vation process, on a molecular layer basis, holds the possibility for many exciting future experiments. An obvious one is to probe how electric fields alter the ion's ability to penetrate the water-oil interfacial barrier. Another possibility takes advantage of the much faster net motion of ions relative to neutrals at these field strengths: We can epitaxially create structured liquids and measure ion motion or trapping in them. In this way we can closely mimic complex interfaces in electrochemistry and in cell membranes.

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Oligotrophy and Nitrogen Fixation During Eastern Mediterranean Sapropel Events

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Nitrogen isotopic measurements in fossil chlorophyll from late Pleistocene organic-rich sediments (sapropels) in the eastern Mediterranean Sea provide geochemical evidence for stratified, nutrient-depleted surface water and extensive nitrogen fixation. This evidence is reconciled with previous indications of high productivity by invoking a model of sapropel formation in which increased river discharge facilitates development of a specialized phytoplankton population whose annual mass sinking provides the organic flux to generate sapropels. This interpretation is consistent with the widespread occurrence of mat-forming diatoms that thrive in stratified water and can harbor diazotrophic bacterial symbionts, but does not support eutrophication of surface waters by enhanced river runoff or a circulation reversal.

The eastern Mediterranean Sea is a well-ventilated, nutrient-depleted basin (*1*) characterized by low primary productivity (*2*) and organic-deficient sediments (*3*). However, during the late Pleistocene, a series of organic-rich sequences, sapropels, were deposited under what must have been dramatically different depositional conditions than those of today (*4*). These green-brown to black deposits with organic carbon concentrations of 2 to 5% are interspersed between gray nannofossil and foraminiferal marl oozes with organic carbon concentrations of 0.1 to 0.3% (*3, 5*). They are typically 1 to 30 cm thick (*4*), were formed over periods of 1000 to 10,000 years, and appear to be basin-wide events at water depths below 300 m (*6*). Seven sapropels, numbered S7 through S1, were deposited during the last 200,000 years, the most recent of which occurred in the early Holocene (*4*). The cause of these sedimentary layers is most likely enhanced primary productivity and fluxes of organic carbon to the seafloor (*3, 7, 8*), improved preservation rates of organic matter in oxygen-deficient water (*9*), or a combination of the two (*6, 10*). We conclude from nitrogen isotopic ratios in chlorophyll derivatives (chlorins) that surface waters were oligotrophic, deep waters were anoxic, and nitrogen fixation was widespread during these events. By invoking micropaleontological-based models of sapropel formation (*6, 7, 11*) in which increased river runoff induces shoaling of intermediate waters, the formation of a deep algal community, and diminished deep-water ventilation, we reconcile these findings with existing evidence for high export production.

Large fluctuations in sedimentary nitrogen isotopic ratios occur when sapropel layers are present. Whole-sediment $\delta^{15}N$ (*12*) values within sapropels S2 through S7 are nearly constant at $-0.1 \pm 0.5‰$ ($\pm 1\sigma$; $n = 26$) and significantly lower than non-sapropel values between those events (Fig. 1, B and C) that average $5.3 \pm 1.0‰$ ($n = 27$), irrespective of sample age or core location. There are two fundamentally different interpretations of these data. One is that the non-sapropel $\delta^{15}N$ value of 5.3‰ represents the sinking flux of nitrogen, or new production, under normal, oligotrophic conditions, and the sapropel $\delta^{15}N$ value of $-0.1‰$ indicates new production from nutrient-replete surface waters (*5*). As demonstrated in a variety of oceanographic settings, high nutrient concentrations in surface waters lead to the production of organic matter with low $\delta^{15}N$ values (*13*) because faster uptake kinetics cause preferential assimilation of ^{14}N (relative to ^{15}N) when nutrients are abundant (*14*). Our alternative interpretation of the sedimentary $\delta^{15}N$ record is that the low values in sapropels are typical of eastern Mediterranean new production both today and throughout the late Pleistocene, and the high values in organic-deficient marl sediments result from extensive diagenetic alteration of nitrogen isotopic ratios in the presence of oxygen.

Support for our interpretation comes from nitrogen isotopic measurements of contemporary and fossil chlorins and dissolved nitrate. These measurements demonstrate that the contemporary eastern Mediterranean is characterized by very low isotopic values of phytoplankton and deep-water nitrate (Fig. 1A) that are similar to phytoplankton and sedimentary $\delta^{15}N$ values in all six sapropels studied (Fig. 1, B and C). The deposition of recent (non-sapropel) sediments with a $\delta^{15}N$ value of 4.3‰ (Fig. 1A) is an enigma that must be reconciled with the very low isotopic values of reactive nitrogen reservoirs within the eastern Mediterranean.

We determined the nitrogen isotopic composition of living and ancient phytoplankton by measuring the $\delta^{15}N$ value of chlorins (*15*) and correcting for an empirically determined isotopic difference between chlorophyll and total

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algal nitrogen (*16*). Chlorophyll, a photosynthetic pigment synthesized by all oxic photoautotrophs, is an excellent biomarker for total algal biomass. Biosynthetic partitioning of nitrogen within microalgae yields chlorophyll that is isotopically depleted by 5.1 ± 1.1‰ (95% confidence interval; n = 8 species) relative to whole algae (*16*). This result was corroborated by measurements of the isotopic difference between chlorophyll and suspended particles in a variety of marine settings (*16*) that averaged 5.3 ± 1.5‰ (n = 6). Although early diagenesis results in some structural changes to the chlorophyll molecule, transformations that remove chlorins from our analytical window, such as macrocycle cleavage, or that involve functional groups on the macrocycle periphery are not expected to alter chlorin $\delta^{15}N$ values because they occur at least two bond lengths from all nitrogen atoms.

Pyropheophorbide *a* (*17*), the most abundant chlorin in sapropels S2 through S7, had a nearly constant $\delta^{15}N$ value of −5.0 ± 0.4‰ (n = 7) (Fig. 1, B and C), which was close to the isotopic composition of chlorophyll from living phytoplankton collected in the eastern Mediterranean in May and June 1996 of −6.4 ± 1.4‰ (n = 3) (Fig. 1A). Adjusting for the isotopic depletion of chlorophyll relative to total algal nitrogen yields mean $\delta^{15}N$ values for phytoplankton of 0.0 ± 1.4‰ in the sapropels, and −1.4 ± 1.9‰ in the contemporary eastern Mediterranean. The similar or slightly higher $\delta^{15}N$ value of phytoplankton during sapropel events compared with today is evidence for oligotrophic surface waters, an inference that is supported by micropaleontological evidence (*6*, *7*) for stratified, nutrient-impoverished surface waters at those times. If nutrient supply had exceeded demand by phytoplankton, then lower isotopic values than those measured under nutrient-depleted (that is, contemporary) conditions should be observed (*13*).

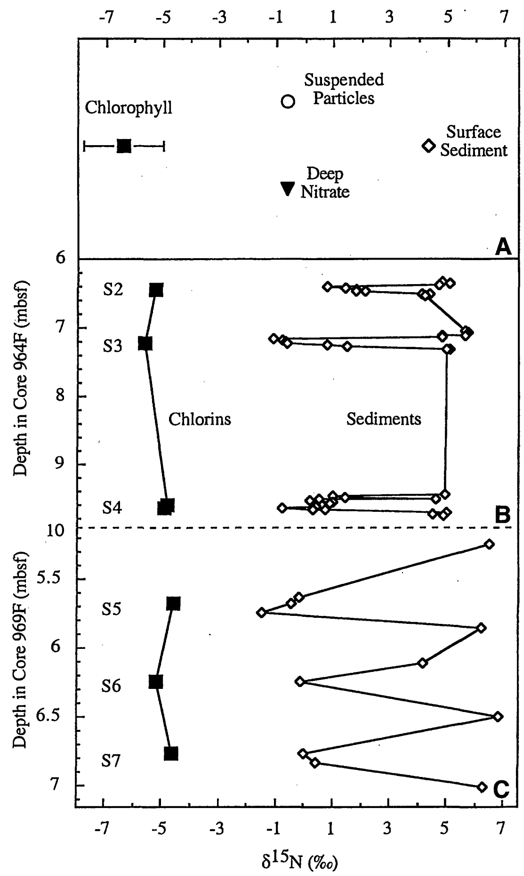

Fig. 1. Nitrogen isotopic values in the (**A**) contemporary and (**B** and **C**) late Pleistocene eastern Mediterranean Sea. Error bars (1σ) are shown for all values, but are smaller than the plot symbol in most cases. Sediments (◇), from which pyropheophorbide *a* (■) was purified (*15*), were collected by the Ocean Drilling Program, Leg 160, between March and April 1995. Sapropels range in age from 55,000 years for S2 to 193,000 years for S7 (*4*). S2 to S4 are from site 964F (36°16′N, 17°45′E, 3657 m). S5 to S7 are from site 969C (33°50′N, 24°53′E, 2196 m). Contemporary water (▼) (36°.00′N, 22°16′E), particulate (○), chlorophyll (■), and sediment (◇) (35°43′N, 15°27′E) samples were collected aboard R/V *Suroit* between May and June 1996. Suspended particulate and chlorophyll *a* $\delta^{15}N$ values are from the chlorophyll maximum and are averaged from three stations along 36°N at 17°59′E, 20°20′E, and 22°16′E. Suspended particles were collected by filtration through a Gelman A/E filter. Deep-water nitrate (▼) was collected from a depth of 1000 m and its nitrogen isotopic composition determined on two $HgCl_2$-preserved 400-ml samples from a single 10-liter Niskin bottle by the ammonia diffusion method (*39*). Sedimentary pyropheophorbide *a* was isolated chromatographically (*15*) to an average purity of 94% before isotopic analysis. Sapropel S4 was split into an upper and a lower half for chlorin isotopic analysis. The similarity of the two values suggests little or no isotopic gradient from event beginning to end. Attempts to measure chlorin $\delta^{15}N$ values in surface sediments were unsuccessful due to extremely low chlorin concentrations.

Table 1. Nitrogen isotopic alteration during early diagenesis.

Bottom-water O_2	Location	$\Delta\delta^{15}N_{sed/trap}$*	$\Delta\delta^{15}N_{sed/susp}$	$\Delta\delta^{15}N_{sed/phyt}$
Well-oxygenated	Southern Ocean	7.5	4.5	
	Eastern Mediterranean		4.9	5.7
	Equatorial Pacific	4	6	
Low oxygen	Arabian Sea	2–4		
Anoxic	Peru Margin		2	−0.5
	Black Sea		−1	0.7
	Cariaco Trench		−1.5	
	Framvaren Fjord	−0.4	−2	

*The isotopic difference between surface sediments and either deep-water sediment trap material (trap), suspended particles in overlying surface waters (susp), or phytoplankton (phyt). Phytoplankton $\delta^{15}N$ values were calculated from chlorin $\delta^{15}N$ values by adding 5.1 per mil (*16*). Additional nitrogen isotopic data are from (*13*, *29*).

Although our phytoplankton samples were collected during a single spring-time cruise, the nitrogen isotopic composition of deep-water nitrate, −0.7 ± 0.1‰ (n = 2) (Fig. 1A), provides support for very low mean annual $\delta^{15}N$ values in phytoplankton. Nitrate in the deep eastern Mediterranean is the principal reservoir of reactive nitrogen in the basin (*1*). With a residence time of 50 to 80 years (*18*), it represents a spatial and temporal integration of new production over the entire basin for many decades. Thus, the time-averaged $\delta^{15}N$ value of material sinking from the euphotic zone must approximate this value in the steady state. The remarkably light isotopic value of abyssal nitrate [versus the global deep-ocean average of 5.7 ± 0.7‰ (*19*)] is good evidence for very low mean annual $\delta^{15}N$ values of phytoplankton in the contemporary eastern Mediterranean. Also consistent with the low isotopic values of phytoplankton and deep nitrate is the $\delta^{15}N$ value of suspended particulate material in the euphotic zone, −0.6 ± 0.1‰ (n = 3) (Fig. 1A). This mixture of algal biomass and detritus is expected to have a longer residence time than living phytoplankton, and therefore to have an isotopic composition similar to that of deep nitrate.

The extremely low isotopic values of contemporary phytoplankton, nitrate, and suspended particles require that nitrogen fixation supply a substantial fraction of new nitrogen to the Mediterranean Sea. Microbial nitrogen fixation imparts an isotopic fractionation to atmospheric N_2 ($\delta^{15}N$ = 0‰), the nitrogenous substrate, producing organic matter with a mean $\delta^{15}N$ value of −2.6 ± 1.3‰ (*20*). When this biomass is remineralized it yields isotopically depleted nitrate. Other ocean basins where extensive nitrogen fixation occurs, such as the Gulf of Mexico, the southern Arabian Sea, and the subtropical Pacific, are characterized by low nitrogen isotopic ratios (*21*, *22*).

Extensive N_2 fixation in the Mediterranean Sea has been inferred from nutrient budgets and elevated N/P ratios in deep waters (that is, N/P = 22 to 29 versus the marine average of 15) (*23*–*25*). Whereas the budget calculations imply a 7 to 41% contribution of biological N_2 fixation to the Mediterranean Sea reactive nitrogen inventory (*25*), the isotopic data indicate that diazotrophy supplies 46 to 70% of eastern basin new nitrogen (*26*). Large increases of fixed nitrogen in phosphorous addition experiments with surface water, and extreme phosphorous limitation of primary production provide additional evidence for high rates of diazotrophy in the eastern Mediterranean (*24*). That widespread nitrogen fixation has been overlooked by field studies is perhaps not surprising in light of recent evidence (*22*, *23*) for dramatically higher global fixation rates than previously reported. In addition to contemporary populations of picocyanobacteria, *Synechococcus* (cyanobacterium), and *Posidonia* (sea grass) (*24*, *25*), extensive rhizosolenid diatom mats living during sapropel episodes (*7*) may have supported nitrogen-fixing bacterial symbionts (*27*). Other sources of nitrogen to the Mediterranean Sea, such as rivers, rain, and north Atlantic seawater, have isotopic values between 1 and 6‰ (*19*, *28*). Altering the contribution of any of these nitrogen sources cannot produce an eastern Mediterranean nitrogen inventory with an isotopic value less than 0‰; nitrogen fixation must be invoked.

With nitrogen isotopic values of 0‰ or lower in phytoplankton and the large abyssal nitrate reservoir, it remains to be explained why sediments between sapropel layers and in core-tops have high $\delta^{15}N$ values of 4 to 7‰ (Fig. 1). We hypothesize that decomposing organic matter becomes enriched in ^{15}N in the presence of oxygen. The severity of the isotopic enrichment appears to be inversely related to bottom-water oxygen concentrations. When bottom waters are well oxygenated, as they are in the Southern Ocean, the central equatorial Pacific, and the eastern Mediterranean, sediments are enriched in ^{15}N by 4 to 6‰ relative to sinking and suspended particles (*13*, *29*), and phytoplankton (Table 1). Under low bottom-water oxygen conditions, such as in the Arabian Sea, surface sediments are 2 to 4‰ enriched in ^{15}N relative to deep-sinking particles (*29*). When bottom waters are anoxic, such as in the Peru Margin, the Black Sea, the Cariaco Trench, and the Framvaren Fjord, surface sediments are within 2‰ of sinking and suspended particles (*29*) and phytoplankton (Table 1). Because phytoplankton $\delta^{15}N$ values in the sapropels are nearly identical to the associated whole-sediment $\delta^{15}N$ values, bottom waters were likely anoxic during those events (*30*), corroborating faunal (*4*) and geochemical (*31*) evidence for bottom-water oxygen deficiency.

Our nitrogen isotopic measurements support a model of sapropel generation in which lowered salinities (*4*) in regions where intermediate waters form cause pycnocline shoaling and diminished ventilation of eastern basin deep water (*6*, *32*). A shallower pycnocline would allow the incursion of nutrient-enriched intermediate water into the euphotic zone to fuel new production by a deep-dwelling algal community (*6*), while diminished ventilation rates would facilitate deep-water anoxia (*6*) and the preservation of organic matter (*9*). Whereas the contemporary eastern Mediterranean pycnocline lies below the euphotic depth, numerical simulations and micropaleontological studies indicate that it shoaled to 50 to 120 m during sapropel events (*6*, *32*). This would account for the occurrence in sapropel layers of rhizosolenid diatoms (*7*) and certain calcareous plankton species (*6*, *11*) adapted to a deep nutrient source (*33*). High abundances of rhizosolenids in sapropels are consistent with nitrogen isotopic evidence for surface-water nutrient depletion because these algae live in stratified, oligotrophic water (*27*).

Enhanced discharge of east African monsoonal rains through the Nile River and increased runoff from Eurasian rivers (*34*) likely triggered the incursion of nutrient-rich intermediate waters into the euphotic zone (*6*, *32*) but, contrary to previous inferences (*3*), did not supply appreciable quantities of nitrogen for phytoplankton growth. Global mean isotopic values of freshwater and estuarine total nitrogen are 4.3 ± 2.7‰ (n = 64) and 4.6 ± 2.0‰ (n = 199), respectively (*28*), and contemporary groundwater nitrate in the lower Nile region is between 2.9 to 14.5‰ (*35*). Phytoplankton $\delta^{15}N$ values of 0‰ in the sapropels thus preclude any dramatic increase in the flux of freshwater nitrogen. Two additional lines of evidence arguing against appreciable nutrient loading by runoff are observations of efficient biological removal of nutrients in estuaries (*36*), and mass balance calculations indicating that a flooding Nile could increase new nitrogen fluxes by no more than 10% (*37*).

Nitrogen isotopic measurements in fossil chlorophyll provide a new tool for understanding the oceanographic conditions during eastern Mediterranean sapropel events. Stratified, nutrient-impoverished surface water supported high rates of nitrogen fixation that contributed substantially to reactive nitrogen pools. Nitrogen from enhanced river runoff was insignificant compared with diazotrophy as a new nitrogen source. In contrast to the contemporary eastern Mediterranean, where well-oxygenated deep water facilitates the diagenetic enrichment of ^{15}N in decomposing organic matter, anoxic bottom waters during sapropel deposition preserved nitrogen isotopic ratios.

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$$\delta^{15}N = \left[\frac{^{15}N/^{14}N_{sample}}{^{15}N/^{14}N_{standard}} - 1 \right] \times 1000$$

and the isotopic standard is atmospheric N_2 with $\delta^{15}N$ = 0‰.
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Heavy Nitrogen in Carbonatites of the Kola Peninsula: A Possible Signature of the Deep Mantle

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Nitrogen and argon isotopes were measured in carbonatites and associated rocks from the Kola Peninsula in Russia. The Kola mantle source, which is thought to be located in the deep mantle, is enriched in heavy nitrogen (+3 per mil relative to air) as compared to Earth's surface (atmosphere and crust, +2 per mil) and the shallow mantle (−4 per mil). Recycling of oceanic crust (+6 per mil) or metal-silicate partitioning may account for the nitrogen isotopic composition of the deep mantle.

Determining the structure and composition of the mantle is necessary in order to understand current and past mantle dynamics and mantle-to-crust interactions. For example, some have argued that part of the mantle has been isolated from mantle convection for most of Earth's history, allowing the preservation of a primitive component that is only sampled by plumes. Evidence in support of this view arises mainly from noble gases, because plume-derived magmas often show lower radiogenic/primordial isotope ratios than do mid-ocean ridge basalts (MORBs) (*1*). At variance with these models are geophysical (*2*), experimental (*3*), and geochemical (*4*) lines of evidence that suggest that some of the subducting slabs sink through the 670-km-deep seismic discontinuity, implying global stirring of the mantle.

The nitrogen isotopic composition of the shallow mantle that feeds MORs, which is expressed as per mil (‰) deviation relative to the composition of air [in $\delta^{15}N$ notation (*5*)], is estimated to be ~−4‰ (*6*–*13*). This signature may be a remnant of the nitrogen isotopic composition of Earth-forming planetesimals, which later evolved as a result of (i) addition of meteoritic (*14*, *15*) and cometary (*15*) volatiles, or (ii) fractional loss of atmospheric volatiles (*16*), or both. Biologic activity leads to a fractionation of nitrogen isotopes and gives sedimentary rocks a specific composition [$\delta^{15}N \sim +6$‰ (*17*)]. Nitrate is used by denitrifying bacteria as the terminal electron acceptor in energy generation when oxygen is unavailable. Associated with denitrification is a kinetic isotope effect that enriches the residual nitrate in ^{15}N (*18*). Because NO_3^- is the main nitrogen-bearing nutrient, marine organisms and sediments are enriched in ^{15}N relative to the atmosphere (*17*). The oceanic crust thus enriched in ^{15}N is subducted back into Earth at convergent plate margins, which makes nitrogen a potentially powerful tracer of volatile recycling in the mantle.

Mantle plumes, which are assumed to be fixed relative to plate motion, sample a deeper region than that feeding MORs (*19*). The isotopic composition of nitrogen in plumes has not been documented (*20*). Low $^4He/^3He$ ratios and a steep $^{20}Ne/^{22}Ne$-$^{21}Ne/^{22}Ne$ correlation (*21*) indicate that a mantle plume contributed to the 370-million-year-old (*22*) ultrabasic-alkaline-carbonatite magmatism in the Kola Peninsula in Russia (the eastern segment of the Baltic Shield). The Kola rocks crystallized at depth (*23*), which prevented them from being extensively outgassed, minimizing any subsequent

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