown to be similar to that of the present day MMWL (McGarry et al., 2004). For evaporative basins, such as the eastern Mediterranean, it has been shown that the ratio of changes in δD_{water} and $\delta^{18}O_{water}$ (i.e. $\Delta\delta D_{water}/\Delta\delta^{18}O_{water}$ or the slope of the meteoric waterline) is lower than that of the general meteoric waterline (Craig and Gordon, 1965; Gat, 1996). As a first approximation, we assume that the ratio was closer to 6 before and after S5 (when net evaporation was more dominant), and higher during S5 (when net evaporation was reduced). For our salinity estimations we assumed a constant slope of 7 and constant d of 22‰ (the effect of different slopes and intercepts on the SSS estimates is discussed below). The $\delta^{18}O$–δD relationship of the eastern Mediterranean surface water thus becomes:

$$\delta D_{water} \approx 7 \times \delta^{18}O_{water} + 22 \tag{3}$$

At the onset of sapropel deposition, $\delta^{18}O_{water}$ decreased by 2.2‰ and thus the reconstructed changes in δD_{water} are at most 15‰, which cannot explain the entire 25‰ shift in the δD of alkenones (Fig. 1D). Thus, fractionation between δD of alkenones and δD_{water} has substantially increased at the onset of the S5 sapropel deposition and, in view of the culture results (Schouten et al., 2006), salinities must thus have decreased substantially. The substantial lowering of

SSS is in agreement with results from many previous studies based on ^{18}O of carbonate tests of foraminifera (Rossignol-Strick et al., 1982; Rossignol-Strick, 1983, 1985; Rohling et al., 2002; Marino et al., 2007).

3.2. Estimation of paleosalinities of the Aegean Sea during S5 sapropel deposition

Based on the results above we can estimate paleosalinities from the hydrogen isotopic fractionation of alkenone-producing algae. The dominant haptophyte alga in the eastern Mediterranean during isotope stage 5e was *G. oceanica* (Giunta et al., 2006). We can estimate SSS using the isotopic fractionation factor α:

$$\alpha_{\text{alkenones-water}} = \frac{1000 + \delta D_{\text{alkenones}}}{1000 + \delta D_{\text{water}}} \tag{4}$$

and the results of Schouten et al. (2006) for hydrogen isotope fractionation by *G. oceanica*:

$$\alpha_{\text{alkenones-water}} = 0.0030 \times S + 0.676 \tag{5}$$

where α (Fig. 1E) is the fractionation factor and S is salinity (Fig. 1F). The δD_{water} can be estimated from the combination of δ^{18}O of the carbonate tests of *G. ruber*, the $U^{k'}_{37}$ SST (see Marino et al., 2007) and the MMWL as described above. Our salinity reconstruction suggests absolute SSS at the base of the S5 sapropel to be ~ 39 followed by a ~ 6 decrease at the onset of S5 sapropel deposition to ~ 33 (Fig. 1F). After the initial freshening the SSS slowly returns to more or less pre-sapropel values (Fig. 1F).

The estimated SSS values seem quite reasonable as they, for example, yield similar SSS as the present day Aegean Sea, i.e. 39, before sapropel deposition. Furthermore, the pattern and magnitude of change in SSS look remarkably similar to those modeled by Rohling et al. (2004) for the upper surface water layers during deposition of different S5 sapropels. Thus, it seems that the hydrogen isotopic composition of alkenones can yield reasonable estimates for the patterns and amplitudes of past SSS changes.

The absolute SSS estimates (Fig. 1F), however, should be interpreted with care as they are subject to relatively large uncertainties. Besides the above assumptions that have been made in order to calculate the SSS estimates, error propagation, especially in the empirically determined correlation between α and salinity (Eq. (5)), results in a large error in the estimated SSS values. To investigate this we performed a sensitivity analysis of our salinity estimates for the different parameters used in our calculations. One uncertainty relates to the slope in the MMWL which can range between 6 and 8 (see above). Changing the slope from 6 to 8 yields only relatively small changes in SSS estimates of less than 1. An uncertainty in the deuterium excess *d* of the MMWL of 1‰ results in an uncertainty of ± 0.3 in the SSS estimates. Hence, the uncertainties in Eq. (3) are leading to an error in the SSS estimates of < 1. The by far largest uncertainty comes from the α salinity relationship because of the relatively large scatter (r^2 = 0.61). The uncertainty in the slope 0.003 ± 0.001 results in uncertainty in SSS estimates of ± 16 from the estimates presented here. The uncertainty in the intercept, 0.676 ± 0.03 results in uncertainty in the salinity estimates of ± 10. Thus, to reduce the uncertainties in our SSS estimates, the δD–salinity relationship has to be better constrained in cultures and also tested in field studies. Nevertheless, the reasonable SSS estimates calculated here for the S5 sapropel in the Aegean Sea show that the combined use of δD of alkenones, $U^{k'}_{37}$ of alkenones and δ^{18}O of the carbonate tests of planktonic foraminifera may be a promising tool for SSS reconstructions.

4. Conclusions

Our δD record of C_{37} alkenones, produced by haptophyte algae, from the Eastern Mediterranean shows a large and abrupt shift towards more negative values at the onset of sapropel deposition. This change runs parallel with that of the δ^{18}O of the carbonate tests of surface dwelling foraminifera suggesting that δD of C_{37} alkenones accurately record the large decrease in sea surface salinity during freshwater flooding. Based on the δD of the water, calculated from the δ^{18}O of foraminifera and $U^{k'}_{37}$ sea surface temperatures, and the δD of C_{37} alkenones we can estimate that the salinity shift at the onset of S5 sapropel deposition was approximately 6, from ~39 to ~33.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2007.08.014.

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