Oxygenation and organic-matter preservation in marine sediments: Direct experimental evidence from ancient organic carbon–rich deposits

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ABSTRACT

Clarification of the factors involved in the formation of unusual ancient organic carbon–rich deposits (like eastern Mediterranean sapropels) is central in understanding oceanic carbon cycling. The role of oxygenation remains a subject of controversy primarily due to two major uncertainties: (1) it is unknown if ancient organic-rich deposits reflect an accumulation of refractory organic matter (OM) or oxygenation-related aberrant sediment OM recycling, and (2) although marine OM degradation may be slower under anoxic conditions, its ultimate impact on organic carbon (C_{org}) preservation over geological time remains unclear. Here we provide direct experimental evidence that the C_{org} in eastern Mediterranean S1 sapropels (deposited >5 ka) is still highly reactive and that a shutdown in labile organic matter degradation under anoxic conditions played a key role in the formation of these deposits.

INTRODUCTION

The question of what variables control organic matter (OM) preservation in marine sediments is one of the most complex and controversial issues in contemporary biogeochemistry (Hedges et al., 1999) and complicates the application of uniformitarianism: the use of the present as a key to the past. More specifically, the role of oxygenation in the formation of ancient organic carbon–rich deposits such as eastern Mediterranean sapropels remains a subject of debate (e.g., Calvert et al., 1992; Rohling, 1994; Hartnett et al., 1998; Sachs and Repeta, 1999; Gelinas et al., 2001; Kennedy et al., 2002). Laboratory experiments examining the effect of oxygen on present-day sedimentary OM degradation have utilized mainly carbon-rich coastal sediments and have revealed that, except for the most reactive fraction, the degradation of OM is slower in the absence of oxygen (e.g., Sun et al., 1993, 2002; Kristensen et al., 1995; Harvey et al., 1995; Kristensen and Holmer, 2001). However, trends may be different in well-oxygenated, organic-deficient deep-sea sediments and it still remains to be established whether anoxic conditions result in enhanced OM preservation over geological time. In this study we report on experiments that directly examine the effect of oxygen on the degradation of OM in ancient eastern Mediterranean organic carbon–rich sediments (S1 sap-

ropels, deposited >5 ka) and on the remineralization of fresh algal carbon in eastern Mediterranean deep-sea surface sediment.

Sapropels, layers of dark colored sediments relatively rich in OM, are common features of the sedimentary record of the Mediterranean Sea otherwise characterized by organic-deficient sediments. At present, the eastern Mediterranean Sea is oligotrophic with a well-mixed, warm, and oxygenated water column. Primary productivity is low, and sediments are deficient in OM (Bethoux, 1993). However, interspersed sapropels are common features in the Pliocene–Holocene sedimentary record (Calvert et al., 1992). Recent and old nonsapropel sediments have low organic carbon (C_{org}) contents (~0.3%), whereas as much as 30% C_{org} has been recorded in Pliocene sapropels (Passier et al., 1999a). Earlier observations have revealed the presence of living bacteria in sapropel sediments but, in accordance with the presence of these OM-rich layers even after >5–200 ka, bacteria activity under in situ conditions is limited (Cragg et al., 1998; Coolen et al., 2002).

We assessed the effect of oxygen on the degradation of sapropel OM by measuring the production of CO_2 in sediment-water slurries of sediments taken from within and around the sapropel. Bulk sediment C_{org} and nitrogen (N_{tot}) content and $\delta^{15}N_{tot}$ were measured to delineate depositional events. Additionally,

the effect of redox conditions on the degradation of fresh algal carbon in oligotrophic deep-sea surface sediment was examined using ^{13}C-labeled diatoms as a tracer, including a treatment with sulfidic conditions that may retard OM degradation through metabolic inhibition or diagenetic OM transformation (Kohnen et al., 1990; Canfield, 1994; Harvey et al., 1995).

MATERIAL AND METHODS

Sediment was collected from four sites (668–2765 m water depth) in the eastern Mediterranean in August 1999 on board the RV *Logachev*. Sediment was extruded in 1-cm-thick slices from Perspex cores (6 cm inner diameter) that were taken from undisturbed box-core samples. Approximately one-third of the sediment slice was used for bulk sediment measurements (stored at −20 °C) and the rest divided between the oxic and anoxic incubations. The C_{org} and N_{tot} content and $\delta^{15}N_{tot}$ measurements for selected intervals were done on ground freeze-dried sediments. Organic carbon and nitrogen contents have been measured using an elemental analyzer following in situ acidification for organic carbon (Nieuwenhuize et al., 1994). Nitrogen isotope ratios were measured using a Finnigan Delta S isotope ratio mass spectrometer coupled on line with an elemental analyzer. For the sediment-slurry incubations, a volume of ~10 mL sediment was directly transferred into 80 mL glass incubation bottles, diluted with 10 mL 0.2 μm filtered seawater and sealed with screw caps fitted with rubber septa. Slurries were then thoroughly mixed (vigorously hand shaken) and headspaces purged for 5 min with N_2 for anoxic incubations and $N_2:O_2$ (80:20) for the oxic incubations. All slurries and controls (bottles containing only gas or bottles containing gas and filtered water) were incubated in the dark at 14 °C for 75–80 days. Slurries were vigorously shaken once a week in order to allow a good exchange between slurry and headspace gas. The amount of CO_2 produced was calculated from the increase in concentration of ΣCO_2 minus the ΣCO_2 ini-

tially present in the pore water and added water. Details of the methods are described in Dauwe et al. (2001). The amount of CO_2 produced was calculated as the sum of accumulated headspace and dissolved concentrations. The equilibrium concentration of CO_2 in the sediment-water slurry was based on measured headspace concentration and the temperature- and salinity-dependent solubility coefficients and pH-dependent speciation.

The effect of oxygenation on the degradation of fresh OM in oligotrophic eastern Mediterranean deep-sea surface sediments was examined using ^{13}C-labeled diatoms (*Thalassiosira pseudonana* labeled with 20% [13]C) as a tracer of labile carbon (Moodley et al., 2002). Surface sediment (0–2 cm), collected in July 2002 north of Crete (35.66°N, 25.1°E, 950 m water depth), was homogenized and used for sediment-water slurries prepared as described here. Two quantities of diatoms (equivalent to 15.1 and 146.7 mmol C m^{-2}) were added to slurries maintained under different redox conditions. A relatively high load and an extremely high load of OM were chosen to mimic an unusual high OM input of otherwise oligotrophic sediments. The effect of anoxic conditions with or without sulfide (20 μmol per incubation bottle or 1.25 mM, added from a stock solution 100 mL 200 mM solution of $Na_2S \cdot 9H_2O$) was also examined in triplicate incubations. All slurries were incubated in the dark at 14 °C for 4 days. Remineralization of the added carbon was followed through ^{13}C enrichment in ΣCO_2 and measured separately both in the headspace and in the water phase following acidification in glass vials (Moodley et al., 2002).

RESULTS AND DISCUSSION

The S1 sapropels (dark green-brown) examined in this study were ~22–32 cm below the seafloor (Fig. 1) and were overlain by yellow-brownish sediments intercepted by a 3–5-cm-thick brown manganese-oxide layer (e.g., Thomson et al., 1999). This layer with diminished C_{org} contents (oxidized layer) results from postdepositional oxidation of the upper part of the original sapropel (van Santvoort et al., 1996). Light gray pyrite-rich sediment is beneath the sapropel layer (Passier et al., 1999a). Surface sediments contained ~0.3% C_{org}, and the organic carbon contents of sapropel layers ranged from 1.07% to 3.95% (Fig. 1A), typical of S1 sapropels (Murat and Got, 2000). The N_{tot} contents ranged from 0.02% to 0.30% (Fig. 1B) and closely correlated with C_{org} contents ($r^2 = 0.98$, p <0.001, n = 51). Similar to observations across older sapropels (Calvert et al., 1992; Sachs and Repeta, 1999; Struck et al., 2001), $\delta^{15}N_{tot}$ profiles show large systematic variation, with lighter values in sapropel layers

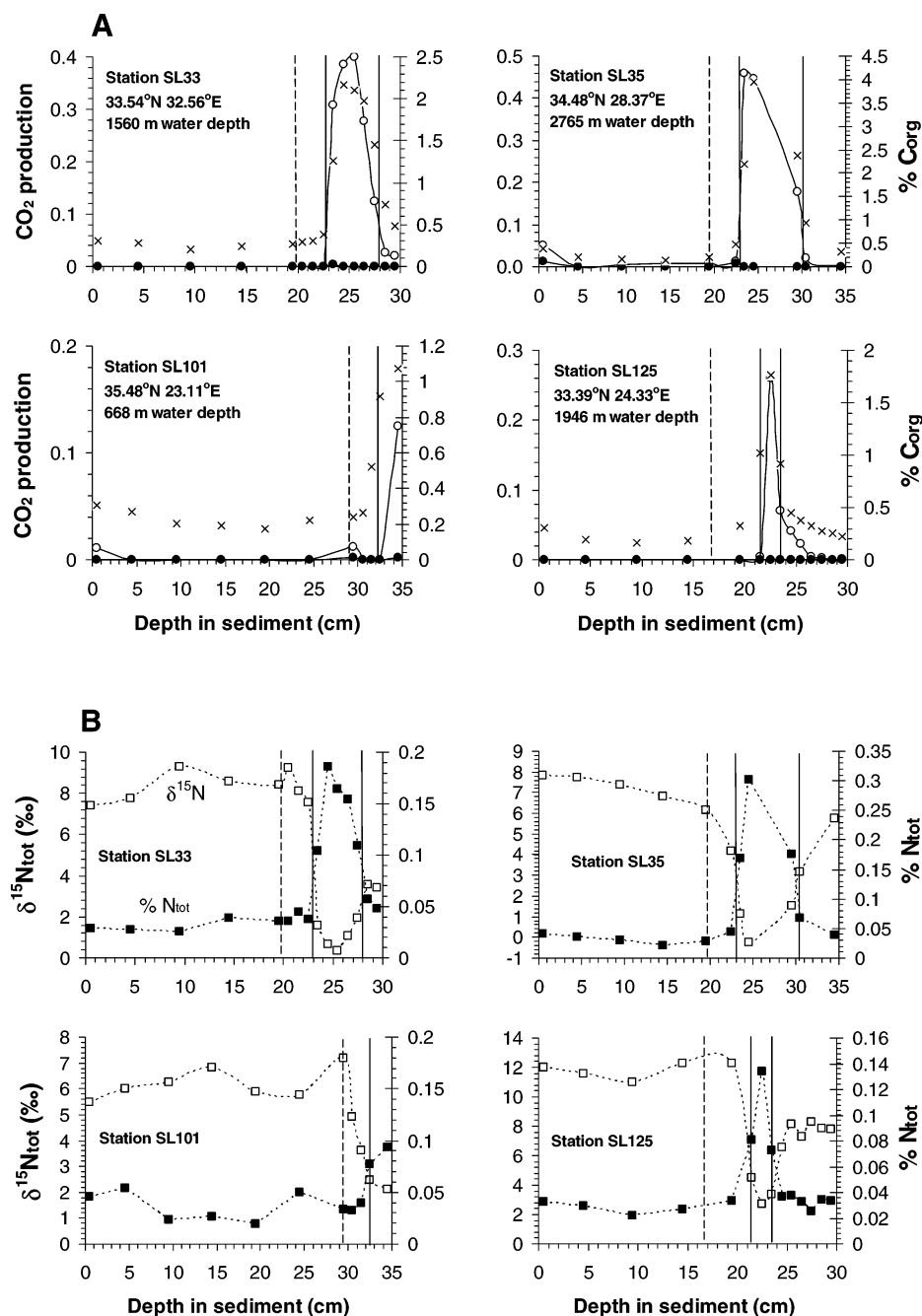(Fig. 1B). These bulk sediment characteristics underline the aberrant conditions during sapropel events.

Sapropel OM degradation, examined through CO_2 production in sediment-water slurry incubations, was evident under oxic conditions but not in the absence of oxygen, indicating that sulfate reduction was limited (Fig. 1A). This is the first direct experimental evidence for the key role of anoxic preservation of OM in eastern Mediterranean sapropel formation. Oxic CO_2 production rates show a

strong linear correlation with organic carbon content in the sediments ($r^2 = 0.82$, p <0.001, n = 51), indicating a close relationship with preservation. First-order oxic mineralization rate constant k (0.07 ± 0.02 yr^{-1}, n = 10, calculated for distinct individual sapropel intervals as quotients of CO_2 production rates and C_{org} content) indicates that the OM in these ancient sediments is of relatively high reactivity with a half-life [$-\ln(0.5)/k$] of 12.0 ± 4.5 yr under oxic conditions. This is direct evidence that sapropels are not an accumula-

Figure 1. Profiles across S1 sapropel of sediment. A: Weight percent organic C_{org} content ($\times$), and CO_2 production rates [μmol C (g dry sediment)$^{-1}$ day^{-1}] under oxic (open symbols) vs. anoxic (closed symbols) conditions. B: $\delta^{15}N_{tot}$ and % N_{tot}. Vertical solid lines indicate visual upper and lower boundary of sapropel (dark-colored sediment) and dashed lines indicate upper boundary of postdepositional oxidized sapropel layer.
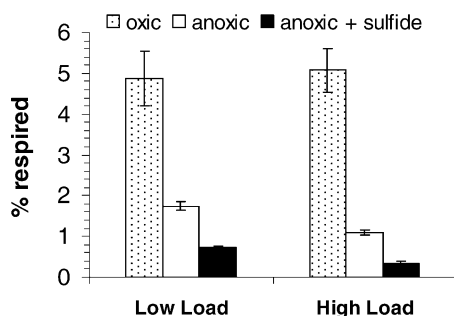
Figure 2. Percent of added diatom carbon respired in eastern Mediterranean deep-sea surface sediment under different treatments. Effect of anoxic conditions with or without sulfide under two loads of carbon: 15.1 mmol C m^{-2} (low load) and 146.7 mmol C m^{-2} (high load) incubated for 4 days (n = 3 ± standard errors).

tion of refractory OM and shows that sapropel OM is readily oxidized by oxygen. The undetectable degradation of sapropel OM in the absence of oxygen, however, is in strong contrast with the situation in modern sediments with similar C_{org} lability under oxygenated conditions (calculated as the amount of CO_2 produced per gram C), e.g., shelf sediments in the northeastern North Sea [~4–18 μmol C d^{-1} gC$_{org}$$^{-1}$ (Hulthe et al., 1998) and 7–24 μmol C d^{-1} gC$_{org}$$^{-1}$ in the sapropel layers], even more so as sapropel OM is primarily of marine origin (Bouloubassi et al., 1999). This indicates the importance of a shutdown mechanism that strongly inhibited further degradation of OM evidenced as S1 sapropels.

Using ^{13}C-labeled diatoms as a tracer of fresh OM it was evident that, under oxic conditions, fresh OM is rapidly remineralized in eastern Mediterranean deep-sea surface sediments (Fig. 2). Approximately 5% of the added carbon was respired within 4 days regardless of the amount of carbon added, indicating that this short-term respiration involved the most reactive fraction of the added diatoms (Moodley et al., 2005). However, in contrast to experiments with organic-rich coastal sediments, remineralization of even this fresh OM was much slower under anoxic conditions, and in particular it was strongly inhibited in the presence of sulfide (Fig. 2). This inhibition was stronger under the higher load of OM, probably due to additional production of sulfide (only ~0.3% of the added diatom was respired within 4 days). Sulfidic conditions, either directly through toxicity or metabolic inhibition or indirectly through diagenetic OM transformation (Kohnen et al., 1990; Canfield, 1994; Harvey et al., 1995), may have been an important inhibitor of OM degradation. This would have contributed significantly to the large difference between S1 and Pliocene sapropels. Pliocene sapropels have higher C_{org} contents (as much as 25%–30% C_{org}) but otherwise have geochemical properties similar to

S1 sapropels (Warning and Brumsack, 2000). In contrast to S1 sapropel events, during the formation of some Pliocene sapropels it has been established that reducing conditions prevailed throughout a large part of the water column (Passier et al., 1999b). Consequently, a larger fraction of OM would have escaped water-column degradation. However, the amount of OM ultimately preserved would depend on the extent of sediment anoxic OM degradation. This study demonstrates that not just oxygen-poor or depleted bottom-water conditions, but the subsequent shutdown in labile OM degradation, played a key role in the formation of ancient organic-rich deposits; anoxic conditions followed by the exhaustion of sedimentary reactive Fe probably triggered the shutdown in OM degradation. High sulfide production could have resulted in Fe limitation for pyrite formation (Passier et al., 1999a), an important sink of sulfide, thereby promoting sulfidization of organic compounds that reduce OM bioavailability (Kohnen et al., 1990).

Oxygen not only has an effect on the amount of OM preserved, but also affects the composition. The S1 sapropel intervals have lighter $\delta^{15}N_{tot}$ values ranging from $-0.26‰$ to $+2.7‰$ compared to $+5.5‰$ to $+12.0‰$ in surface sediments (Fig. 1B). The $\delta^{15}N_{tot}$ profiles were a mirror image of OM content (in particular the nitrogen content, Fig. 1B), implying that the systematic lighter values in sapropel layers are closely related to anoxic preservation. This is supported by the relative enrichment in $\delta^{15}N_{tot}$ in the low-carbon–containing postdepositional oxidized upper part of the original sapropel ($\delta^{15}N_{tot}$ enrichment ranging from $+2.5‰$ to $+12.2‰$, Fig. 1B) and points to significant oxygen-induced postdepositional modification of $\delta^{15}N$ (Altabet et al., 1999; Sachs and Repeta, 1999; Lehmann et al., 2002; Brummer et al., 2002). At the same time, this relationship indicates that sedimentary OM remineralization was strongly reduced during sapropel formation.

Although OM $\delta^{15}N_{tot}$ may undergo diagenetic depletion under anoxic conditions (Lehmann et al., 2002), the characteristic light values found in sapropel intervals are not products of diagenetic alteration. Older sapropels with a wider range in OM content (1%–9%) than that in this study (1%–4%) have a similar range in nitrogen isotopes ($-1‰$ to $+4‰$; Calvert et al., 1992; Sachs and Repeta, 1999; Struck et al., 2001), but a maximum depletion in $\delta^{15}N_{tot}$ ($-1‰$ to $+0.5‰$) is encountered in sapropel intervals with C_{org} >3.5%. This suggests that these light values reflect primarily the original sapropel OM, in accordance with a greater importance of water-column nitrogen fixation during sapropel events (Kemp et al., 1999; Sachs and Re-

peta, 1999; Struck et al., 2001). Enhanced primary and export production during sapropel events have been attributed to major changes in the primary producers. It is well established that enhanced stratification of the water column prevailed during sapropel events (Rohling, 1994; Emeis et al., 2003); this allowed the development of specific mat-forming diatoms that harbor endosymbiotic nitrogen-fixing bacteria (Sancetta, 1994; Kemp et al., 1999; Struck et al., 2001). Given that hydrological anomaly may have varied between sapropel events (Rohling, 1994; Emeis et al., 2003), variations in the intensity and duration of the sapropel specific primary production may have prevailed. The trends in $\delta^{15}N_{tot}$ suggest that variation in OM content coupled with shifts in nitrogen isotopes such as in sapropel intervals with C_{org} <3% (Fig. 1B) reflect different oxygen exposure time and/or lower contribution of sapropel specific primary producers. At the higher end of OM content, similar nitrogen isotopes but strong differences in C_{org} contents may indicate increasing export production with increasing sediment OM content. However, it has been established that the relative extent of sediment anoxic degradation was lowest in sapropels with high OM content (Passier et al., 1999a), indicating that the differences in the C_{org} content of sapropels reflect primarily the intensity of shutdown in OM degradation.

Our experimental evidence for an oxygen effect on carbon preservation in eastern Mediterranean sapropels corroborates field evidence from deep-sea turbidites (Wilson et al., 1986; Cowie and Hedges, 1994) and correlative evidence (Hartnett et al., 1998). It is also consistent with the presence of a postdepositional oxidized layer on the top of a sapropel layer, and supports that sapropel OM is readily oxidized by oxygen (van Santvoort et al., 1996; Thomson et al., 1999). Furthermore, although a shutdown in OM degradation was evidently the common basis for sapropel formation, differences in OM content of sapropels are related to the evolution and duration of environmental conditions that governed the prevalence of sapropel specific primary producers and water-column oxygenation. The high sulfide production and consequent exhaustion of Fe necessitates a high input of reactive carbon and supports that export production must have been significantly higher during sapropel events (Struck et al., 2001; Calvert and Fontugne, 2001, and references therein). Finally, although explaining past geological events depends on our understanding of present-day processes, crucial insight into key ecological processes may be gained directly from the geological past.

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