Evidence from chlorin nitrogen isotopes for alternating nutrient regimes in the Eastern Mediterranean Sea

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ABSTRACT

Nitrogen isotopes of chlorins, degradation products of chlorophyll, reflect the isotopic composition of nutrient N utilized by marine phytoplankton communities. Here we show that in sediments of the eastern Mediterranean Pleistocene and Holocene, values of $\delta^{15}N$ for chlorins and total nitrogen vary in concert, with a consistent offset of ~5‰ reflecting the fractionation imparted during chlorophyll biosynthesis. Samples from the Integrated Ocean Drilling Program Sites 964 and 969 were analyzed at a sampling resolution of ~4–10 cm, clustered around sapropel events 2, 3, 4 and 5 (~100–170 ka). In low organic content sediments, chlorin values of ~0‰ coincident with total nitrogen values of ~+5‰ indicate that the latter reflects the original biomass and is not a consequence of diagenetic isotope enrichment. In sapropel horizons, the chlorin and total nitrogen values are 5‰ more negative (~−5‰ and ~0‰, respectively), resembling previously-reported, modern-day water-column particulates (~0‰). We suggest that nutrient conditions in the Eastern Mediterranean correspond to three scenarios and that the similarity between sapropel and modern-day bulk $\delta^{15}N$ is coincidental. Organic-poor marl sediments formed under oligotrophic conditions where surface productivity resulted from upwelling of Atlantic-sourced nitrate. Sapropels were characterized by enhanced diazotrophy that was likely fueled by increased riverine P fluxes to surface waters. Present-day conditions are dominated by anthropogenic N sources. These scenarios agree with a model of sapropel formation in which stratification caused by increased fresh-water inputs led to N fixation due to P:N nutrient imbalance. Enhanced production combined with stratification promoted and maintained anoxic deep waters, consequently increasing organic matter preservation. Such a model may be relevant to interpreting other episodes of intense organic matter deposition in past oceans.

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1. Introduction

The modern Mediterranean Sea is an ultra-oligotrophic system with fully oxygenated deep waters. The Pleistocene sedimentary record of its eastern basin typically consists of organic-lean (0.1–0.3% total organic carbon; TOC; Calvert et al., 1992) nannofossil marl oozes. These calcareous marls are interrupted by organic-rich sapropel layers (2–5% TOC; e.g. Calvert, 1983), which occasionally represent Mediterranean-wide events as evidenced by the co-occurrence of sapropels in the western basin (Bouloubassi et al., 1999). It is generally proposed that sapropel layers reflect a combination of nutrient-enhanced primary productivity and/or reduced oxygenation of deep waters that allowed increased organic matter preservation (Rohling, 1994 and references therein).

Sedimentary nitrogen isotope records are useful tracers of paleoceanographic nutrient conditions. Exported phytoplankton biomass theoretically preserves the $\delta^{15}N$ value of the surface waters. Nitrogen carries the isotopic composition of dissolved inorganic nitrogen (DIN) if the nutrient source is nitrate or ammonia, and of atmospheric N_2 if the source is from microbial nitrogen fixation, with the additional overprint of any biological processing in the water column. In the Mediterranean Sea, where surface DIN is completely consumed annually, nitrogen isotopes have been used to infer nutrient sources under baseline (presumably oligotrophic) and sapropel-forming conditions (Calvert et al., 1992; Sachs and Repeta, 1999; Struck et al., 2001; Meyers and Bernasconi, 2005). In general, sapropel sediments are characterized by low bulk $\delta^{15}N$ values of ~0‰, whereas marl layers are characterized by more enriched bulk $\delta^{15}N$ values of ~5‰ (Calvert et al., 1992).

Nitrogen isotope values of contemporary surface sediments in the Eastern Mediterranean (~+4.3‰) resemble the bulk $\delta^{15}N$ values of marl sediments (~+5‰). However, surface sediments are about 5‰ enriched compared to suspended PON in the photic zone (~−0.6‰; Sachs and Repeta, 1999). Evidence from several ocean basins indicates that under

oxic, low-TOC depositional conditions, diagenetic remineralization can alter the $\delta^{15}N$ signature of bulk organic nitrogen (Wada et al., 1987; Altabet, 1996; Gaye-Haake et al., 2005). Diagenetic enrichment of about 5‰ relative to sinking fluxes has been measured in Southern Ocean sediments (Wada et al., 1987; Altabet and Francois, 1994a). Since newly-fixed nitrogen results in biomass $\delta^{15}N$ values of ~0‰, and Mediterranean source waters from the North Atlantic supply NO_3^- with a $\delta^{15}N$ value of 4.8–5‰ (Pantoja et al., 2002), Sachs and Repeta (1999) suggested that productivity in the modern Eastern Mediterranean is fuelled by diazotrophic nitrogen, and that the discrepancy between modern PON and sediments could be due to diagenetic alteration of bulk nitrogen.

Since a similar enrichment of ~5‰ exists between sapropel and marl bulk $\delta^{15}N$ values, Sachs and Repeta (1999) proposed that the consistent difference in the nitrogen isotopic record between times of sapropel and marl deposition is a diagenetic artifact. Chlorins, the tetrapyrrole degradation products of chlorophyll, are not subject to isotopic fractionation during diagenesis because diagenetic transformations that degrade the tetrapyrrole macrocycle do not occur on bonds containing nitrogen (Sachs and Repeta, 1999). Therefore, chlorins can be used to avoid or evaluate the effect of diagenesis on bulk $\delta^{15}N$ values. The average $\delta^{15}N$ value of chlorins in sapropel layers is similar to the $\delta^{15}N$ value of chlorophyll in surface waters of the present-day eastern basin (-5.0 ± 0.4‰ vs. -6.4 ± 1.4‰, respectively; Sachs and Repeta, 1999). Because the fractionation associated with chlorophyll biosynthesis is ~5‰ (Sachs et al., 1999), these values represent bulk biomass with $\delta^{15}N$ values near -1‰ in the modern Eastern Mediterranean, and 0‰ in sapropels. These biomass values could imply that the isotopic signal of primary production during both sapropel and non-sapropel depositional resulted from an invariant diazotrophic nutrient budget in surface waters throughout the Pleistocene (Sachs and Repeta, 1999).

Due to analytical limitations, Sachs and Repeta were not able to measure $\delta^{15}N$ values of chlorins directly from marl oozes. Rather, the values of modern phytoplankton, particulate matter, and deep basinal NO_3^- were extrapolated to represent organic matter deposition under non-sapropel conditions. In this paper we use a new method for measuring compound-specific nitrogen isotopes that is applicable to both organic-lean and organic-rich sediments (Higgins et al., 2009) in order to re-examine the nitrogen isotope record of the Eastern Mediterranean, including direct examination of the marls.

2. Materials and methods

Samples were analyzed from Ocean Drilling Program (ODP) Leg 160, Sites 964 (Ionian Sea) and 969 (Mediterranean Ridge) from the Eastern Mediterranean basin (Fig. 1). These samples spanned sapropels S2, S3 and S4 (Site 964) and S4 and S5 (Site 969),
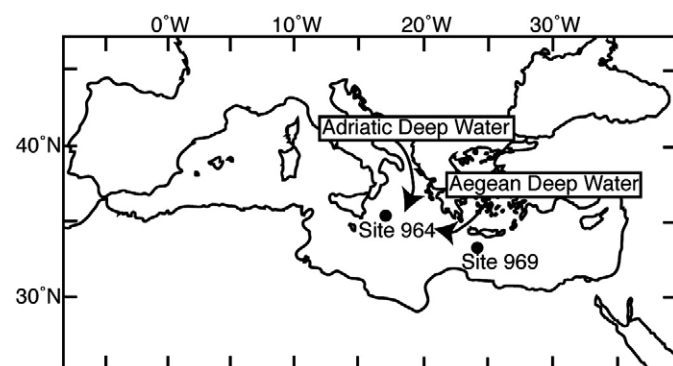

Fig. 1. Map of the Mediterranean Sea showing sample locations as well as sources of deep-water formation. Modified after Cramp and O'Sullivan, 1999.

corresponding to 6.21–9.31 meters below sea floor (mbsf) at Site 964, and 3.16–4.27 mbsf at Site 969. Samples (≤ 2 cm thick horizons) were obtained at a resolution of 4–10 cm, except for an unsampled 1.6 m gap between S3 and S4 in Site 964. Each horizon was measured for % total nitrogen (TN), % total organic carbon (TOC), bulk $\delta^{15}N$, and $\delta^{13}C_{org}$. Chlorin $\delta^{15}N$ values were measured for each sapropel sample individually. Due to the low organic content of marl ooze sediments, two to three samples, each spanning a total of ≤ 16 cm were combined for non-sapropel chlorin $\delta^{15}N$ measurements.

Samples were analyzed using a modification of the methods described in Higgins et al. (2009). Sediments (3–27 g) were freeze dried, subsampled for bulk analysis (~1 g), and extracted with 90:10 dichloromethane (DCM)/methanol (MeOH) using an Accelerated Solvent Extractor (ASE 200 and ASE 350; Dionex Corporation). Lipid extracts were separated using a Biotage FLASH + 12i system with a SiO_2 column. Fraction one (F1) was eluted using 100% DCM, and fraction two (F2) was eluted using 60:40 ethyl acetate (EtOAC)/DCM. In order to determine chlorin concentrations and elution times, Flash fractions were concentrated and analyzed by normal-phase (NP-) HPLC (Agilent) on a Zorbax-SIL column (4.6 mm × 250 mm, 5 μm) using a gradient from hexane to 75:25 MeOH/EtOAC in 30 min. Care was taken to minimize light exposure during sample handling. Absorbance was monitored at 410 nm and 686 nm, and peak areas at these wavelengths were integrated. Nitrogen concentration in each sample was estimated using an empirically-determined conversion factor (~2e-3 nmol N*mAU^{-1} min^{-1}; calculated from the analysis of a pheophorbide a standard). Based on estimated N concentrations, samples containing ~50 nmol N were prepared for preparative NP-HPLC and fraction collection. Each sample (<100 μL) was separated using the same elution program as above, with fraction collection at times corresponding to absorbance peaks (typically ~6–16 min). Chlorin-concentrated fractions (CCFs) from F1 and F2 subfractions were oxidized quantitatively to NO_3^- following the methods of Higgins et al. (2009).

Samples were analyzed for nitrate concentrations by reduction of nitrate to NO followed by detection using a Monitor Labs Inc. N Oxides Analyzer model 884 (Braman and Hendrix, 1989). Nitrate $\delta^{15}N$ values were measured using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002), with average reproducibility of ~0.3‰. Bulk samples were analyzed for percent total nitrogen (TN), $\delta^{15}N$ values of bulk nitrogen, percent TOC, and $\delta^{13}C_{org}$. For carbon analyses, samples were decarbonated by acidification with 8% sulfurous acid. Bulk analyses were done on a Costech 4010 elemental analyzer coupled to a Thermo Scientific Delta V isotope ratio mass spectrometer.

3. Results

Bulk elemental abundances of nitrogen and organic carbon showed consistent patterns and agree with previous reports (Calvert et al., 1992; Sachs and Repeta, 1999; Struck et al., 2001; Meyers and Bernasconi, 2005). Non-sapropel samples averaged 0.25 ± 0.11% TOC, while sapropels averaged 3.6 ± 2.4% TOC (Fig. 2A,F). TN values averaged 0.037 ± 0.010% and 0.27 ± 0.13% in marls and sapropels, respectively (Fig. 2B,G). These elemental concentrations correspond to average C:N values of 8 in marl horizons and 16 in sapropels. Although the values of $\delta^{13}C_{TOC}$ were equivalent in both types of sediment, averaging -23.1 ± 1.4‰ in marls and -23.0 ± 1.0‰ in sapropels (Fig. 2C,H), bulk nitrogen isotopes demonstrated the expected enrichment in ^{15}N in non-sapropel horizons. The average $\delta^{15}N_{TN}$ values were 5.17 ± 0.94‰ and 0.35 ± 1.14‰ in marls and sapropels, respectively (Fig. 2D,I).

In all cases, $\delta^{15}N$ values for chlorins (CCFs) corresponded well to the values of $\delta^{15}N_{TN}$, with an offset equal to the fractionation associated with chlorophyll biosynthesis (Fig. 2E,J). The $\delta^{15}N$ values for CCFs from sapropel horizons averaged -4.7 ± 0.4‰. Assuming a 5‰ offset between chlorophyll and biomass (Sachs et al., 1999), these values correspond to $\delta^{15}N_{TN}$ values of ~0.3‰. This confirms that the
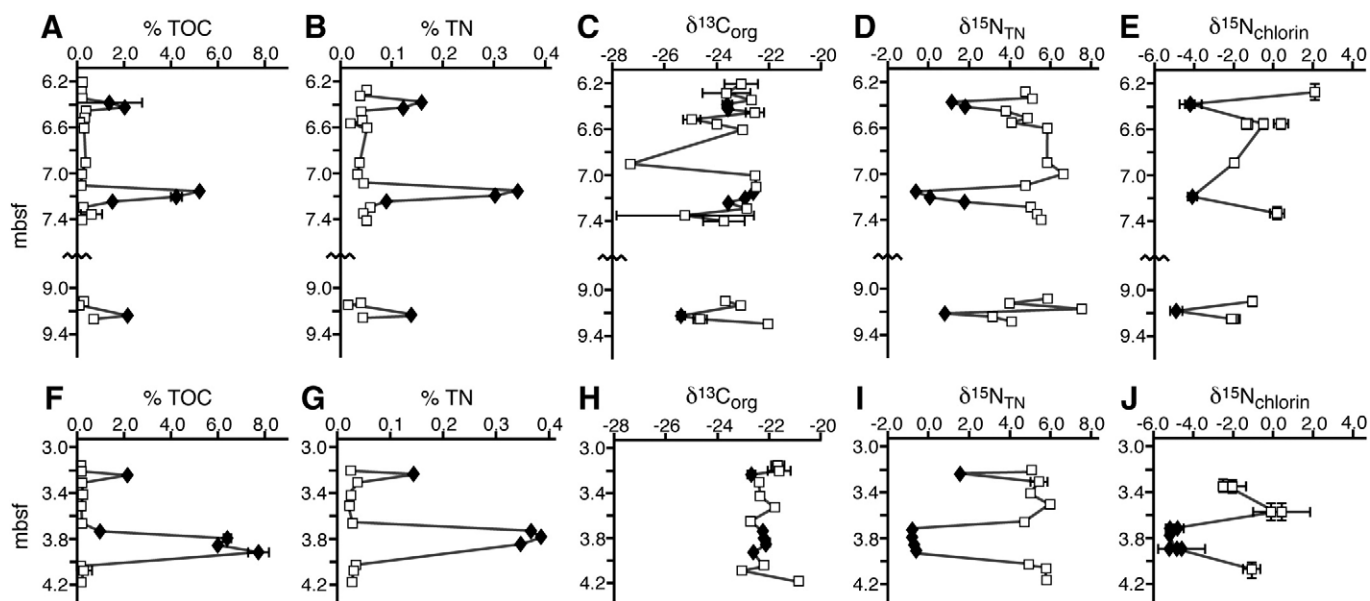
Fig. 2. Isotopic and elemental data from Sites 964 (A–E) and 969 (F–J). A, F: %TOC. B, G: %TN. C, H: $\delta^{13}C_{org}$. D, I: $\delta^{15}N_{TN}$. E, J: $\delta^{15}N_{chlorin}$. Data from sapropel horizons are shown as black diamonds, and data from marl horizons are shown as white squares.

total primary producer community during sapropel events had $\delta^{15}N_{biomass}$ values near 0‰, consistent with previous reports. In non-sapropel horizons, however, chlorin $\delta^{15}N$ values were enriched in ^{15}N. Chlorins in marl ooze sediments averaged $-0.8 \pm 1.3‰$, which with the 5‰ offset would correspond to phytoplankton isotopic values of $\sim +4.2‰$.

Control measures were employed to ensure that the $\delta^{15}N$ values of CCFs primarily represented chlorins and not other, trace sources of organic nitrogen that may be present in organic-lean samples. Samples were measured for $\delta^{15}N$ values only when their oxidized NO_3^- yields did not exceed expected quantities as determined by HPLC absorbance quantification. Since sapropel horizons contain abundant quantities of readily identifiable chlorins, we estimated the average chlorin-to-NO_3^- conversion factor from integrated absorbances at 410 and 686 nm for all sapropel samples. The average conversion factor at 410 nm for sapropel F1s was 0.0013 ± 0.0008 nmol $N*mAU^{-1}*min^{-1}$ (1σ), and for sapropel F2s it was 0.0023 ± 0.0006 nmol $N*mAU^{-1}*min^{-1}$ (1σ). Average conversion factors at 686 nm were 0.00094 ± 0.00074 nmol $N*mAU^{-1}*min^{-1}$ (1σ) and 0.0018 ± 0.0006 nmol $N*mAU^{-1}*min^{-1}$ (1σ) for F1 and F2, respectively. F1 largely contains chlorin steryl esters and other non-polar chlorins, as well as carotenoids, and the greater variability of the conversion factor for F1 is probably due to interfering absorbance of carotenoids at these wavelengths. In addition, this diminishes the average conversion factor for F1 samples (nitrogen yield is proportionally lower at a given value of absorbance), because although co-eluting carotenoids absorb at these wavelengths, they do not contain any nitrogen.

Since the concentration of chlorins in organic-lean, non-sapropel CCFs was much lower than for sapropels, and the identity of specific structures was less certain, we applied these empirical F1 and F2 conversion factors above to calculate expected yield to reduce potential influences of non-chlorin N. We report values of $\delta^{15}N$ for CCFs from marl horizons only when oxidized NO_3^- yield is within a 50–150% range of the expected concentration. This corresponds to a $<1\sigma$ window of variance in the conversion equations for N yield. While this may have resulted in artificial exclusion of some samples yielding low N concentrations (relatively high carotenoid influence; yields ≤50% of expected), only three samples were excluded based on this criterion. More important was the exclusion of samples having yields much greater than expected, as these were likely to contain significant non-chlorin nitrogen (four data points excluded).

4. Discussion

Our data show that chlorins in calcareous marl sediments deposited in the Eastern Mediterranean during the late Pleistocene have $\delta^{15}N$ values consistent with primary biomass that was enriched in ^{15}N ($\sim +4$ to $+5‰$). This implies that the bulk organic nitrogen isotopes in these sediments have not been heavily overprinted by diagenesis. The data contrast markedly with the suggestion by Sachs and Repeta (1999) that present-day Mediterranean surface waters are typical of Pleistocene conditions that led to the formation of low-TOC marl oozes in the Eastern Mediterranean. By extension, the data exclude the possibility that marls and sapropel sediments were deposited under similar oceanographic conditions.

Depleted nitrogen isotope values of modern PON and chlorophyll have been interpreted to derive from newly-fixed nitrogen, which carries a $\delta^{15}N$ value of $\sim 0‰$ (Sachs and Repeta, 1999; Pantoja et al., 2002). The $\delta^{15}N$ values of contemporary deep nitrate also are depleted, suggesting that low ^{15}N content is a persistent characteristic of the modern Eastern Mediterranean, at least for the residence time of nitrate in the deep basin (~ 50 years; Bethoux et al., 1990). As an alternative to endogenous N fixation, we suggest that the nitrogen budget of the modern Mediterranean has an overprint from the atmospheric deposition of exogenous fixed nitrogen (Mara et al., 2009). Anthropogenic influences obscure what would otherwise be an oceanographic nutrient regime typical of conditions during marl deposition. The present-day total particulate nitrogen and deep basin NO_3^- therefore are not analogues for the Pleistocene background conditions. If so, the Eastern Mediterranean in the Pleistocene and Holocene is best described by three different biogeochemical scenarios, rather than two: 1) conditions that lead to sapropel formation, 2) baseline conditions that lead to calcareous ooze formation, and 3) modern conditions. These three states more easily reconcile with the total available isotope data.

1. Suggested causes for sapropel formation have focused on the relative contributions of enhanced primary productivity (Calvert et al., 1992; Kemp et al., 1999; Struck et al., 2001; Weldeab et al., 2003; Meyers and Bernasconi, 2005) vs. decreased oxygenation of bottom waters and sediments (Cheddadi and Rossignol-Strick, 1995; Hartnett et al., 1998). Sapropel horizons tend to coincide with precessional minima, which are characterized by warm, wet conditions in the Mediterranean caused by the North African monsoon and

Mediterranean depressions (Rossignol-Strick, 1985; Rohling, 1994; Emeis et al., 2000). Oxygen isotopes measured in planktonic foraminifera demonstrated inputs of fresh water into Mediterranean surface waters during the onset of sapropel formation (Tang and Stott, 1993; Kallel et al., 2000; Rohling et al., 2004). Consistent with this observation, van der Meer et al. (2007) have estimated a decrease of 6 in sea surface salinity based on hydrogen isotopes of alkenones. The timing of these events, taken together with the increased abundance of terrestrial biomarkers (Bouloubassi et al., 1999) in sapropel sediments, supports a model in which increased riverine runoff caused a freshening of surface waters. This large input of fresh water disrupted the thermohaline circulation of the Mediterranean, which led to shoaling of the pycnocline, stratification, stagnation and decreased oxygen advection to bottom waters. (Rohling and Gieskes, 1989; Rohling, 1994; Rohling et al., 2006).

Excess runoff carried phosphorus into surface waters, enhancing productivity (Diester-Haass et al., 1998). Ti/Al ratios in Nile Delta sediments suggest that reduced sediment fluxes from the Nile may have increased P inputs by reducing adsorption onto Fe minerals (Krom et al., 2002). Estimates for the $\delta^{15}N$ values of riverine nitrogen are uncertain and depend on local, terrigenous nitrogen sources. Brandes and Devol (2002) have estimated an average pre-anthropogenic value of $\sim 4 \pm 4‰$ for global terrestrial runoff.

The density stratification simultaneously reduced the amount of upwelling of deep nitrate whose original source is the North Atlantic ($\delta^{15}N \sim 5‰$). To compensate for the excess supply of P, diazotrophic nitrogen, with $\delta^{15}N$ values of $\sim 0‰$, would have been the primary N source (Sachs and Repeta, 1999). The combination of runoff-enhanced primary productivity and suboxic conditions promoted the preservation of organic matter in the deep basin. Evidence for extensive production by diatoms that are adapted to stratified water columns and harbor diazotrophic symbionts supports this theory of sapropel formation (Kemp et al., 1999).

2. Stratified conditions contrast markedly with the baseline conditions in which organic-lean calcium carbonate oozes accumulate. Circulation in the Mediterranean in the late Pleistocene likely was similar to today − water flowed in from the Atlantic over the shallow sills of Gibraltar and Sicily, filling the deep waters of the western and eastern basins (Rohling, 1994). Phytoplankton blooms occurred in response to deep winter mixing events, and therefore biomass utilized nitrate originating from the North Atlantic, yielding $\delta^{15}N_{TN}$ values of $\sim 5‰$. Any contribution of nitrogen fixation or incomplete utilization of nitrate under conditions of phosphorus limitation may have slightly decreased the expressed nitrogen isotopic values (Altabet and Francois, 1994b), possibly accounting for the somewhat greater scatter in the data for marl horizons relative to the general consistency of $\delta^{15}N$ values in sapropel horizons (Fig. 2D,E). Regardless, the correspondence between chlorin $\delta^{15}N$ values and bulk nitrogen isotope data shows that values of bulk $\delta^{15}N_{TN}$ near 5‰ are not an artifact of diagenesis.

Although diagenetic enrichment of sedimentary ^{15}N occurs frequently in open-ocean settings (Altabet and Francois, 1994a), absence of diagenetic artifacts often is observed on continental margins (Pride et al., 1999; Altabet et al., 1999; Emmer and Thunell, 2000; Thunell et al., 2004; Thunell and Kepple, 2004). The enclosed Mediterranean Sea appears to more closely resemble the latter examples. Oxygen exposure time in both the water column and surface sediments is a key factor in total organic matter preservation (Hartnett et al., 1998). However, >99% of surface production is remineralized before sedimentary burial (Martin et al., 1987), and the relative contributions of water column vs. sedimentary processes to nitrogen isotopic fractionation are not well understood (Altabet, 1996). Varying degrees of boundary-layer transport and sedimentary re-working also may contribute significantly to the magnitude of post-depositional fractionation (Freudenthal et al., 2001; Kienast et al., 2005), but the impact of such processes appears to be lower in the Mediterranean. Burial of TN with a $\delta^{15}N$ value of $\sim +5‰$

is consistent with an ultimate source from the Atlantic, to maintain overall isotopic mass balance in the system.

3. Snapshot measurements of the present-day Eastern Mediterranean may not be accurate analogues for Pleistocene hydrography, i.e., neither for sapropel nor for baseline conditions. Deep nitrate in the eastern basin should reflect an integrated $\delta^{15}N$ signal of remineralized phytoplankton plus Atlantic nitrate. However, currently there is regional and temporal isotopic variability in deep nitrate, with values in the eastern basin ranging from $+0.7 \pm 0.1‰$ to $+2.5 \pm 0.1‰$; and averaging $+3.4 \pm 0.5‰$ in the western basin (Sachs and Repeta, 1999; Pantoja et al., 2002). The residence time of nitrate in the Eastern Mediterranean deep waters is ~ 50 years (Bethoux et al., 1990). This suggests that values of $\delta^{15}N$ should be spatially homogeneous if major, temporally-stable oceanographic states are the primary influence. However, circulation in the Mediterranean is dynamic, and in the early 1990s a major shift in deep water formation occurred (Roether et al., 1996; Fig. 1). The Eastern Mediterranean Transient (EMT) represented an abrupt switch from the Adriatic Sea to the Aegean Sea as a main source of deep water. This new source water (Cretan Deep Water; CDW) is characterized by low preformed nutrient concentrations. Biomass and nitrate $\delta^{15}N$ values of $\sim 0‰$ were sampled in the spring of 1996 (Sachs and Repeta, 1999), under minimum influence of North Atlantic Intermediate Water and a maximum potential influence of exogenous and/or diazotrophic nitrogen. The circulation apparently shifted abruptly back in 2007, reverting to Adriatic Sea deep-water formation, which is saltier and denser than that of the Aegean (Rubino and Hainbucher, 2007).

Nutrient budgets also suggest that present-day (Anthropocene) conditions are unrepresentative for either the Pleistocene or Holocene (d'Alcalà et al., 2003; Krom et al., 2004). The Eastern Mediterranean acts as a net source of nitrogen to the Western Mediterranean, which in turn is a net source of nitrogen to the Atlantic (d'Alcalà et al., 2003). The most recent estimates of nitrogen sources to the Eastern Mediterranean claim that atmospheric deposition of preformed nitrogen accounts for >50% (111×10^9 mol/y out of 180×10^9 mol/y; Krom et al., 2004). It is believed to largely arise from biomass burning, combustion of fossil fuels, and production and use of agricultural fertilizers (Guerzoni et al., 1999; Duce et al., 2008). Duce et al. (2008) estimate up to a $4\times$ increase in atmospheric N deposition to the Mediterranean since 1860. This non-biological source may also explain N:P ratios in the Mediterranean, which are $\sim 30:1$ in deep water − far above the Redfield ratio (Redfield et al., 1963; Krom et al., 2004). High N:P ratios in the Mediterranean also have been attributed to nitrogen fixation, and the presence of phylogenetically-diverse nifH genes is consistent with this capacity (Man-Aharonovich et al., 2007). Since atmospheric deposition events are sporadic, and the Eastern Mediterranean is an oligotrophic system, it is not surprising that it contains a high diversity of diazotrophic microbes. However, data suggest that expressed fixation rates are too low to invoke diazotrophy as the main source of fixed nitrogen (Bar Zeev et al., 2008). Additionally, large blooms of marine diazotrophs such as Trichodesmium spp., or of diatoms that contain diazotrophic symbionts, are not presently observed (Krom et al., 2004; Bar Zeev et al., 2008).

Although measurements of aerosol $\delta^{15}N$ are not numerous, existing data suggest that aerosol N is more likely to be responsible for the modern, isotopically-depleted signals. Wankel et al. (in press) measured an isotopically-depleted ^{15}N content of aerosol NOx over the Gulf of Aqaba, Red Sea (range $-6.9‰$ to $+1.9‰$; flux-weighted average $= -2.6‰$). Based on their calculations of back trajectories of air masses, >50% of this aerosol NOx came from the Mediterranean and Western Europe, and these dust particles carried an anthropogenic trace element signal (Chen et al., 2008). Estimates of $\delta^{15}N$ values of NOx were $-2.3‰$ from Western Europe, $-2.9‰$ from Eastern Europe, and $-1.3‰$ from the Mediterranean region. Mara et al. (2009) also measured $\delta^{15}N$ values of wet and dry atmospheric deposition on the island of Crete on a bi-weekly basis for six months, and

calculated an integrated value of −3.1‰. With deep nitrate residence times of ~50 years (Bethoux et al., 1990), and possibly shorter due to changing hydrographic conditions, this anthropogenic signal likely has persisted long enough to influence deep-water nitrate isotope values. However, since sedimentation rates in the eastern Mediterranean are very low (2–3 cm/ka) and oxic sediments experience extensive bioturbation, organic nitrogen in surface sediments still reflects mostly pre-anthropocene biomass accumulation.

5. Conclusions

Chlorin $\delta^{15}N$ values in both sapropel and marl sediments of the eastern Mediterranean show that heavy values of $\delta^{15}N_{TN}$ in organic-lean sediments are not diagenetic artifacts; they reflect the isotopic composition of nitrogen used by surface water biomass. During non-sapropel sediment deposition, this nitrogen was supplied from the North Atlantic, while during sapropel events, enhanced diazotrophy likely was fueled by increased riverine P fluxes to surface waters. In contrast, modern conditions represent a nutrient regime that is not characteristic of the Pleistocene or Holocene. The Mediterranean nitrogen budget in the Anthropocene is largely sourced by atmospheric deposition of anthropogenic preformed nitrogen.

These findings show that care must be taken when extrapolating modern-day nutrient conditions to the geologic record, because anthropogenic effects potentially are large and may mask as natural processes within the nitrogen cycle. Additionally, the consistent difference between chlorin and bulk values of $\delta^{15}N$ in both sapropel and marl sediments suggests that diagenetic alteration of bulk nitrogen isotopes may not be as prevalent as previously assumed for oxygenated sedimentary environments. Further work must be done to elucidate factors that control diagenetic isotopic alteration in sediments. Finally, our data confirm that sapropel formation is controlled by hydrographic and redox conditions in the Mediterranean; changes in nutrient sources and budgets alone do not necessarily explain cases of anomalous organic matter preservation. Similar hydrographic profiles of salinity-enhanced stratification may also have contributed to earlier episodes of enhanced organic matter burial and ocean anoxic events.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.epsl.2009.12.009.

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