New neodymium isotope data quantify Nile involvement in Mediterranean anoxic episodes

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ABSTRACT

The development of widespread anoxic conditions in the deep oceans is evidenced by the accumulation and preservation of organic-carbon–rich sediments, but its precise cause remains controversial. The two most popular hypotheses involve (1) circulation-induced increased stratification resulting in reduced oxygenation of deep waters or (2) enhanced productivity in the surface ocean, increasing the raining down of organic matter and overwhelming the oxic remineralization potential of the deep ocean. In the periodic development of deep-water anoxia in the Pliocene–Pleistocene Mediterranean Sea, increased riverine runoff has been implicated both as a source for nutrients that fuel enhanced photic-zone productivity and a source of a less dense freshwater cap leading to reduced circulation, basin-wide stagnation, and deep-water oxygen starvation. Monsoon-driven increases in Nile River discharge and increased regional precipitation due to enhanced westerly activity—two mechanisms that represent fundamentally different climatic driving forces—have both been suggested as causes of the altered freshwater balance. Here we present data that confirm a distinctive neodymium (Nd) isotope signature for the Nile River relative to the Eastern Mediterranean—providing a new tracer of enhanced Nile outflow into the Mediterranean in the past. We further present Nd isotope data for planktonic foraminifera that suggest a clear increase in Nile discharge during the central intense period of two recent anoxic events. Our data also suggest, however, that other regional freshwater sources were more important at the beginning and end of the anoxic events. Taken at face value, the data appear to imply a temporal link between peaks in Nile discharge and enhanced westerly activity.

Keywords: anoxia, Mediterranean, Nile River, monsoon, foraminifera, neodymium isotopes.

INTRODUCTION

Considerably enhanced freshwater fluxes into the Mediterranean are widely interpreted to be key to the collapse of deep-water ventilation and/or to the elevated supply of nutrients (fueling enhanced productivity) that led to the deposition of organic-rich sediments (sapropels) during Mediterranean anoxic events (e.g., Rossignol-Strick et al., 1982; Rossignol-Strick, 1983, 1987; Rohling and Hilgen, 1991; Calvert et al., 1992; Rohling, 1994; Sancetta, 1994; Kallel et al., 1997; Sachs and Repeta, 1999; Casford et al., 2002). It is well established that sapropel deposition coincided systematically with Northern Hemisphere insolation maxima related to the orbital cycle of precession, which intensified the African monsoon (e.g., Rossignol-Strick et al., 1982; Rossignol-Strick, 1983; Rohling and Hilgen, 1991). Ethiopian rivers, fed by these monsoonal rains in summer, cause a strong seasonal flood in the Nile River's discharge into the Mediterranean (Adamson et al., 1980). Other work has suggested that there were concomitant increases in direct precipitation over the Mediterranean region, related to increased westerly activity (e.g., Rossignol-Strick, 1987; Rohling and Hilgen, 1991; Kallel et al., 1997; Bar-Matthews et al., 2000). That there was an increase in freshwater supply to the Mediterranean during sapropel-generating events is evidenced by $\delta^{18}O$ anomalies in fossil planktonic foraminifera from sediment cores (Rossignol-Strick et al., 1982; Emeis et al., 1998, 2000). However, oxygen isotope studies have proved unsuccessful at pinpointing the origin of the freshwater. To address this issue, we test the hypothesis that Nile outflow was enhanced; our approach uses neodymium (Nd) isotope analyses of Nile River water, Eastern Mediterranean seawater, and fossil foraminifera from ODP (Ocean Drilling Program) Holes 967C and 967D in the eastern Levantine Basin.

RESULTS

Rising in the Tertiary basalts of the Ethiopian Highlands, two of the main tributaries of the Nile, the Blue Nile and Atbara River, are expected to have Nd isotope signatures enriched in the radiogenic Nd isotope (^{143}Nd). New Nd isotope data for the River Nile and its tributaries confirm that expectation (Fig. 1 and Table DR1[1]). As is typical, the Nd data are reported in epsilon units (parts per 10,000 deviations from chondritic uniform reservoir [CHUR]):

$$\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd_{meas}) \div (^{143}Nd/^{144}Nd_{CHUR}) - 1] \times 10^4, \quad (1)$$

and $^{143}Nd/^{144}Nd_{CHUR} = 0.512638$ (normalized to $^{146}Nd/^{144}Nd = 0.7219$). The Nile River's annually averaged dissolved load has an estimated ε_{Nd} value of ~ -1 to -1.5 (Fig. 1). We assume that this has remained constant over the past 125 k.y. Published data (Spivack and Wasserburg, 1988) show that the seawater flow from the Western into the Eastern Mediterranean, through the Strait of Sicily, has an ε_{Nd} value of ~ -10. Relative to that value, our data for present-day Eastern Mediterranean surface seawater (Fig. 1) are shifted toward more radiogenic values ($\varepsilon_{Nd} = -5$; Fig. 1) as a result of dissolved and particulate-borne Nd from the Nile.

The 3.5–4 epsilon unit contrast between the dissolved Nd isotope composition of Nile water and the ambient Eastern Mediterranean (Fig. 1) may be used to identify increases in Nile outflow during anoxic events, following the identification of a suitable substrate that records past seawater Nd isotope compositions. Planktonic foraminifera have been demonstrated to have the ability to record the Nd isotope composition of surface water (Vance and Burton, 1999; Burton and Vance, 2000; Vance et al., 2004). We use Nd isotope analyses of planktonic foraminifera within and around the sapropels to investigate the role of the Nile in their genesis.

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[1] GSA Data Repository item 2004091, Table DR1 and Table DR2, Nd isotopic data for the Nile and for foraminifera from Ocean Drilling Program Core 967, is available online at www.geosociety.org/pubs/ft2004.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

Geology; July 2004; v. 32; no. 7; p. 565–568; doi: 10.1130/G20419.1; 3 figures; Data Repository item 2004091.

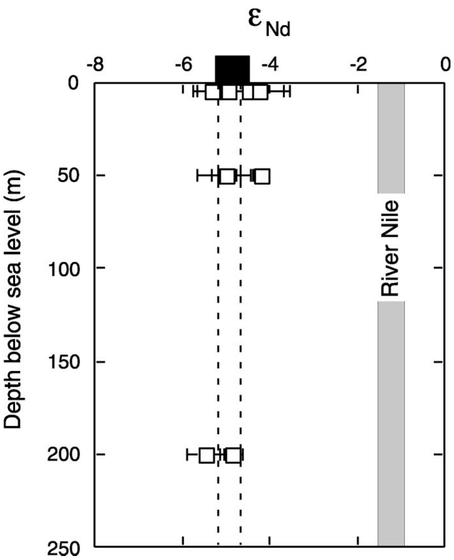

Figure 1. Nd isotope data for Eastern Mediterranean surface seawater (open squares; dashed lines give two standard deviations on either side of weighted mean for all data; data are from Vance et al. [2004] and are for samples taken both close to mouth of Nile and off coast of Israel) and main Nile (light gray band). Also shown (black rectangle) is weighted average for our analyses of nonsapropel planktonic foraminifera at Ocean Drilling Program Site 967. Seawater measurements come from close to Nile outflow and, as result, probably represent maximum ε_{Nd} values for Eastern Mediterranean Basin as whole. Value of ε_{Nd} for main Nile was calculated as weighted average of all main Nile analyses weighted for discharge (means for station at Dongola in Sudan for period 1912–1984; data from Global Runoff Data Centre, http://www.hydrosalt.com/niledata/grade/grdchome.htm) and measured Nd concentration. Upper and lower bounds on weighted average are given by calculations based on (1) discharge data for months during which our samples were taken (February [dry season] and September [wet season]) and (2) discharge data calculated as average for wet and dry seasons. River-water samples were passed through 0.2 μm filters, and Nd was separated from filtered water by using coprecipitation with $Fe(OH)_3$. Analytical techniques for separation and mass spectrometric analysis of Nd have been reported previously (Vance and Thirlwall, 2002). Error bars on all Nd isotope data in this paper are for 95% confidence. Reproducibility within one analytical session, based on 5–10 separate analyses of our in-house Aldrich standard, is ~0.000006–0.000010. Differences between individual analytical sessions were corrected for by normalization to value for this Aldrich standard of 0.511421—equivalent to value for La Jolla Nd of 0.511856 (Vance and Thirlwall, 2002).

ODP Holes 967C and 967D are located on the northern slope of the Eratosthenes Seamount, south of Cyprus in the eastern Levantine Basin (Emeis et al., 1998). The sinking of oxygenated surface waters between Cyprus and Rhodes, forming Levantine Intermediate Water (LIW), has been shown to be extremely sensitive to changes in freshwater input in general and Nile discharge in particular (e.g., Myers, 2002). Pre–Aswan Dam Nile outflow affected this part of the Mediterranean via entrainment in the counterclockwise current along the Levantine coast.

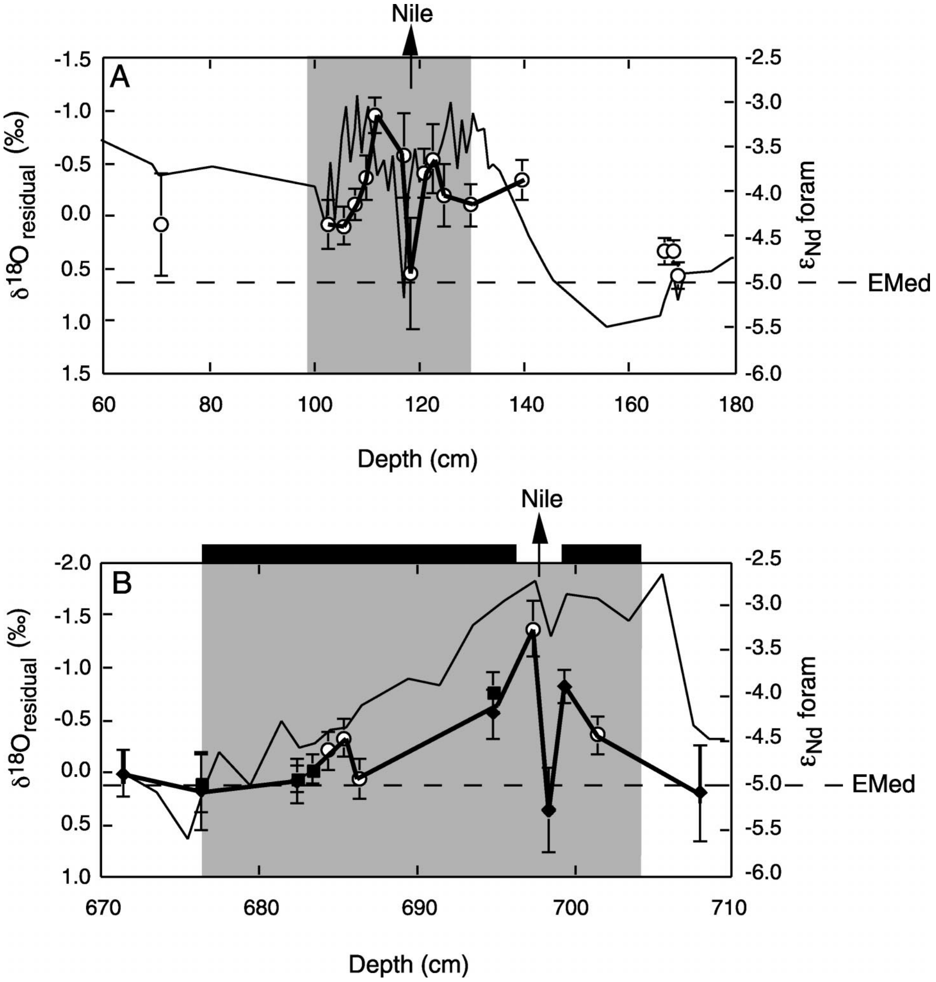

Figure 2. Nd isotope data for sedimentary planktonic foraminifera separated from levels corresponding to (A) sapropel S1 and (B) sapropel S5 at Ocean Drilling Program (ODP) Site 967 in Levantine Basin. Filled diamonds—*Globigerinoides ruber*; filled squares—*Orbulina universa*; open circles—mixed *O. universa* and *G. ruber* samples. Use of mixed samples is justified by fact that in three instances in S5 where both species were analyzed separately for same interval, identical results were obtained. All foraminiferal samples for Nd isotope analysis were cleaned and analyzed by using methods described elsewhere (Vance and Burton, 1999; Burton and Vance, 2000; Vance et al., 2004). Thicker line is line through all Nd data points. Faint line gives $\delta^{18}O$ residuals referenced to present-day value of 0‰ and with ice-volume and temperature contributions to signature removed (data from Emeis et al., 1998, 2000). Gray areas denote extents of two sapropels as defined by Emeis et al. (2000) and Rohling et al. (2002, 2004). Dashed line labeled EMed gives present-day ε_{Nd} value of Eastern Mediterranean (Fig. 1), and arrow labeled Nile indicates direction of expected shift in ε_{Nd} toward Nile (from Fig. 1). Thick black lines at top of B indicate approximate positions of two periods in S5 when monsoon front penetrated northward of central Saharan watershed (from Rohling et al., 2002, 2004). See text for further discussion.

Foraminiferal Nd isotope data for sapropels S1 (ca. 9–6 ka.) and S5 (ca. 124–119 ka) at ODP Site 967 show distinct ε_{Nd} shifts away from the ambient Eastern Mediterranean value of -5 toward the Nile value at -1 to -1.5, reaching values of ~ -3 to -3.5 in both S1 and S5 (Figs. 2A and 2B and Table DR2 [see footnote 1]). The ε_{Nd} shifts coincide with strongly negative $\delta^{18}O$ residuals (i.e., the residual signature after removal of temperature and ice-volume effects—see Emeis et al., 2000, and Fig. 2 for details), which reflect enhanced freshwater dilution. Besides this covariation on the nonsapropel to sapropel scale, we also observe some covariation on smaller scales, with ε_{Nd} dropping back to ambient Eastern Mediterranean values coincident with, or close to, reductions in ^{18}O depletion.

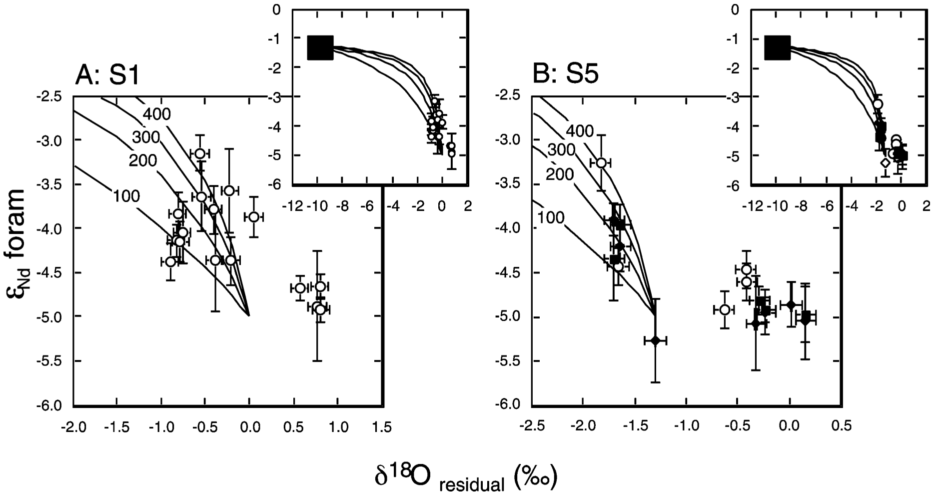

Figure 3. ε_{Nd} **data for foraminifera vs.** $\delta^{18}O$ **residuals (filled diamonds—*Globigerinoides ruber*; filled squares—*Orbulina universa*; open circles—mixed *O. universa* and *G. ruber* samples) for (A) sapropel S1 and (B) sapropel S5. Large black squares denote Nile end member in Nd isotope vs. O isotope space, and labeled curves are mixing hyperbolae between this end member and ambient Eastern Mediterranean end member. Nile end member is assumed to have** $\delta^{18}O$ **(standard mean ocean water, SMOW) value of −8.4‰, i.e., ~10‰ lower than present-day Eastern Mediterranean surface water (McKenzie, 1993). Mixing curves are labeled with modeled effective Nd concentrations (in pmol/kg) for Nile outflow after estuarine removal of rare earth elements. For sapropel S1, Mediterranean end member is assumed to have same Nd isotope and O isotope compositions as modern Eastern Mediterranean foraminifer, whereas for sapropel S5, Mediterranean end member is taken to have** $\delta^{18}O$ **value of −1.3‰, because this is** $\delta^{18}O$ **at which Nd appears to move away from ambient Mediterranean values; i.e.,** $\delta^{18}O$ **interval between 0‰ and −1.3‰ does not have associated** ε_{Nd} **shift. See text for further discussion.**

DISCUSSION

The previously documented shifts in foraminiferal $\delta^{18}O$ residuals associated with the sapropels clearly imply freshwater dilution, but cannot unambiguously identify the sources. Our new Nd data can identify these sources. The shift of the Nd data in the central parts of the sapropels, away from the ‘‘normal’’ Eastern Mediterranean background and toward the more radiogenic Nile value, strongly suggest enhanced Nile flooding during Mediterranean anoxic episodes by waters derived from the Ethiopian Highlands, which have basalts that contain highly radiogenic Nd. No other known regional source of Nd could cause such an isotopic change. Increased discharge from European and Turkish rivers—with ε_{Nd} values of ~ -10 and -6, respectively (Frost et al., 1986)—would cause changes in Mediterranean ε_{Nd} values that are opposite to the trends we observe.

Are the observed Nile Nd concentrations high enough to effect the changes in surface-seawater Nd isotope composition implied by the shifts that are observed in our foraminiferal Nd isotope data? The Nile River Nd concentrations required to produce the mixing curves in Figure 3 (100–400 pmol/kg) are at the lower end of the range observed for the present-day Nile (100–1720 pmol/kg). At face value, the measured Nd concentrations of the Nile are easily capable of causing the shift in Nd isotope ratios in the Eastern Mediterranean during sapropel-generating events. However, several studies (Elderfield et al., 1990; Sholkovitz, 1993) have shown that much of the dissolved Nd pool (traditionally operationally defined as that which passes through a 0.45 μm filter) is transported in the form of colloids and that these colloids are rapidly removed by coagulation processes in estuaries. This process is known to remove 45%–95% of riverine rare earth element (REE, e.g., Nd) loads (Elderfield et al., 1990; Sholkovitz, 1993), so the measured Nile Nd concentrations are not necessarily directly relevant here.

Nozaki et al. (2000) demonstrated that REEs in estuaries show near-conservative mixing (i.e., simple dilution, producing a straight line on a mixing diagram when REE concentration is plotted vs. salinity) when Nd concentrations are measured in the ‘‘truly dissolved’’ (i.e., noncolloidal) fraction as isolated by ultrafiltration. Most ultrafiltration studies of rivers (e.g., Viers et al., 1997; Nozaki et al., 2000; Ingri et al., 2000) report Nd concentrations of 20–920 pmol/kg. One study reports Nd concentrations to 3330 pmol/kg in ultrafiltered samples of northwest Russian rivers (Pokrovsky and Schott, 2002). Clearly, the range of Nile Nd concentrations required by Figure 3 is also consistent with the range obtained for the truly dissolved fraction of riverine Nd. Although these data do not require it, a further contribution to Eastern Mediterranean Nd could derive from isotopic exchange with, or dissolution of, riverine particulates. However, Krom et al. (2002) concluded that the quantity of Nile particulates bearing radiogenic Nd decreased during sapropel-generating events.

Our new foraminifera data also imply that the Nile was not the only factor in the altered freshwater balance of the Eastern Mediterranean during anoxic events. If the Nile were the only source of extra freshwater during sapropel-generating events, then on ε_{Nd} vs. $\delta^{18}O$ mixing plots (Fig. 3), the data should lie on a single hyperbolic mixing line, the curvature of which depends solely on the dissolved Nd concentrations in the ambient Eastern Mediterranean and in the Nile water entering the basin. For S1 (Fig. 3A), three points clearly lie at $\delta^{18}O > 0$‰ and have ε_{Nd} values similar to modern observations; these points represent the last deglaciation, at which time Eastern Mediterranean ε_{Nd} values appear to have been similar to those of the present. All samples with $\delta^{18}O$ residuals of <0‰, which represent sapropel S1, have ε_{Nd} values that are broadly on a mixing trend between the Eastern Mediterranean and the Nile. This finding suggests enhanced Nile flooding into the Eastern Mediterranean relative to the present.

The picture for S5 (Figs. 2B, 3B), however, is slightly more complicated. Sapropel S5 is more intense than S1, with greatly enhanced moisture-bearing summer monsoon circulation (Rohling et al., 2002). Figure 2B shows that the peak ε_{Nd} signature within S5 is narrower than that of the $\delta^{18}O$ signature, so a large part of the $\delta^{18}O$ shift in S5 is associated with little or no change in ε_{Nd} (Fig. 3B). For S5 in particular, the new data clearly imply both a radiogenic Nd Nile component and a nonradiogenic Nd component. Discharge of the latter, presumably runoff from the wider Mediterranean catchment, became enhanced before the Nile flooding, and also outlasted it. Moreover, the return to normal ε_{Nd} values in the center of the sapropel Nd peak (at a depth of 698–699 cm) is accompanied by only a modest dip in the $\delta^{18}O$ profile (Fig. 3B), implying the maintenance of the freshwater source but the disappearance of an enhanced Nile influence on Mediterranean Nd. The gradual decline in ^{18}O depletion following the peaks in the Nd and O data (Fig. 2B) implies that, although the Nile contribution tails off in the center of S5, the enhanced freshwater supply to the Eastern Mediterranean, perhaps associated with increased westerly activity, continues, albeit at a declining rate. We note, however, that Rohling et al. (2002, 2004) concluded, particularly for S5, that non-Nile runoff was probably not restricted to European and Anatolian rivers, but included ^{18}O-depleted African monsoon discharge from paleorivers and/or wadis along the wider North African margin, related to penetration of the monsoon front to the north of the central Saharan watershed. This process has now been inferred for the majority of eastern Mediterranean sapropels deposited during the past 3 m.y. (Larrassoana et al., 2003).

CONCLUDING REMARKS

The theory of increased Nile outflow during sapropel deposition is widely supported, and the relationship with the astronomical cycle of precession is widely acknowledged (Rossignol-Strick et al., 1982; Rossignol-Strick, 1987; Rohling and Hilgen, 1991; Rohling, 1994). Sedimentary Nd and Sr isotope data for Mediterranean deep-sea sediments suggested a generally increased delivery of Nile sediment relative to Saharan dust at times of sapropel deposition (Krom et al., 1999; Freydier et al., 2001). Our Nd isotope data for planktonic foraminifera now considerably refine this picture: the increase in Nile outflow was confined to the depositional period of the central part of the sapropels, whereas other freshwater discharges became elevated prior to, and outlasted, the Nile floods. The Nile clearly was important for sapropel formation in the Eastern Mediterranean, but it was most definitively not exclusively responsible for the recorded freshwater excess in the basin at those times. Our results suggest that the Nile flux enhancement was rivaled in magnitude by that from other freshwater sources (Fig. 2B), especially during the deposition of sapropel S5 ca. 124–119 ka (cf. Rohling et al., 2002, 2004).

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