2012

A review of nitrogen isotopic alteration in marine sediments

Rebecca S. Robinson
University of Rhode Island, rebecca_r@uri.edu

Markus Kienast

Ana Luiza Albuquerque

Mark Altabet

Sergio Contreras

See next page for additional authors

Citation/Publisher Attribution
Robinson, R. S., et al. (2012), A review of nitrogen isotopic alteration in marine sediments, *Paleoceanography*, 27, PA4203, doi: 10.1029/2012PA002321
Available at: https://doi.org/10.1029/2012PA002321

A review of nitrogen isotopic alteration in marine sediments

Rebecca S. Robinson,[1] Markus Kienast,[2] Ana Luiza Albuquerque,[3] Mark Altabet,[4] Sergio Contreras,[5] Ricardo De Pol Holz,[6] Nathalie Dubois,[7] Roger Francois,[8] Eric Galbraith,[9] Ting-Chang Hsu,[10] Tara Ivanochko,[8] Samuel Jaccard,[11] Shuh-Ji Kao,[10] Thorsten Kiefer,[12] Stephanie Kienast,[2] Moritz Lehmann,[13] Philippe Martinez,[14] Matthew McCarthy,[15] Jürgen Möbius,[16] Tom Pedersen,[17] Tracy M. Quan,[18] Evgeniya Ryabenko,[19] Andreas Schmittner,[20] Ralph Schneider,[21] Aya Schneider-Mor,[22] Masahito Shigemitsu,[23] Dan Sinclair,[24] Christopher Somes,[19] Anja Studer,[25] Robert Thunell,[26] and Jin-Yu Yang[27]

Received 16 March 2012; revised 11 September 2012; accepted 12 September 2012; published 23 October 2012.

[1] Nitrogen isotopes are an important tool for evaluating past biogeochemical cycling from the paleoceanographic record. However, bulk sedimentary nitrogen isotope ratios, which can be determined routinely and at minimal cost, may be altered during burial and early sedimentary diagenesis, particularly outside of continental margin settings. The causes and detailed mechanisms of isotopic alteration are still under investigation. Case studies of the Mediterranean and South China Seas underscore the complexities of investigating isotopic alteration. In an effort to evaluate the evidence for alteration of the sedimentary N isotopic signal and try to quantify the net effect, we have compiled and compared data demonstrating alteration from the published literature. A >100 point comparison of sediment trap and surface sedimentary nitrogen isotope values demonstrates that, at sites located off of the continental margins, an increase in sediment $^{15}N/^{14}N$ occurs during early burial, likely at the seafloor. The extent of isotopic alteration appears to be a function of water depth. Depth-related differences in oxygen exposure time at the seafloor are likely the dominant control on the extent of N isotopic alteration. Moreover, the compiled data suggest that the degree of alteration is likely to be uniform through time at most sites so that bulk sedimentary isotope records likely provide a good means for evaluating relative changes in the global N cycle.

Citation: Robinson, R. S., et al. (2012), A review of nitrogen isotopic alteration in marine sediments, *Paleoceanography*, *27*, PA4203, doi:10.1029/2012PA002321.

[1]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island, USA.
[2]Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada.
[3]Departamento de Geoquímica, Instituto de Química, Universidade Federal Fluminense, Rio de Janeiro, Brazil.
[4]School for Marine Science and Technology, University of Massachusetts Dartmouth, New Bedford, Massachusetts, USA.
[5]Large Lakes Observatory, University of Minnesota Duluth, Duluth, Minnesota, USA.
[6]Department of Oceanography, University of Concepcion, Concepcion, Chile.
[7]School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, UK.
[8]Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada.
[9]Earth and Planetary Sciences, McGill University, Montreal, Quebec, Canada.
[10]Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan.

Corresponding author: R. S. Robinson, Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA. (rebeccar@gso.uri.edu)

0883-8305/12/2012PA002321

[11]Geologisches Institut, ETH Zurich, Zurich, Switzerland.
[12]PAGES, Bern, Switzerland.
[13]Institute for Environmental Geoscience, University of Basel, Basel, Switzerland.
[14]EPOC, UMR CNRS 5805, University of Bordeaux, Talence, France.
[15]Ocean Sciences Department, University of California, Santa Cruz, California, USA.
[16]Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Hamburg, Germany.
[17]School of Earth and Ocean Sciences, University of Victoria, Victoria, British Columbia, Canada.
[18]Boone Pickens School of Geology, Oklahoma State University, Stillwater, Oklahoma, USA.
[19]Marine Biogeochemistry IFM-GEOMAR, Kiel, Germany.
[20]College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA.
[21]Institut fuer Geowissenschaften, Christian-Albrechts Universitaet zu Kiel, Kiel, Germany.
[22]School of Earth Sciences, Stanford University, Stanford, California, USA.
[23]Environmental Earth Science, Hokkaido University, Hokkaido, Japan.
[24]Institute of Marine and Coastal Sciences, Rutgers University, Newark, New Jersey, USA.
[25]Earth Sciences, ETH Zurich, Zurich, Switzerland.
[26]Department of Earth and Ocean Sciences, University of South Carolina, Columbia, South Carolina, USA.
[27]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, China.

1. Importance of the Marine N Cycle

[2] Nitrogen (N) is a major component of biomass and is required for photosynthesis. The total oceanic fixed N inventory and its availability in the surface ocean are thus important controls on primary production. Variations in these two parameters over geologic time have significant implications for the global biogeochemical cycling, not only of N, but also of carbon, and oxygen throughout Earth history. Sedimentary N isotope measurements have emerged as a powerful tool for monitoring the marine N cycle in the past and for testing important hypotheses explaining the ice core CO_2 records [*Galbraith et al.*, 2008b, and references therein]. However, initial tests of the proxy demonstrated alteration of the primary isotopic signal during sinking and sedimentation and, more significantly, during burial in some settings [*Altabet and Francois*, 1994; *Galbraith et al.*, 2008b]. Because local-to-regional scale spatial patterns of the surface and subsurface water column N isotopic composition of nitrate are largely mirrored in the sediments, despite evidence for alteration, paleoceanographic work proceeded [*Altabet and Francois*, 1994]. However, the focus of this work has been on the continental margins, where alteration is thought to be minimal [*Altabet et al.*, 1999; *Kienast et al.*, 2002; *Thunell et al.*, 2004], or based on isotopic measurements of specific organic N pools (i.e., microfossil-bound and chlorophyll degradation products) [*Higgins et al.*, 2009; *Ren et al.*, 2009; *Robinson et al.*, 2004]. Here, we evaluate evidence for and against alteration of bulk sedimentary N isotope ratios. A comparison of >100 published, co-located sediment trap and surface sediment N isotope values indicates that the degree of alteration increases with water depth in the ocean. The lack of evidence for an increase in $^{15}N/^{14}N$ with increasing sinking depth, tracked by sediment traps at the same geographic location and different depths, implies that alteration occurs largely at/in the seafloor. Despite the evidence for alteration, there exists the potential for a more comprehensive reconstruction of the paleo-marine N cycle that includes the widespread use of bulk measurements in combination with the measurement of specific organic N pools and global circulation models [*Somes et al.*, 2010; E. Galbraith et al., Global nitrogen isotopic constraints on the acceleration of oceanic denitrification during the last deglacial warming, submitted to *Nature Geoscience*, 2012].

2. Processes Reflected by Sedimentary N Isotope Ratios

[3] Nitrogen in the ocean is present in many redox states, and biological processes are largely responsible for the various transformations of N from one form to another. These transformations are usually associated with fractionation of the N isotopes ($^{15}N/^{14}N$) [*Altabet and Francois*, 1994; *Codispoti*, 1989; *Montoya*, 1994; *Wellman et al.*, 1968]. Kinetic isotope effects stem from differences in reaction rates between the heavy and light isotopes. The processes that are known to affect the isotopic composition of dissolved inorganic N (DIN) in the modern ocean include N_2 fixation by diazotrophic bacteria [*Karl et al.*, 1997], nitrification, the extent of surface NO_3^- utilization [*Altabet and Francois*, 1994], denitrification [*Liu and Kaplan*, 1989],

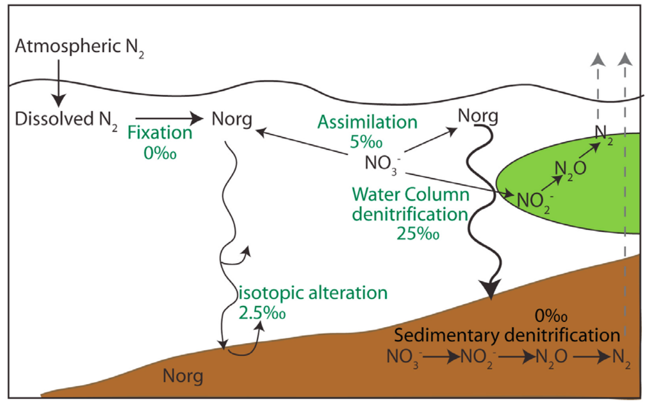


Figure 1. Key steps in the marine N cycle typically recorded in the nitrogen isotopic composition of marine sediments. Estimates of isotopic enrichment factors for the individual transformations are noted. The green shaded area represents suboxic water columns where denitrification occurs (modified from *Sigman et al.* [2009]).

and the anammox reaction (S. Contreras et al., manuscript in preparation, 2012). The external processes, such as N_2 fixation and denitrification/anammox, control the inventory of nutrient N in the ocean while nitrification and uptake reflect internal cycling processes. In the modern ocean, the N isotopic compositions (as $\delta^{15}N$, where $\delta^{15}N = {}^{15}N/{}^{14}N_{sample}/{}^{15}N/{}^{14}N_{standard} - 1*1000‰$, where the standard is atmospheric N_2) of different N pools are used to evaluate the relative roles of these various processes within the N cycle [*Brandes and Devol*, 2002; *Deutsch et al.*, 2004; *Lehmann et al.*, 2004; *Sigman et al.*, 2009]. When organisms assimilate N to produce biomass, the ^{15}N content of their N source is imprinted in the organic matter eventually deposited in sediments. The source is influenced by the preformed $\delta^{15}N$ of the water mass as well as any process that adds or removes N, such as remineralization or water column denitrification, along its flow path in the subsurface. The sub-euphotic "source" signature may be overprinted by alteration of the isotopic signal in the surface ocean, through additions of newly fixed N or the partial consumption of NO_3^-. In sum, sedimentary $\delta^{15}N$ can reflect changes in ocean circulation, the biological pump, and large scale N cycling (Figure 1) [*Brandes and Devol*, 2002; *Deutsch et al.*, 2004; *Galbraith et al.*, 2008b; *Robinson and Sigman*, 2008; *Sigman et al.*, 2010]. N isotopes also may be viewed as a paleoredox proxy because denitrification, the respiration of organic matter using NO_3^-, occurs under suboxic conditions [*Galbraith et al.*, 2004; *Jaccard and Galbraith*, 2012; *Kashiyama et al.*, 2008] (Figure 1).

[4] The $\delta^{15}N$ values of bulk sedimentary organic nitrogen reflect the $\delta^{15}N$ of the sinking flux of organic matter, plus any secondary isotopic alteration that occurs during sinking and burial due to either the removal or addition of N. To use the N isotopic composition of bulk sediments as a paleoceanographic tracer for surface waters, the extent of any alteration-related fractionation must be well constrained. Studies of sinking particles in the North Atlantic, Norwegian Sea, Sargasso Sea, Southern Ocean, and Southern California Bight have shown alteration of the $\delta^{15}N$ in sinking particles with depth during periods of low flux, or in low-productivity

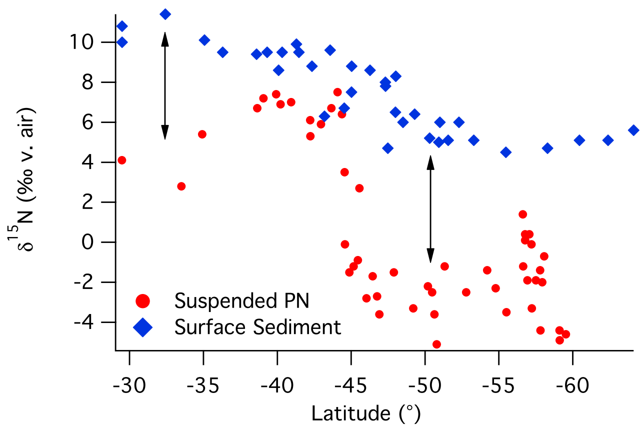


Figure 2. Southern Ocean suspended and surface sediment $\delta^{15}N$ versus latitude [*Altabet and Francois*, 1994]. The large offset between suspended and surface sediment $\delta^{15}N$ values collapses in the region of higher accumulation rates under the Antarctic Polar Front (~44°S).

regions, perhaps due to the addition of nitrogen from other sources [*Altabet and Francois*, 2001; *Altabet et al.*, 1991; *Lehmann et al.*, 2002; *Lourey et al.*, 2003] or the loss of specific N_{org} fractions [*Macko and Estep*, 1984]. The observed changes are not unidirectional, but include both increases and decreases of $\delta^{15}N$ [*Lehmann et al.*, 2002]. However, during blooms, the $\delta^{15}N$ of sinking PN does not change with depth [*Altabet et al.*, 1991; *Altabet and Francois*, 1994]. Since high flux events contribute the majority of organic matter accumulating in sediments, organic N (N_{org}) that reaches the sediment-water interface generally should preserve the $\delta^{15}N$ signal of N_{org} in the surface.

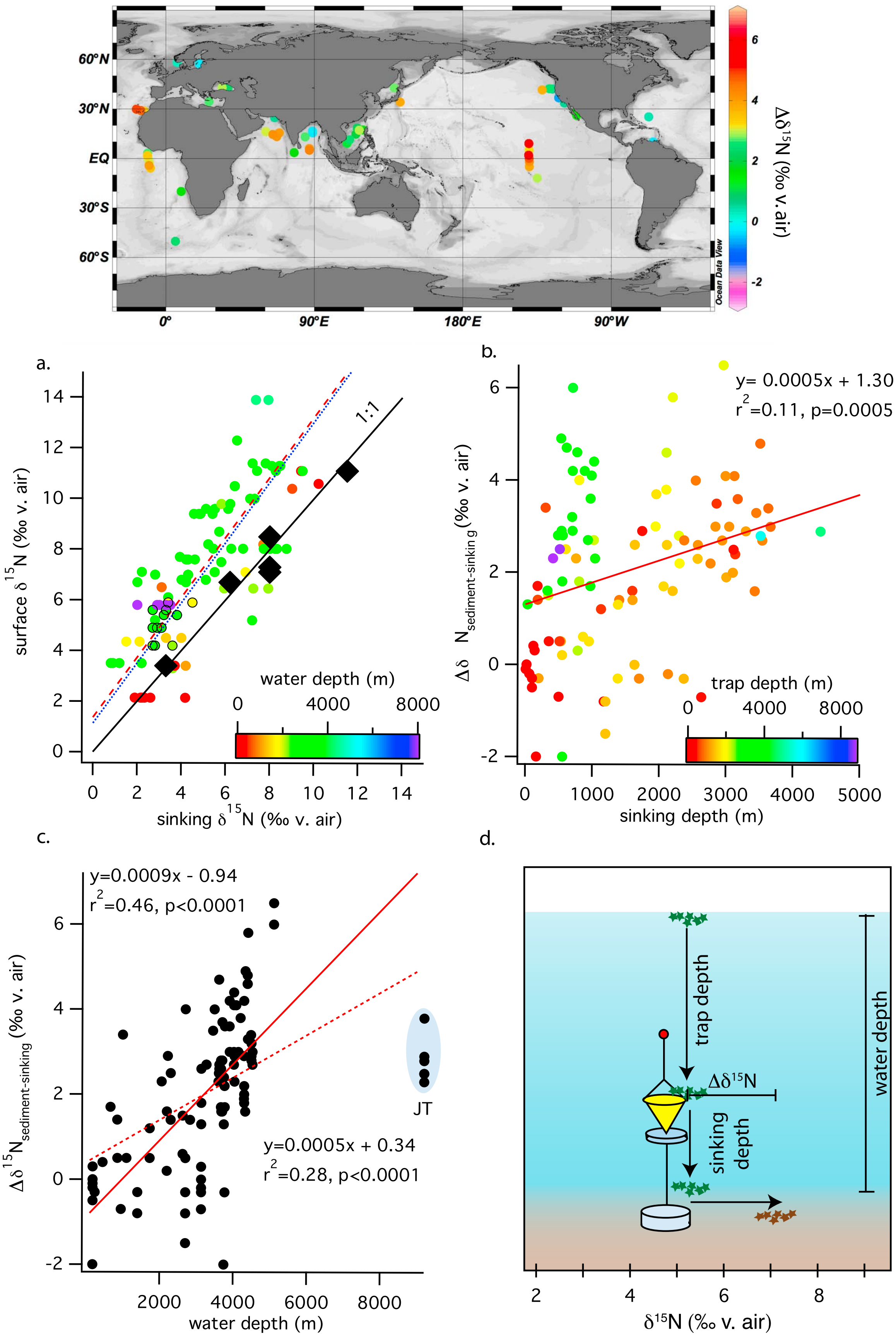
3. Isotopic Alteration of the $\delta^{15}N$ Signal in Sediments

[5] Significant isotopic alteration of the organic N signal appears to occur at the sediment-water interface during early burial [*Altabet and Francois*, 1994]. Comparisons of sinking, suspended, and surface sedimentary $\delta^{15}N$, led to the assertion that in low organic N flux regions such as the Southern Ocean, there is the potential for a large (3–6‰) increase in the $\delta^{15}N$ values recorded in bulk sediments at the seafloor (Figure 2) [*Altabet and Francois*, 1994]. However, spatial variation in sedimentary $\delta^{15}N$ values fit expectations based on both surface nitrate concentration changes and $\delta^{15}N$ of nitrate values [*Altabet and Francois*, 1994; *Farrell et al.*, 1995; *Sigman et al.*, 1999]. In high sediment accumulation regions, such as on continental margins, the $\delta^{15}N$ values of surface sediments are essentially equal to the $\delta^{15}N$ of the sinking flux and/or subeuphotic zone nitrate, suggesting that no significant alteration occurs in these regions [*Altabet et al.*, 1999; *Kienast et al.*, 2002; *Thunell et al.*, 2004] (Figure 3a).

[6] Several attempts to understand isotopic alteration of sedimentary N in the natural environment were made [*Altabet et al.*, 1999; *Freudenthal et al.*, 2001a; *Prokopenko et al.*, 2006a; *Velinsky et al.*, 1991]. Sequential extractions from margin sediments led to the operational definition of four sedimentary nitrogen pools: (1) organic nitrogen, (2) acid released/mineral bound, (3) weakly bound ammonium (NH_4^+), and (4) tightly bound NH_4^+ [*Freudenthal et al.*, 2001a]. For example, the $\delta^{15}N$ of the organic N pool sampled off the Moroccan coast increased within the top 10 cm and then stabilized, suggesting that even in margin sediments, some alteration may occur [*Freudenthal et al.*, 2001a]. In a second study, measurements of sedimentary $\delta^{15}N$ and pore water-NH_4^+ $\delta^{15}N$ from the same horizons suggest that there is little or no offset between the two N pools in organic-rich, marine dominated margin sediments (<1‰), despite oxidation of a significant proportion of the organic nitrogen delivered to the seafloor and the large buildup of pore water NH_4^+ [*Prokopenko et al.*, 2006a, 2006b]. This is consistent with the observation that in rapidly accumulating sediments there is no offset between sinking flux $\delta^{15}N$ and bulk $\delta^{15}N$ of surface sediment (Figure 3a) [*Altabet et al.*, 1999; *Kienast et al.*, 2002; *Thunell et al.*, 2004]. One explanation for the lack of offset, despite clear evidence for loss of organic N, is that at high organic matter concentrations there is no preferential removal of specific organic fractions. That is, the fraction that is lost has a N isotopic composition that is equivalent to that of the residual organic matter. Alternatively, and probably less likely, the diversity of the sedimentary microbial consortium may lead to the cancellation of the various fractionating processes.

[7] In lower flux environments, where organic matter content is low and the $\delta^{15}N$ of the sinking flux is lower than that of the surface sediments, the processes must be different. The increase in bulk $\delta^{15}N$ appears to occur at/in the seafloor and is generally attributed to the preferential loss of components of the bulk organic matter with lower $\delta^{15}N$. While there is some field and experimental evidence for a decrease in $\delta^{15}N$ of the bulk organic pool during early sedimentary diagenesis, at least under anaerobic preservation conditions [*Altabet et al.*, 1991, *Libes and Deuser*, 1988, *Lehmann et al.*, 2002], the majority of existing studies to date suggests that the $\delta^{15}N$ of sedimentary organic matter increases during alteration. Evidence for the increase in $\delta^{15}N$ of organic nitrogen comes from both downcore profiles of $\delta^{15}N$ in the uppermost, oxic zone of the sediment column [*Freudenthal et al.*, 2001a] as well as incubation experiments [*Holmes et al.*, 1998]. Experimental investigation of the N isotope effect associated with deamination suggests that generally low $\delta^{15}N$ NH_4^+ is produced [*Macko and Estep*, 1984]. Leakage of low $\delta^{15}N$ NH_4^+ into pore waters could explain the increase in the bulk sedimentary $\delta^{15}N$, provided this NH_4^+ is not reincorporated into bacterial biomass or readily adsorbed onto the sediment matrix. This is plausible in oxic sedimentary environments where ammonium pools are small or negligible due to the rapid and essentially complete oxidization to NO_3^- (e.g., near sediment/water interface or beneath the oligotrophic gyres) and/or where clay/organic matter content is minimal (i.e., biogenic sediments dominate).

[8] Bulk $\delta^{15}N$ values can also be influenced by interference from terrestrial materials, NH_4^+ absorption into clay minerals, and winnowing/size fractionation [*Mollenhauer et al.*, 2005; *Kienast et al.*, 2005; *Schubert and Calvert*, 2001]. The impact of these processes is more significant in organic-poor sediments. NH_4^+ is associated with the solid



60°N
30°N
EQ
30°S
60°S
0°
90°E
180°E
90°W
Ocean Data View
Δδ15N (‰ v.air)
a.
surface δ15N (‰ v. air)
sinking δ15N (‰ v. air)
1:1
water depth (m)
0
4000
8000
b.
y= 0.0005x + 1.30
r2=0.11, p=0.0005
Δδ Nsediment-sinking (‰ v. air)
trap depth (m)
sinking depth (m)
c.
y=0.0009x - 0.94
r2=0.46, p<0.0001
y=0.0005x + 0.34
r2=0.28, p<0.0001
Δδ15Nsediment-sinking (‰ v. air)
JT
water depth (m)
d.
trap depth
Δδ15N
sinking depth
water depth
δ15N (‰ v. air)

Figure 3

phase of the sediment in fixed and exchangeable forms. Exchangeable NH_4^+ is adsorbed by ion exchange reactions on the surfaces of organics and minerals and makes up only a small proportion of the bulk sedimentary N (typically <1%) in pelagic sediments [*de Lange*, 1992; *Freudenthal et al.*, 2001a; *Müller and Suess*, 1979]. It can account for a significantly larger fraction in anoxic, organic-rich sediments, as the amount of exchangeable NH_4^+ increases with the $[NH_4^+]$ of the pore waters [*Rosenfeld*, 1979]. Fixed NH_4^+, on the other hand, is incorporated into clay mineral structures and can comprise a significant to dominant proportion of the bulk N [*Carman et al.*, 1996; *Freudenthal et al.*, 2001a; *Kienast et al.*, 2005; *Schubert and Calvert*, 2001]. In organic-poor sediments, inorganic N can make up 94% of the total N [*Schubert and Calvert*, 2001]. The fixed fraction is made up of an inherited component, that is NH_4^+ delivered with the lithogenic sediments, as well as what is adsorbed in situ. As with the exchangeable NH_4^+, the fixed fraction tends to increase with increasing pore water $[NH_4^+]$, but to a lesser degree [*Rosenfeld*, 1979]. The adsorptive potential of any given sediment depends upon its clay content and mineralogy, NH_4^+ availability, and potassium content of the sediments and interstitial waters [*Carman et al.*, 1996; *Mackin and Aller*, 1984; *Rosenfeld*, 1979]. Because fixed NH_4^+ substitutes for a cation within the lattice structure of clay minerals, it occurs at a slower rate than the ion-exchange involved in adsorption of exchangeable NH_4^+. Although this slow rate makes substitution difficult to evaluate quantitatively in the lab, it is likely relevant on geologic timescales. The consequences for bulk $\delta^{15}N$ depend upon the size of the NH_4^+ pool relative to the ON pool, the $\delta^{15}N$ of the NH_4^+ pool (s) (both what was inherited with clay minerals and produced in situ), the proportion of the NH_4^+ that is fixed relative to what may be oxidized to NO_3^-, and any fractionation associated with the adsorption process [*Karamanos and Rennie*, 1978]. In sum, alteration of the bulk N isotopic value from that of the sinking flux may occur in organic poor sediments where NH_4^+ may make up a significant portion of total sedimentary N because it may have several fates (oxidation, adsorption, utilization) with fractionation effects associated with each process.

4. Case Studies

[9] In this section we present two case studies highlighting the challenges and complexities of investigations into the cause of "diagenetic" alterations of the $\delta^{15}N$ signal, and review some of the approaches taken/progress made over the last 20 years. The first, from the South China Sea (SCS), illustrates how alteration, due to diagenesis and variable contributions of inorganic N from land, can result in misleading bulk $\delta^{15}N$ results [*Kienast et al.*, 2005]. Based on a minor offset between $\delta^{15}N$ values in the fluff layer and the uppermost sediment sample of only 0.3–1.2‰, and the absence of a correlation between increasing $\delta^{15}N$ and decreasing percent TN in the downcore records, *Kienast* [2000] argued modification of the $\delta^{15}N$ signal in the water column or during sediment burial in the SCS to be insignificant. This seemed to be in line with expectations for minimal alteration in marginal settings with high C_{org} burial rates, compared to oligotrophic sites with low sedimentation rates [*Altabet*, 1996]. The downcore record that accompanied this assertion in *Kienast* [2000] is widely cited, as it remains one of the few sedimentary $\delta^{15}N$ records from an oligotrophic site. Three lines of evidence, however, suggest that the conclusion of no alteration, and thus the significance of this record, need to be reevaluated. First, since the study in 2000, trap time series from the SCS have become available [*Gaye et al.*, 2009], which suggest that "$\delta^{15}N$ in sediments underlying trap locations were 1.5–3‰ higher than the annual average of sinking particles," comparable to other sites studied (Figure 3a). Second, analysis of fluff samples from many more of the stations within the SCS (n = 32) reveals that the average offset between fluff samples and the topmost sediment sample of 0.6‰ at four of the core sites presented in *Kienast* [2000] is a minimum estimate (Figure 4). Indeed, there is a significant correlation between increased sedimentary $\delta^{15}N$ and a higher offset between fluff and sediment surface (Figure 4). To a first approximation, this trend implies that surface sediment values above 5–5.5‰ in the SCS are caused by an isotopic enrichment during early sedimentary diagenesis of >1‰ and up to 3‰ during the transition from fluff to surface sediment. Third, *Kienast et al.* [2005] showed that 35–65% of TN in the SCS is (operationally defined) inorganic N, with an isotopic composition of 3.1–4.8‰. These authors argued that "the significant percentage of N_{inorg} and the distinct isotopic signature will… dampen any variability associated with N_{org} in the bulk $\delta^{15}N$ signal" [*Kienast et al.*, 2005, p. 5] Closer inspection of two of the records from the southern SCS (sites 17961 and 17964) reveals how a significant post-depositional alteration of the organic nitrogen could have been effectively masked in the sedimentary record: A substantial loss of organic nitrogen (ca. 20–25%) in the top 1–3 m, equivalent to the last 10 ka, of these two cores is paralleled by an increase in $\delta^{15}N$ of organic N by up to 2‰, which results in a near constant $\delta^{15}N$ of total N, similar to *Freudenthal et al.*'s [2001a] results. Finally, physical processing of sediment may also have contributed to spatial differences in downcore records in the South China Sea. Size-related differences in

Figure 3. Site locations of the global sediment trap compilation with color coding to highlight the geographic distribution of $\Delta\delta^{15}N$ values (sediment-sinking $\delta^{15}N$) (map panel). Surface versus sinking sedimentary $\delta^{15}N$ values with color coding to denote water depth differences for each location (a) The *Gaye et al.* [2009] South China Sea sediment trap data are outlined in black. Surface sedimentary versus nitrate $\delta^{15}N$ values (black diamonds) and surface versus sinking values from several margin locations fall along the 1-to-1 line (solid black line). Reduced major axis linear regression for all sites (dotted line) as well as a subset of sites made up of those with depths >1000 m (dashed line), suggest a line with a slope of 1.2 and an intercept of ∼1‰ (1.1–1.4‰). (c) $\Delta\delta^{15}N$ (sediment-sinking $\delta^{15}N$) shows a strong relationship to water depth (r^2 = 0.46, Japan Trench samples highlighted in gray oval marked JT are excluded from this correlation) but (b) not to sinking depth (r^2 = 0.11), suggesting (d) that the alteration takes place at the seafloor. See Table 1 for full details on data, including location, trap depths, and references.

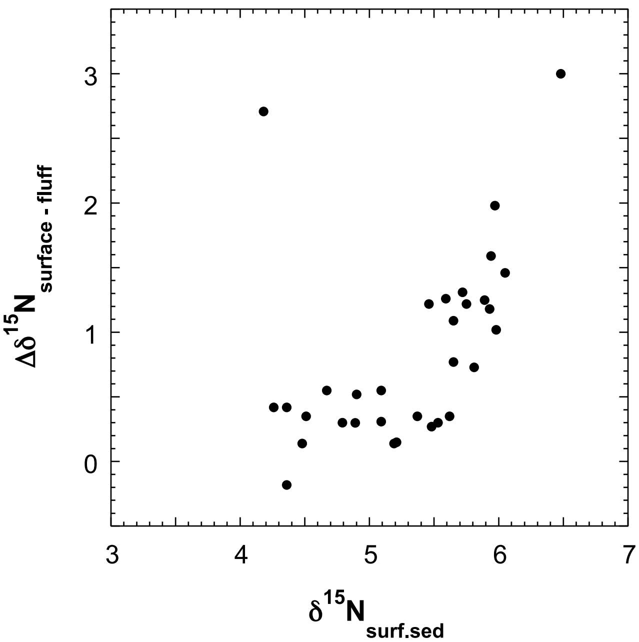


Figure 4. Crossplot of $\Delta\delta^{15}$N (surface δ^{15}N-fluff δ^{15}N) and surface sediment δ^{15}N values from the South China Sea showing the variability in preservation across the basin. The first order increase in sedimentary δ^{15}N values appears to be due to isotopic alteration (M. Kienast, unpublished data, 2006).

the δ^{15}N of particles exist and sediments that witness either winnowing or focusing will record an altered bulk δ^{15}N record. This is most likely to occur where there are heterogeneous mixtures of organic matter, such as on the continental margins and in marginal seas [*Kienast et al.*, 2005]. The end result is that the sediments in the South China Sea experience variable degrees of alteration and the *Kienast* [2000] records are not likely faithfully recording water column variations.

[10] The next case study involves the well-studied sediments of the Mediterranean Sea. The Mediterranean sediments present striking evidence for variability in their preservation of sedimentary organic matter (e.g., alternating marl and sapropel layers). Accompanying this variability are large systematic changes in the bulk N isotopic composition of the sediments with higher δ^{15}N values in the low TOC marls and lower δ^{15}N values in the organic rich sapropels. Some interpretations of the isotope records have inferred significant overprinting of the primary δ^{15}N values by alteration [*Möbius et al.*, 2010; *Sachs and Repeta*, 1999], while others have interpreted the records to reflect primary signatures [*Calvert et al.*, 1992; *Higgins et al.*, 2010].

[11] The evidence for isotopic alteration comes from observed increases in bulk δ^{15}N associated with post depositional oxidation of sapropelic organic carbon [*Moodley et al.*, 2005] and from the comparison of bulk δ^{15}N values to the amino acid (AA) Degradation Index (DI) [*Dauwe et al.*, 1999; *Möbius et al.*, 2010]. DI is the result of statistical evaluation of systematic compositional changes of the 14 most common protein AAs during remineralization [*Dauwe et al.*, 1999]. DI scores sediments with a value of 1 for fresh organic matter toward low values (<−0.5) with intensive organic matter degradation. Sediments from the Mediterranean, both surface sediments from a spatially distributed survey and downcore profiles, show a linear relationship between DI and bulk δ^{15}N values [*Möbius et al.*, 2010], suggesting that changes in δ^{15}N may be linked to organic matter quality. *Möbius et al.* [2010] suggested that the low δ^{15}N values that occur in the sapropel intervals are the result of enhanced preservation, and that diagenetic isotopic alteration raised the δ^{15}N values of the marl sedimentary organic matter. However, the correlation between DI and δ^{15}N does not, on its own, indicate causality.

[12] This interpretation is at odds with results comparing the δ^{15}N of chlorins, chlorophyll *a* degradation products, and bulk δ^{15}N from Mediterranean sedimentary sequences containing both sapropel and marl horizons. Throughout the profiles, δ^{15}N values from chlorins are consistently offset from bulk values by 4–5‰, implying that the bulk δ^{15}N values recorded in the organic poor marl sequences are not heavily overprinted by alteration, and that the low δ^{15}N values during sapropel formation represent significantly different N biogeochemical conditions in the overlying surface waters [*Higgins et al.*, 2010]. These data call into question the basic assumption that δ^{15}N data from organic-poor sediments should be discounted categorically and suggest that, at least in this case, the degradation index reflects good preservation at times when the water column above produced low δ^{15}N organic matter. This would be consistent with abundant N_2 fixation and rapid accumulation of organic matter and/or O_2-poor bottom waters during sapropel formation, for example.

5. Sediment Trap and Surface Sediment Compilation

[13] In an effort to evaluate the degree of isotopic alteration from a global data set and to put some of the individual sediment trap studies discussed into a larger context, we compiled published, co-located, sediment trap-sinking particle and surface sediment δ^{15}N values (Figure 3 and Table 1). The term co-located describes trap and surface sediment sampling stations that are nominally within the same location. In most cases, both data types were presented together, but in the case that we assigned surface sediment values from separate studies to available trap data, we defined co-location as being within 1° of latitude/longitude of one another and most are within 0.5°. The sites, not surprisingly, are largely located on the margins and in the Northern Hemisphere (see map in Figure 3). The compilation includes sites at a range of water depths (180–9200 m), primary production (based on Chl a 0.09–5 mg/m^3) and sedimentation rates (2–>200 cm/kyr), as well as distances from land. Overall, the compilation reveals a fairly consistent relationship between the sinking flux and the sedimentary δ^{15}N values, despite the fairly large range of $\Delta\delta^{15}$N values of −2 to 6.5‰ ($\Delta\delta^{15}$N = surface sediment - sinking δ^{15}N). The mean is 2.3 ± 1.8‰ (1σ) (Figure 3a). Only a handful of surface sediment samples fall along the 1:1 line in the crossplot of sediment versus sinking δ^{15}N (Figure 3a) and they are from highly productive continental margin locations. Surface sediment δ^{15}N versus subeuphotic zone $\delta^{15}N_{nitrate}$ from several margin locations also fall along the

Table 1. Tabulated Data From Sediment Trap and Surface Sediment $\delta^{15}N$ Comparison With References

Region	Latitude	Longitude	Bottom Depth (m)	Trap Depth (m)	Flux Weighted $\delta^{15}N$ (‰ v. air)	Surface $\delta^{15}N$ (‰ v. air)	$\Delta\delta^{15}N$ (‰ v. air)	Chl a (mg/L)	Sed Rates (cm/kyr)	BW [O2] (mg/L)	Source[a]
Black Sea	42.35	37.57	2055	1300	2.1	2	−0.1	0.80	300.00	0.00	M. Altabet, unpublished data, 1991; *Fry et al.* [1991] (sediments)
Black Sea	43.00	34.01	2220	477	1.5	2	0.5	0.68	300.00	0.00	M. Altabet, unpublished data, 1991; *Fry et al.* [1991] (sediments)
Mediterranean Sea	34.43	26.1792	3750	3720	2.2	3.5	1.3	0.11	6.00	4.15	*Möbius et al.*, 2010; J. Möbius (personal communication, 2012) (SR)
Mediterranean Sea	34.44	26.19	3600	2560	1.2	3.5	2.3	0.11	6.00	4.00	*Möbius et al.*, 2010; J. Möbius (personal communication, 2012) (SR)
Mediterranean Sea	34.44	26.193	3620	1508	0.9	3.5	2.6	0.11	6.00	4.00	*Möbius et al.*, 2010; J. Möbius (personal communication, 2012) (SR)
Mediterranean Sea	34.44	26.193	3620	2689	0.8	3.5	2.7	0.11	6.00	4.00	*Möbius et al.*, 2010; J. Möbius (personal communication, 2012) (SR)
Canary Island region	28.72	346.85	996	700	3.1	6.5	3.4	0.29	9.1	3.37	*Freudenthal et al.* [2001b]
Canary Island region	29.13	344.55	3610	500	4.2	6.7	2.5	0.13	29.13	5.48	*Freudenthal et al.* [2001b]
Canary Island region	29.13	344.55	3610	3000	2.0	6.7	4.7	0.13	29.13	5.48	*Freudenthal et al.* [2001b]
Canary Island region	29.77	342.05	4327	900	5.5	7.1	1.6	0.11	1.5	5.47	*Freudenthal et al.* [2001b]
Canary Island region	29.77	342.05	4327	3800	2.2	7.1	4.9	0.11	1.5	5.47	*Freudenthal et al.* [2001b]
Cariaco Basin	10.08	295.33	1400	225	4.2	3.4	−0.8	0.63	30.00	0.00	*Thunell et al.* [2004]
Cariaco Basin	10.08	295.33	1400	1200	3.7	3.4	−0.3	0.63	30.00	0.00	*Thunell et al.* [2004]
Framvaren Fjord, Norway	58.13	6.75	180	15	4.18	2.14	−2.0		21.58	0.00	*Velinsky and Fogel* [1999]; *Næs et al.* [1988]
Framvaren Fjord, Norway	58.13	6.75	180	40	1.89	2.14	0.3		21.58	0.00	*Velinsky and Fogel* [1999]; *Næs et al.* [1988]
Framvaren Fjord, Norway	58.13	6.75	180	80	2.6	2.14	−0.5		21.58	0.00	*Velinsky and Fogel* [1999]; *Næs et al.* [1988]
Framvaren Fjord, Norway	58.13	6.75	180	120	2.33	2.14	−0.2		21.58	0.00	*Velinsky and Fogel* [1999]; *Næs et al.* [1988]
Framvaren Fjord, Norway	58.13	6.75	180	160	2.16	2.14	0.0		21.58	0.00	*Velinsky and Fogel* [1999]; *Næs et al.* [1988]
Framvaren Fjord, Norway	58.13	6.75	180	175	2.23	2.14	−0.1		21.58	0.00	*Velinsky and Fogel* [1999]; *Næs et al.* [1988]
Gotland Sea (Baltic)	57.30	20.24	240	140	3.7	3.4	−0.3		108.89		*Struck et al.* [2004]; *Kotilainen* [2006] (SR)
Eq. Guinea Basin	−0.08	349.23	4141	1097	5.2	8.2	3.0	0.34	3.71	5.71	*Lavik* [2001]; *Sarnthein* [2003a, 2003b] (SR)
N Guinea Basin	1.78	348.75	4399	953	4.3	7.6	3.3	0.19	3.01	5.74	*Lavik* [2001]; *Bickert and Wefer* [1996] (SR)
N Guinea Basin	1.79	348.86	4522	859	4.6	7.6	3.0	0.19	3.01	5.74	*Lavik* [2001]; *Bickert and Wefer* [1996] (SR)
N Guinea Basin	1.79	348.87	4481	853	4.2	7.6	3.4	0.19	3.01	5.72	*Lavik* [2001]; *Bickert and Wefer* [1996] (SR)
N Guinea Basin	3.17	348.84	4524	984	3.4	6.1	2.7	0.17	2.20	5.80	*Lavik* [2001]; *Jahns et al.* [1998] (SR)
S Guinea Basin	−5.79	350.58	3450	598	6.1	9.6	3.5	0.19	5.17	5.53	*Lavik* [2001]; *Meinecke* [1992] (SR)
S Guinea Basin	−4.19	349.74	3490	948	5.4	9.4	4.0	0.26	3.54	5.53	*Lavik* [2001]; *Meinecke* [1992] (SR)
S Guinea Basin	−2.19	349.91	3906	1068	5.7	8.7	3.0	0.30	5.49	5.62	*Lavik* [2001]; *Sarnthein* [2003a, 2003b] (SR)
South Atlantic	−50.13	5.83	3750	614	2.8	5.2	2.4	0.22	10.83	4.97	*Holmes et al.* [2003]; *Frank and Mackensen* [2002] (SR)
South Atlantic	−50.13	5.83	3750	3196	7.2	5.2	−2.0	0.22	10.83	4.97	*Holmes et al.* [2003]; *Frank and Mackensen* [2002] (SR)
Walvis Ridge	−20.05	9.15	2196	599	5.5	7.1	1.6	0.62	3.1	5.10	*Holmes et al.* [2002]; *Bickert and Mackensen* [2003] (SR)
Walvis Ridge	−20.05	9.15	2196	1648	6.9	7.1	0.2	0.62	3.1	5.10	*Holmes et al.* [2002]; *Bickert and Mackensen* [2003] (SR)
Indian Ocean	13.1	84.33	3271	2250	4.3	7.0	2.7	0.17		2.46	*Gaye-Haake et al.* [2005]
Indian Ocean	13.1	84.33	3271	900	4.3	7.0	2.7	0.17		3.46	*Gaye-Haake et al.* [2005]
Indian Ocean	5.0	86.92	4020	3000	5.1	9.6	4.4	0.24		3.92	*Gaye-Haake et al.* [2005]
Indian Ocean	6.0	86.92	4020	900	5.5	9.6	4.1	0.28		3.96	*Gaye-Haake et al.* [2005]
Indian Ocean	15.5	68.67	3770	2800	5.8	9.8	4.0	0.26	7.75	3.20	*Gaye-Haake et al.* [2005]; *Sirocko et al.* [2000]
Indian Ocean	15.5	68.67	3770	1400	6.2	9.8	3.6	0.26	7.75	3.20	*Gaye-Haake et al.* [2005]; *Sirocko et al.* [2000]
Indian Ocean	13.2	67.13	4075	3090	6.4	10.5	4.1	0.34		3.36	*Gaye-Haake et al.* [2005]
Indian Ocean	13.2	67.13	4075	1090	6.4	10.5	4.1	0.34		3.36	*Gaye-Haake et al.* [2005]
Indian Ocean	16.3	60.50	4020	2080	7.1	10.0	3.0	0.38	4.13	3.46	*Gaye-Haake et al.* [2005]; *Sirocko et al.* [2000]
Indian Ocean	16.3	60.50	4020	1080	7.3	10.0	2.7	0.38	4.13	3.46	*Gaye-Haake et al.* [2005]; *Sirocko et al.* [2000]
Indian Ocean	24.8	65.82	1100	590	7.7	8.2	0.5			0.28	*Gaye-Haake et al.* [2005]
Indian Ocean	15.5	88.83	2700	1900	3.6	3.3	−0.3	0.17		3.14	*Gaye-Haake et al.* [2005]
Indian Ocean	16.5	88.83	2700	1000	3.6	3.3	−0.3	0.17		3.14	*Gaye-Haake et al.* [2005]
Indian Ocean	3.5	77.68	3770	2800	5.8	7.5	1.7	0.19		3.77	*Gaye-Haake et al.* [2005]
Indian Ocean	14.5	64.77	3900	730	7.8	11.4	3.6	0.29	2.38	3.30	*Gaye-Haake et al.* [2005]; *Sirocko et al.* [2000]

Table 1. (continued)

Region	Latitude	Longitude	Bottom Depth (m)	Trap Depth (m)	Flux Weighted $\delta^{15}N$ (‰ v. air)	Surface $\delta^{15}N$ (‰ v. air)	$\Delta\delta^{15}N$ (‰ v. air)	Chl a (mg/L)	Sed Rates (cm/kyr)	BW [O2] (mg/L)	Source[a]
Indian Ocean	14.5	64.77	3900	3020	7.2	11.4	4.2	0.29	2.38	3.30	*Gaye-Haake et al.* [2005]; *Sirocko et al.* [2000]
South China Sea	9.15	109.72	1730	600	3.3	4.5	1.2	0.12	2.15	2.15	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	9.15	109.72	1730	1200	4.0	4.5	0.5	0.12	2.15	2.15	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	11.40	111.28	2300	900	4.5	5.9	1.4	0.11	2.40	2.40	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	11.40	111.28	2300	1700	3.4	5.9	2.5	0.11	2.40	2.40	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	14.62	115.12	4300	1200	2.9	4.9	2.0	0.10	2.60	2.60	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	14.62	115.12	4300	2000	2.7	4.9	2.2	0.10	2.60	2.60	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	14.62	115.12	4300	3750	3.1	4.9	1.8	0.10	2.60	2.60	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	17.07	117.18	4038	1465	3.3	5.6	2.3	0.11	2.58	2.58	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	17.07	117.18	4038	3500	2.7	5.6	2.9	0.11	2.58	2.58	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	17.27	119.52	2826	1225	3.6	4.2	0.6	0.11	2.40	2.50	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	17.27	119.52	2628	1765	2.7	4.2	1.5	0.11	2.40	2.40	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	17.27	119.52	2628	2287	2.8	4.2	1.4	0.11	2.40	2.40	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	18.47	116.02	3766	1000	3.8	5.4	1.6	0.13	2.58	2.58	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
South China Sea	18.47	116.02	3677	3350	3.2	5.4	2.2	0.13	2.58	2.58	*Gaye et al.* [2009]; *Wang et al.* [1995] (SR)
Equatorial Pacific	−11.97	224.97	4294	1292	13.64	15.5	1.9	0.11	3.93	3.93	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	−11.97	224.97	4294	3594	12.63	15.5	2.9	0.11	3.93	3.93	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	−4.95	220.27	4198	2099	3.92	7.7	3.8	0.13	3.84	3.84	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	−1.95	220.27	4293	3593	2.80	7	4.2	0.33	3.87	3.87	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	0.07	220.18	4385	880	4.55	9.4	4.8	0.36	3.81	3.81	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	0.07	220.18	4385	3618	4.85	9.4	4.6	0.36	3.81	3.81	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	0.07	220.18	4385	2284	4.78	9.4	4.6	0.36	3.81	3.81	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	2.00	219.87	4397	2203	6.50	12.3	5.8	0.23	3.77	3.77	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	5.02	220.22	4493	1200	8.42	11.3	2.9	0.15	3.77	3.78	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	5.02	220.22	4493	2200	8.46	11.3	2.8	0.15	3.77	3.78	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	5.02	220.22	4493	3800	8.07	11.3	3.2	0.15	3.77	3.78	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	9.00	220.02	5100	2150	7.35	13.9	6.5	0.11	3.99	3.99	*Altabet* [2001]; *Murray et al.* [2000] (SR)
Equatorial Pacific	9.00	220.02	5100	4400	7.91	13.9	6.0	0.11	3.99	3.99	*Altabet* [2001]; *Murray et al.* [2000] (SR)
California Current; Carmen B	26.03	249.08	848	665	9	10.4	1.4	0.80	260.00	0.22	*Altabet et al.* [1999]; *Thunell et al.* [1994]
California Current; Guaymas B	27.88	248.33	665	485	9.4	11.1	1.7	1.03	118.00	0.00	*Altabet et al.* [1999]; *Thunell et al.* [1994]
California Current; San Pedro B	33.55	241.50	850	500	8	8.5	0.5	1.10	100.00		*Altabet et al.* [1999]
California Current; Monterey Bay	36.75	237.95	950	450	7.8	7.1	−0.7		200.00	0.57	*Altabet et al.* [1999]; *Lewis et al.* [2002]
California Current; Soledad B	25.2	292.7	450	330	10.2	10.6	0.4	0.35	108.00	0.32	*Silverberg et al.* [2004]; R. Thunell (personal communication, 2011)
California Current	42.192	−127.578	3133	500	8.75	8.03	−0.7	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	42.192	−127.578	3133	1500	5.43	8.03	2.6	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	42.192	−127.578	3133	1750	6.78	8.03	1.3	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	42.192	−127.578	3133	2330	6.25	8.03	1.8	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	42.192	−127.578	3133	1000	8.24	8.03	−0.2	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	42.192	−127.578	3133	1500	8.01	8.03	0.0	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	42.192	−127.578	3133	1750	8.31	8.03	−0.3	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	42.192	−127.578	3133	2350	7.72	8.03	0.3	0.31	9.40	2.51	S. Kienast (unpublished data, 2002); *Kienast et al.* [2002] (SR)
California Current	41.564	−131.99	3700	3218	8.26	11.1	2.8	0.20	1.30	2.75	S. Kienast (unpublished data, 2002); *Lyle et al.* [1992] (SR)
California Current	41.564	−131.99	3700	1500	9.47	11.1	1.6	0.20	1.30	2.75	S. Kienast (unpublished data, 2002); *Lyle et al.* [1992] (SR)
California Current	41.564	−131.99	3700	1750	7.4	11.1	3.7	0.20	1.30	2.75	S. Kienast (unpublished data, 2002); *Lyle et al.* [1992] (SR)
California Current	42.084	−125.761	2700	1500	7.93	6.46	−1.5	0.39	27.00	2.10	*Kienast et al.* [2002]
California Current	42.049	−125.762	2700	1500	7.25	6.46	−0.8	0.38	27.00	2.10	*Kienast et al.* [2002]
California Current	42.108	−125.832	2700	1750	5.93	6.46	0.5	0.39	27.00	2.10	*Kienast et al.* [2002]

Table 1. (continued)

Region	Latitude	Longitude	Bottom Depth (m)	Trap Depth (m)	Flux Weighted $\delta^{15}N$ (‰ v. air)	Surface $\delta^{15}N$ (‰ v. air)	$\Delta\delta^{15}N$ (‰ v. air)	Chl a (mg/L)	Sed Rates (cm/kyr)	BW [O2] (mg/L)	Source[a]
Japan Sea	42.73	138.28	3665	1090	4.2	6.8	2.6	0.49	4.52	5.19	*Nakanishi and Minagawa* [2003]; *Crusius et al.* [1999]
Japan Sea	42.73	138.28	3665	1600	5.1	6.8	1.7	0.49	4.52	5.19	*Nakanishi and Minagawa* [2003]; *Crusius et al.* [1999]
Japan Sea	42.73	138.28	3665	3110	4.0	6.8	2.8	0.49	4.52	5.19	*Nakanishi and Minagawa* [2003]; *Crusius et al.* [1999]
Japan Trench	34.17	142.0	9200	4789	2.9	5.8	2.9	0.22	23.00		*Nakatsuka et al.* [1997]; *Boggs* [1984]
Japan Trench	34.17	142.0	9200	8789	3.5	5.8	2.3	0.22	23.00		*Nakatsuka et al.* [1997]; *Boggs* [1984]
Japan Trench	34.17	142.0	9200	1674	3.3	5.8	2.5	0.22	23.00		*Nakatsuka et al.* [1997]; *Boggs* [1984]
Japan Trench	34.17	142.0	9200	4180	2.0	5.8	3.8	0.22	23.00		*Nakatsuka et al.* [1997]; *Boggs* [1984]
Japan Trench	34.17	142.0	9200	5687	3.0	5.8	2.8	0.22	23.00		*Nakatsuka et al.* [1997]; *Boggs* [1984]
Japan Trench	34.17	142.0	9200	8688	3.3	5.8	2.5	0.22	23.00		*Nakatsuka et al.* [1997]; *Boggs* [1984]

[a]"SR" following a citation indicates that citation is the source of the data in the Sedimentation Rate column.

1:1 line (Figure 3a). The remaining data tend to lie above the 1:1 line and these data are broadly distributed geographically, without an apparent pattern of variation. A reduced major axis linear regression (which accounts for error in both the x and y data sets) yields a slope close to 1 (1.2) and a y-intercept of 1.1‰. If sites with depths <1000 m are excluded (this includes all of the sites on the 1:1 line), the slope is the same, 1.2, and the intercept is 1.4 ‰. In both cases, the relationship is significant, with a p value <0.001 at 95% confidence limit. This suggests that the offset between bulk and sinking $\delta^{15}N_{PN}$ values is relatively consistent across a range of depositional environments but that there is an increase in the offset with increasing water depth (Figures 3a). The $\Delta\delta^{15}N$ values increase with water depth by 0.5‰/km using the entire data set and by ~1‰/km if the samples from the Japan trench, which fall off of the trend, are excluded (Figure 3c). This is similar to the increase in $\delta^{15}N$ values observed with water depth for a larger, surface sediment database (0.4‰/km) (Galbraith et al., submitted manuscript, 2012). No such linear trend is observed if we compare $\Delta\delta^{15}N$ to sinking depth (water depth - trap depth) (Figure 3b). Nor is any systematic change observed when one examines data from locations with trap data from multiple depths; in some cases it is unchanged, in others it decreases and in still others it increases. This suggests that while there is isotopic alteration in the water column, the systematic increase that is observed is likely a product of early burial diagenesis at the seafloor [*Altabet and Francois*, 1994], rather than in the water column between the trap and the seafloor. This is consistent with the observations from the South China Sea fluff-sediment comparison (see above). The variability observed when comparing $\delta^{15}N$ values between traps also suggests that the controls in the water column are more complex.

[14] The discrepancy between the $\delta^{15}N$ values in trap material and sediments could have several causes. It may simply be due to differences in the sources of organic matter to traps and to the seafloor. This is caused by differences in the timescale of deposition between traps and sediments, where short-term perturbations, either natural such as blooms or dust storms or anthropogenic including plumes and agricultural runoff, have the potential to heavily influence what is captured in traps but may not appear in the seafloor signal. It can also be due to "swimmers" in the traps or lateral transport at the seafloor. Transport at the seafloor has the potential to fractionate the sediments by size, which in turn may alter the isotopic signal. Transport-related processes in particular may be important in this data set, given its bias toward the margins, where organic matter may be moved downslope beneath surface waters with a strong gradient in $\delta^{15}N_{nitrate}$ values [e.g., *Freudenthal et al.*, 2001a] and toward open ocean sites located in regions with active sediment focusing (e.g., Equatorial Pacific, Southern Ocean) [*Francois et al.*, 2004; *Mollenhauer et al.*, 2005]. However, we compiled as large a data set as possible in order to highlight first order trends in the data and to avoid bias by site specific effects, and despite the broad scatter in the data, the observed trends are significant. We attribute the majority of the isotopic change between traps and surface sediments to early diagenesis of the isotopic signal.

[15] Preservation of organic matter, while not perfectly understood, is likely a function of the length of time that

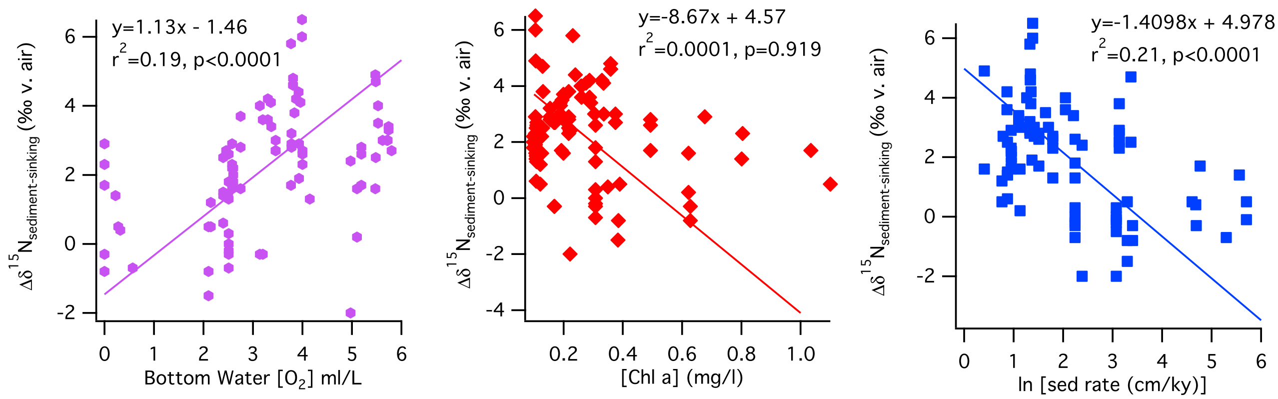


Figure 5. Crossplots of (left) $\Delta\delta^{15}N$ versus bottom water [O_2], (middle) Chl-a concentration, and (right) sedimentation rate for the sites in the sediment trap database. Sites close to the margins were excluded from the Chl-a comparison because of the large error associated with nearshore-site Chl-a estimates from satellites. In all cases but Chl-a, the correlations are statistically significant at a 95% confidence interval.

organic matter is exposed to molecular O_2 in pore waters [*Hartnett et al.*, 1998], which is a function of bottom water oxygen concentrations and total sediment and organic carbon accumulation rates. For comparison, we have plotted our $\Delta\delta^{15}N$ values against first order estimates of these parameters (Figure 5). In each case, values are estimated from gridded data sets; bottom water oxygen estimates are from WOA09 [*Garcia et al.*, 2010] and chlorophyll-*a* concentrations (Global SeaWIFS chlorophyll mean Sept. 1997–Dec. 2004). Nearshore sites were omitted from the chlorophyll-*a* comparison because the data are unreliable. Sedimentation rate estimates are based on published age models (see Table 1 for references). Oxygen concentrations, sedimentation rates, and chlorophyll-*a* concentrations are not completely independent from one another and all are related to $\Delta\delta^{15}N$ for the trap sites. Oxygen is linearly related while the relation to sedimentation rates is log linear. In both cases, the correlations are statistically significant at a 95% confidence interval. The linear correlation between $\Delta\delta^{15}N$ and Chl-*a* is weaker and is not statistically significant, although this may be related to the omission of the highly productive margin sites from this analysis (Figure 5). In addition, all are linearly related to water depth. The water depth versus $\Delta\delta^{15}N$ comparison gives the best fit, with an r^2 value of 0.46, suggesting that the degree of sedimentary $\Delta\delta^{15}N$ alteration is a function of oxygen exposure time, consistent with the suggestion of *Möbius et al.* [2010, 2011]. Water depth is a robust proxy for exposure time because early burial, or the period in which sediments are exposed to oxygen-rich bottom waters and active microbial processes, is generally prolonged in the deep sea due to slower sediment accumulation and microbial metabolic rates [*D'Hondt et al.*, 2009; *Roy et al.*, 2012]. However, these are not strictly depth related processes, but are also a function of distance from land, sediment type, productivity in the overlying surface water and the chemistry of the water bathing the seafloor at a given site [*Alkhatib et al.*, 2012]. The Japan Trench samples serve as a good example of an exception to the water depth generalization, in that they do not fall along the trend of ~1‰ of alteration per km of water depth, but rather more like 0.5‰ [*Nakatsuka et al.*, 1997]. The lower degree of alteration for their given depth (9200 m) is likely due to the sites proximity to land and relatively rapid sediment accumulation rates when compared to the deep gyres.

[16] If we take depth as a robust proxy for the controls on alteration and consider significant changes in burial depth at a given site unlikely on orbital timescales or without major changes in the site location (e.g., tectonic transport away from a spreading ridge), then significant temporal changes in the degree of alteration at a given site are unlikely as well. Furthermore, regionally coherent downcore records of $\delta^{15}N$ changes, across a range of sedimentation rates and sediment compositions, from the continental margin to the central/western Equatorial Pacific argue against significant changes in preservation as a function of realistic changes in accumulation rates at a single site [*Galbraith et al.*, 2008a; *Kao et al.*, 2008; *Martinez et al.*, 2006]. The data suggest that spatial comparisons using absolute $\delta^{15}N$ values should consider the potential impact of alteration at deeper/more distal sites. However, when comparing the average offset of 2.3‰ to the total range of surface sedimentary $\delta^{15}N$ values compiled in the NICOPP database of 15‰, this seems minor (Galbraith et al., submitted manuscript, 2012). Finally, the ~2.3‰ average offset gleaned from the sediment trap compilation is, interestingly, approximately equal to the 2.5‰ mean offset between predicted surface sediment $\delta^{15}N$ values derived from simulations with a global ocean biogeochemical model incorporating nitrogen isotopes [*Somes et al.*, 2010] and the global compilation of observed surface sediment $\delta^{15}N$ values (Galbraith et al., submitted manuscript, 2012).

6. Avoiding Alteration in Paleo Reconstructions

[17] In order to avoid alteration, work with sedimentary N isotopes proceeded with a two-pronged approach, using bulk $\delta^{15}N$ measurements on the margins where fidelity was fairly certain and developing new N archives that were less prone to alteration for the study of relatively slowly accumulating sediments, such as the Southern Ocean and the oligotrophic regions [*Altabet and Curry*, 1989; *Higgins et al.*, 2009; *Ren et al.*, 2009; *Robinson et al.*, 2004; *Sachs and Repeta*, 1999; *Shemesh et al.*, 1993]. These include microfossil bound N isotope proxies, developed to tap into a mineral bound

organic fraction, and compound specific measurements of chlorophyll and chlorophyll degradation products such as those discussed in the Mediterranean Sea example. Both proxy types assume that the δ^{15}N value being measured is 1) a reflection of water column variability, rather than species- or molecule-specific biases, and 2) protected from alteration during sinking and burial.

[18] These alternative δ^{15}N proxies all have the potential to allow a fresh look at the nitrogen cycle by opening up the field of reconstructions to include the margins and open ocean pelagic settings where preservation of bulk organic nitrogen is questionable or the organic matter content is so low that it precludes a robust measurement by EA-IRMS. Both culture work and downcore reconstructions that compare bulk δ^{15}N values to the δ^{15}N values of the novel N isotope proxies themselves allow for added investigations into the integrity of the two signals.

[19] The predominance of sedimentary δ^{15}N records from the margins and a potentially unjustified skepticism of downcore records from low productivity regions have impeded our ability to study the global marine nitrogen cycle in the past. Bulk analyses are inexpensive and rapid and appear more robust than previously perceived. Testing regional patterns of alteration by comparing the δ^{15}N of nitrate, sinking particles and surface sediments is useful but not always feasible. Moreover, it does not exclude the possibility of differences in preservation in the past. We suggest that the routine adoption of simple evaluation tools can help detect potential problems with bulk δ^{15}N in sediment cores. For example, a nonzero y-intercept in a plot of total organic carbon versus total nitrogen is indicative of the presence of inorganic nitrogen, likely NH_4^+ fixed in clays [*Calvert*, 2004; *Kienast et al.*, 2005; *Schubert and Calvert*, 2001] or inputs of terrestrial organics, with their distinct C/N. Given significant deviations from a 1:1 line, the inorganic N pool can be measured and the organic N δ^{15}N calculated. This correction gives a value for ON, but it does not avoid variable preservation of the ON.

7. Summary and Outlook

[20] Over the last several decades the use of sedimentary δ^{15}N as a tool to study the marine nitrogen cycle has expanded. We have an excellent picture of variability in rapidly accumulating sediments from the last ~50–100 kyr. However, data from the oligotrophic ocean are few, due to concern regarding alteration. Studies that have sought to unravel the exact mechanisms responsible for isotopic shifts in the bulk sedimentary organic N pool have been largely inconclusive due to the difficulty of discerning slow sediment alteration directly. However, empirical data, including the sediment trap results compared here, suggest that even in slowly accumulating regions of the ocean, bulk sedimentary δ^{15}N records will primarily reflect changes in the δ^{15}N of exported N in most cases, rather than differential alteration. This is consistent with recent comparisons between chlorin/porphyrin δ^{15}N and bulk sedimentary δ^{15}N profiles that indicate that in sediments of poor organic matter preservation, such as the Mediterranean marls, or those millions of years old, like the Cretaceous black shales [*Higgins et al.*, 2010, 2012], the bulk δ^{15}N presents a robust picture of biogeochemical cycling of N.

[21] The future of N isotope studies is likely to lead to an improved understanding of the proxy itself as well as the evolution of the long-term N cycle and its importance for modulating climatic and ecological changes. At present, published N isotope records largely span the last 100 kyr with only a few on the order of 3–5 Ma and older (e.g., Ocean Anoxic Events/the Archean [*Garvin et al.*, 2009; *Higgins et al.*, 2012; *Jenkyns et al.*, 2007; *Junium and Arther*, 2007]). While there is value in examining relative changes in sedimentary δ^{15}N across an ancient interval, it is difficult to place the data in context without a continuous, robust record of δ^{15}N in the ocean. This is essential for distinguishing between global marine nitrogen cycle processes and regional phenomena. Examining N cycle processes in ancient sediments will also require further evaluation of isotopic alteration on extremely long timescales.

[22] **Acknowledgments.** This contribution was made possible by the efforts of many people who shared their time, data and expertise, and through discussions at the NICOPP working group meetings. The authors are grateful to three anonymous reviewers and the Editor, Rainer Zahn, for thorough and constructive reviews of earlier versions of the manuscript. NICOPP (Nitrogen Cycle in the Ocean, Past and Present) is a joint working group of PAGES and IMAGES.

References

Alkhatib, M., C. J. Schubert, P. del Giorgio, Y. Gelina, and M. F. Lehmann (2012), Organic matter reactivity indicators in sediments of St. Lawrence Estuary, *Estuarine Coastal Shelf Sci.*, *102–103*, 36–47, doi:10.1016/j.ecss.2012.03.002.

Altabet, M. A. (1996), Nitrogen and Carbon Isotopic Tracers of the Source and Transformation of Particles in the Deep Sea, in *Particle Flux in the Ocean*, edited by V. Ittekkot et al., pp. 155–171, John Wiley, New York.

Altabet, M. A. (2001), Nitrogen isotopic evidence for micronutrient control of fractional NO_3^- utilization in the equatorial Pacific, *Limnol. Oceanogr.*, *46*, 368–380, doi:10.4319/lo.2001.46.2.0368.

Altabet, M. A., and W. B. Curry (1989), Testing models of past ocean chemistry using foraminifera ^{15}N/^{14}N, *Global Biogeochem. Cycles*, *3*(2), 107–119, doi:10.1029/GB003i002p00107.

Altabet, M. A., and R. Francois (1994), Sedimentary nitrogen isotopic ratio as a recorder for surface nitrate utilization, *Global Biogeochem. Cycles*, *8*(1), 103–116, doi:10.1029/93GB03396.

Altabet, M., and R. Francois (2001), Nitrogen isotope biogeochemistry of the Antarctic Polar Frontal Zone at 170°W, *Deep Sea Res., Part II*, *48*, 4247–4273, doi:10.1016/S0967-0645(01)00088-1.

Altabet, M. A., W. G. Deuser, S. Honjo, and C. Stienen (1991), Seasonal and depth-related changes in the source of sinking particles in the North Atlantic, *Nature*, *354*, 136–139, doi:10.1038/354136a0.

Altabet, M. A., C. Pilskaln, R. Thunell, C. Pride, D. Sigman, F. Chavez, and R. Francois (1999), The nitrogen isotope biogeochemistry of sinking particles from the margin of the Eastern North Pacific, *Deep Sea Res., Part I*, *46*, 655–679, doi:10.1016/S0967-0637(98)00084-3.

Bickert, T., and A. Mackensen (2003), Last Glacial to Holocene changes in South Atlantic deep water circulation, in *The South Atlantic in the Late Quaternary: Reconstruction of Material Budgets and Current Systems*, edited by G. Wefer et al., pp. 671–695, Springer, New York.

Bickert, T., and G. Wefer (1996), Late Quaternary deep water circulation in the South Atlantic: Reconstruction from carbonate dissolution and benthic stable isotopes, in *The South Atlantic: Present and Past Circulation*, edited by G. Wefer et al., pp. 599–620, Springer, Berlin.

Boggs, S. (1984), Quaternary sedimentation in the Japan arc-trench system, *Geol. Soc. Am. Bull.*, *95*(6), 669–685, doi:10.1130/0016-7606(1984)95<669:QSITJA>2.0.CO;2.

Brandes, J. A., and A. H. Devol (2002), A global marine-fixed nitrogen isotopic budget: Implications for Holocene nitrogen cycling, *Global Biogeochem. Cycles*, *16*(4), 1120, doi:10.1029/2001GB001856.

Calvert, S. E. (2004), Beware intercepts: Interpreting compositional ratios in multi-component sediments and sedimentary rocks, *Org. Geochem.*, *35*, 981–987, doi:10.1016/j.orggeochem.2004.03.001.

Calvert, S. E., B. Nielsen, and M. R. Fontugne (1992), Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels, *Nature*, *359*, 223–225, doi:10.1038/359223a0.

Carman, R., J. Aigars, and B. Larsen (1996), Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea, *Mar. Geol.*, *134*, 57–76, doi:10.1016/0025-3227(96)00033-3.

Codispoti, L. A. (1989), Phosphorus vs. Nitrogen Limitation of New and Export Production, in *Productivity of the Ocean: Present and Past*, edited by W. H. Berger et al., pp. 377–394, John Wiley, New York.

Crusius, J., T. F. Pedersen, S. E. Calvert, G. L. Cowie, and T. Oba (1999), A 36kyr geochemical record from the Sea of Japan of organic matter flux variations and changes in intermediate water oxygen concentrations, *Paleoceanography*, *14*(2), 248–259, doi:10.1029/1998PA900023.

Dauwe, B., J. J. Middelberg, P. M. J. Herman, and C. H. R. Heip (1999), Linking diagenetic alteration of amino acids and bulk organic matter reactivity, *Limnol. Oceanogr.*, *44*(7), 1809–1814, doi:10.4319/lo.1999.44.7.1809.

D'Hondt, S., et al. (2009), Subseafloor sedimentary life in the South Pacific Gyre, *Proc. Natl. Acad. Sci. U. S. A.*, *106*, 11,651–11,656.

de Lange, G. J. (1992), Distribution of exchangeable, fixed, organic and total nitrogen in interbeded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic, *Mar. Geol.*, *109*, 95–114, doi:10.1016/0025-3227(92)90223-5.

Deutsch, C., D. M. Sigman, R. C. Thunell, A. N. Meckler, and G. H. Haug (2004), Isotopic constraints on glacial/interglacial changes in the oceanic nitrogen budget, *Global Biogeochem. Cycles*, *18*, GB4012, doi:10.1029/2003GB002189.

Farrell, J. W., T. F. Pedersen, S. E. Calvert, and B. Nielsen (1995), Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean, *Nature*, *377*, 514–517, doi:10.1038/377514a0.

Francois, R., M. Frank, M. M. Rutgers van der Loeff, and M. P. Bacon (2004), 230Th normalization: An essential tool for interpreting sedimentary fluxes during the late Quaternary, *Paleoceanography*, *19*, PA1018, doi:10.1029/2003PA000939.

Frank, M., and A. Mackensen (2002), Age model of sediment core PS1768-8, http://doi.pangaea.de/10.1594/PANGAEA.81105, PANGAEA, Network for Geol. and Environ. Data, Germany.

Freudenthal, T., T. Wagner, F. Wenzhofer, M. Zabel, and G. Wefer (2001a), Early diagenesis of organic matter from sediments of the eastern subtropical Atlantic: Evidence from stable nitrogen and carbon isotopes, *Geochim. Cosmochim. Acta*, *65*(11), 1795–1808, doi:10.1016/S0016-7037(01)00554-3.

Freudenthal, T., S. Neuer, H. Meggers, R. Davenport, and G. Wefer (2001b), Influence of lateral partical advection and organic matter degradation on sediment accumulation and stable nitrogen isotope ratios along a productivity gradient in the Canary Islands region, *Mar. Geol.*, *177*, 93–109, doi:10.1016/S0025-3227(01)00126-8.

Fry, B., H. W. Jannasch, S. J. Molyneaux, C. O. Wirsen, J. A. Muramoto, and S. King (1991), Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and the Cariaco Trench, *Deep Sea Res.*, *38*, S1003–S1019, doi:10.1016/S0198-0149(10)80021-4.

Galbraith, E. D., M. Kienast, T. F. Pedersen, and S. E. Calvert (2004), Glacial-interglacial modulation of the marine nitrogen cycle by high-latitude O_2 supply to the global thermocline, *Paleoceanography*, *19*, PA4007, doi:10.1029/2003PA001000.

Galbraith, E. D., M. Kienast, S. L. Jaccard, T. F. Pedersen, B. G. Brunelle, D. M. Sigman, and T. Kiefer (2008a), Consistent relationship between global climate and surface nitrate utilization in the western subarctic Pacific throughout the last 500 ka, *Paleoceanography*, *23*, PA2212, doi:10.1029/2007PA001518.

Galbraith, E. D., D. M. Sigman, R. S. Robinson, and T. F. Pedersen (2008b), Nitrogen in past marine environments, in *Nitrogen in the Marine Environment*, 2nd ed., edited by D. G. Capone et al., pp. 1497–1535, Academic, Burlington, Mass.

Garcia, H. E., R. A. Locarnini, T. P. Boyer, J. I. Antonov, O. K. Baranova, M. M. Zweng, and D. R. Johnson (2010), *World Ocean Atlas 2009*, vol. 3, *Dissolved Oxygen, Apparent Oxygen Utilization, and Oxygen Saturation*, *NOAA Atlas NESDIS*, vol. 70, edited by S. Levitus, 344 pp., NOAA, Silver Spring, Md.

Garvin, J., R. Buick, A. D. Anbar, G. L. Arnold, and A. Kaufman (2009), Isotopic evidence for an aerobic nitrogen cycle in the latest Archean, *Science*, *323*, 1045–1048, doi:10.1126/science.1165675.

Gaye, B., M. G. Wiesner, and N. Lahajnar (2009), Nitrogen sources in the South China Sea, as discerned from stable nitrogen isotopic ratios in rivers, sinking particles, and sediments, *Mar. Chem.*, *114*, 72–85, doi:10.1016/j.marchem.2009.04.003.

Gaye-Haake, B., et al. (2005), Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean, *Mar. Chem.*, *96*, 243–255, doi:10.1016/j.marchem.2005.02.001.

Hartnett, H. E., R. G. Keil, J. I. Hedges, and A. H. Devol (1998), Influence of oxygen exposure time on organic carbon preservation in continental margin sediments, *Nature*, *391*, 572–575, doi:10.1038/35351.

Higgins, M. B., R. S. Robinson, K. L. Casciotti, M. R. McIlven, and A. Pearson (2009), Determining the nitrogen isotopic composition of porphyrins by the denitrifier method, *Anal. Chem.*, *81*(1), 184–192, doi:10.1021/ac8017185.

Higgins, M. B., R. S. Robinson, S. Carter, and A. Pearson (2010), Evidence from chlorin nitrogen isotopes for alternating nutrient regimes in the Eastern Mediterranean Sea, *Earth Planet. Sci. Lett.*, *290*, 102–107, doi:10.1016/j.epsl.2009.12.009.

Higgins, M. B., R. S. Robinson, J. M. Husson, S. J. Carter, and A. Pearson (2012), Dominant eukaryotic export production during ocean anoxic events reflects importance of recycled NH_4^+, *Proc. Natl. Acad. Sci. U. S. A.*, *109*, 2269–2274, doi:10.1073/pnas.1104313109.

Holmes, M. E., P. J. Müller, R. R. Schneider, M. Segl, and G. Wefer (1998), Spatial variations in euphotic zone nitrate utilization based on $\delta^{15}N$ in surface sediments, *Geo Mar. Lett.*, *18*, 58–65, doi:10.1007/s003670050052.

Holmes, M. E., G. Lavik, G. Fischer, M. Segl, G. Ruhland, and G. Wefer (2002), Seasonal variability of $\delta^{15}N$ in sinking particles in the Benguela upwelling regions, *Deep Sea Res., Part I*, *49*, 377–394, doi:10.1016/S0967-0637(01)00055-3.

Holmes, M. E., G. Lavik, G. Fisher, and G. Wefer (2003), Nitrogen isotopes in sinking particles and surface sediments in the central and southern Altantic, in *The South Atlantic in the Late Quaternary: Reconstruction of Material Budgets and Current Systems*, edited by G. Wefer, S. Mulitzas, and V. Raymeyer, pp. 143–165, Springer, New York.

Jaccard, S. L., and E. D. Galbraith (2012), Large climate-driven changes in oceanic oxygen concentrations during the last deglacation, *Nat. Geosci.*, *5*, 151–156, doi:10.1038/ngeo1352.

Jahns, S., M. Hüls, and M. Sarthein (1998), Age model of sediment core GIK16776-1, http://doi.pangaea.de/10.1594/PANGAEA.56134, PANGAEA, Network for Geol. and Environ. Data, Germany.

Jenkyns, H. C., A. Matthews, H. Tsikos, and Y. Erel (2007), Nitrate reduction, sulfate reduction, and sedimentary iron isotope evolution during the Cenomanian-Turionian oceanic anoxic event, *Paleoceanography*, *22*, PA3208, doi:10.1029/2006PA001355.

Junium, C. K., and M. A. Arther (2007), Nitrogen cycling during the Creaceous, Cenomaniam-Turian Oceanic Anoxic Event II, *Geochem. Geophys. Geosyst.*, *8*, Q03002, doi:10.1029/2006GC001328.

Kao, S. J., K. K. Liu, S. C. Hsu, Y. P. Chang, and M. H. Dal (2008), North Pacific-wide spreading of isotopically heavy nitrogen from intensified denitrification during the Bølling/Allerød and post-Younger Dryas periods: Evidence from the Western Pacific, *Atmos. Chem. Phys. Discuss.*, *5*, 1017–1033.

Karamanos, R. E., and D. A. Rennie (1978), Nitrogen isotope fractionation during ammonium exchange reactions with soil clay, *Can. J. Soil Sci.*, *58*, 53–60, doi:10.4141/cjss78-005.

Karl, D., R. Letelier, L. Tupas, J. Dore, J. Christian, and D. Hebel (1997), The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean, *Nature*, *388*, 533–538, doi:10.1038/41474.

Kashiyama, Y., N. O. Ogawa, M. Shiro, R. Tade, H. Kitazato, and N. Ohkouchi (2008), Reconstruction of the biogeochemistry and ecology of photoautotrophs based on the nitrogen and carbon isotopic compositions of vanadyl porphyrins from Miocene siliceous sediments, *Biogeosciences*, *5*, 797–816, doi:10.5194/bg-5-797-2008.

Kienast, M. (2000), Unchanged nitrogen isotopic composition of organic matter in the South China Sea during the last glacial cycle: Global implications, *Paleoceanography*, *15*, 244–253, doi:10.1029/1999PA000407.

Kienast, M., M. J. Higginson, G. Mollenhauer, T. I. Eglinton, M.-T. Chen, and S. E. Calvert (2005), On the sedimentological origin of down-core variations of bulk sedimentary nitrogen isotope ratios, *Paleoceanography*, *20*, PA2009, doi:10.1029/2004PA001081.

Kienast, S. S., S. E. Calvert, and T. F. Pedersen (2002), Nitrogen isotope and productivity variations along the northeast Pacific margin over the last 120 kyr: Surface and subsurface paleoceanography, *Paleoceanography*, *17*(4), 1055, doi:10.1029/2001PA000650.

Kotilainen, A. (2006), Age model of sediment core ARA-6/98-GBVH, http://doi.pangaea.de/10.1594/PANGAEA.407733, PANGAEA, Network for Geol. and Environ. Data, Germany.

Lavik, G. (2001), Nitrogen isotopes of sinking matter and sediments in the South Atlantic, PhD thesis, Univ. Bremen, Bremen, Germany.

Lehmann, M. F., S. M. Bernasconi, A. Barbieri, and J. A. McKenzie (2002), Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis, *Geochim. Cosmochim. Acta*, *66*(20), 3573–3584, doi:10.1016/S0016-7037(02)00968-7.

Lehmann, M. F., D. Sigman, and W. M. Berelson (2004), Coupling the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ of nitrate as a constraint on benthic nitrogen cycling, *Mar. Chem.*, *88*, 1–20, doi:10.1016/j.marchem.2004.02.001.

Lewis, R. C., K. H. Coale, B. D. Edwards, M. Marot, J. N. Douglas, and E. J. Burton (2002), Accumulation rate and mixing of shelf sediments in the Monterey Bay National Marine Sanctuary, *Mar. Geol.*, *181*, 157–169, doi:10.1016/S0025-3227(01)00265-1.

Libes, S. M., and W. G. Deuser (1988), The isotope geochemistry of particulate nitrogen in the Peru Upwelling Area and the Gulf of Maine, *Deep Sea Res., Part A*, *35*, 517–533, doi:10.1016/0198-0149(88)90129-X.

Liu, K.-K., and I. R. Kaplan (1989), The eastern tropical Pacific as a source of ^{15}N-enriched nitrate in seawater off southern California, *Limnol. Oceanogr.*, *34*, 820–830, doi:10.4319/lo.1989.34.5.0820.

Lourey, M. J., T. W. Trull, and D. M. Sigman (2003), Sensitivity of delta N-15 of nitrate, surface suspended and deep sinking particulate nitrogen to seasonal nitrate depletion in the Southern Ocean, *Global Biogeochem. Cycles*, *17*(3), 1081, doi:10.1029/2002GB001973.

Lyle, M., R. Zahn, F. Prahl, J. Dymond, R. Collier, N. Pisias, and E. Suess (1992), Paleoproductivity and carbon burial across the California Current: The Multitracer transect, 42°N, *Paleoceanography*, *7*, 251–272, doi:10.1029/92PA00696.

Mackin, J. E., and R. C. Aller (1984), Ammonium adsorption in marine sediments, *Limnol. Oceanogr.*, *29*(2), 250–257, doi:10.4319/lo.1984.29.2.0250.

Macko, S. A., and M. L. F. Estep (1984), Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter, *Org. Geochem.*, *6*, 787–790, doi:10.1016/0146-6380(84)90100-1.

Martinez, P., F. Lamy, R. S. Robinson, L. Pichevin, and I. B. Illy (2006), Atypical d^{15}N variations at the southern boundary of the east Pacific oxygen minimum zone over the last 50 kyr, *Quat. Sci. Rev.*, *25*, 3017–3028, doi:10.1016/j.quascirev.2006.04.009.

Meinecke, G. (1992), Spätquartäre Oberflächenwassertemperaturen im östlichen äquatorialen Atlantik, PhD thesis, 181 pp., Univ. Bremen, Bremen, Germany.

Möbius, J., N. Lahajnar, and K.-C. Emeis (2010), Diagenetic control on nitrogen isotope ratios in Holocene sapropels and recent sediments from the Mediterranean Sea, *Biogeosciences*, *7*, 3901–3914, doi:10.5194/bg-7-3901-2010.

Möbius, J., B. Gaye, N. Lahajnar, E. Bahlmann, and K.-C. Emeis (2011), Influence of diagenesis on sedimentary d15N in the Arabian Sea over the last 130 kyr, *Mar. Geol.*, *284*, 127–138, doi:10.1016/j.margeo.2011.03.013.

Mollenhauer, G., M. Kienast, F. Lamy, H. Meggers, R. R. Schneider, J. M. Hayes, and T. I. Eglinton (2005), An evaluation of C-14 age relationships between co-occurring foraminifera, alkenones, and total organic carbon in continental margin sediments, *Paleoceanography*, *20*, PA1016, doi:10.1029/2004PA001103.

Montoya, J. P. (1994), Nitrogen Isotope Fractionation in the Modern Ocean: Implications for the Sedimentary Record, in *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*, edited by R. Zahn et al., pp. 259–279, Springer, Berlin.

Moodley, L., J. J. Middelberg, P. M. J. Herman, K. Soetaert, and G. J. De Lange (2005), Oxygenation and organic matter preservation in marine sediments: Direct experimental evidence from ancient organic carbon-rich deposits, *Geology*, *33*, 889–892, doi:10.1130/G21731.1.

Müller, P. J., and E. Suess (1979), Productivity, sedimentation rate and seidmentary organic matter in the oceans—I. Organic matter preservation, *Deep Sea Res., Part A*, *26*, 1347–1362, doi:10.1016/0198-0149(79)90003-7.

Murray, R. W., C. Knowlton, M. Leinen, A. C. Mix, and C. H. Polsky (2000), Export production and carbonate dissolution in the central equatorial Pacific Ocean over the past 1 Ma, *Paleoceanography*, *15*, 570–592, doi:10.1029/1999PA000457.

Næs, K., J. Skei, and P. W. Wassman (1988), Total particulate and organic fluxes in anoxic Framvaren waters, *Mar. Chem.*, *23*, 257–268, doi:10.1016/0304-4203(88)90097-7.

Nakanishi, T., and M. Minagawa (2003), Stable carbon and nitrogen isotopic compositions of sinking particles in the northeast Japan Sea, *Geochem. J.*, *37*, 261–275, doi:10.2343/geochemj.37.261.

Nakatsuka, T., N. Handa, N. Harada, T. Sugimoto, and S. Imaizumi (1997), Origin and decomposition of sinking particulate organic matter in the deep water column inferred from the vertical distributions of its d15N, d13C, and D14C, *Deep Sea Res., Part I*, *44*(12), 1957–1979, doi:10.1016/S0967-0637(97)00051-4.

Prokopenko, M., D. E. Hammond, A. J. Spivack, and L. Stott (2006a), Impact of long term diagenesis on δ^{15}N of organic matter in marine sediments: Sites 1227 and 1230, *Proc. Ocean Drill. Program Sci. Results*, *201*, 30 pp.

Prokopenko, M., D. E. Hammond, and L. Stott (2006b), Lack of isotopic fractionation of δ^{15}N of organic matter during long-term diagenesis in marine sediments, ODP Leg 202, Sites 1234 and 1235, *Proc. Ocean Drill. Program Sci. Results*, *202*, 22 pp.

Ren, H., D. Sigman, A. N. Meckler, B. Plessen, R. S. Robinson, Y. Rosenthal, and G. H. Haug (2009), Foraminiferal isotope evidence of reduced nitrogen fixation in the ice age Atlantic Ocean, *Science*, *323*, 244–248, doi:10.1126/science.1165787.

Robinson, R. S., and D. Sigman (2008), Nitrogen isotopic evidence for a poleward decrease in surface nitrate within the ice age Antarctic, *Quat. Sci. Rev.*, *27*, 1076–1090, doi:10.1016/j.quascirev.2008.02.005.

Robinson, R. S., B. G. Brunelle, and D. M. Sigman (2004), Revisiting nutrient utilization in the glacial Antarctic; Evidence from a new diatom-bound N isotope method, *Paleoceanography*, *19*, PA3001, doi:10.1029/2003PA000996.

Rosenfeld, J. K. (1979), Ammonium Adsorption in nearshore anoxic sediments, *Limnol. Oceanogr.*, *24*(2), 356–364, doi:10.4319/lo.1979.24.2.0356.

Roy, H., J. Kallmeyer, R. R. Adhikari, R. Pockalny, B. B. Jørgensen, and S. D'Hondt (2012), Aerobic microbial respiration in 86-Million-year-old deep-sea red clay, *Science*, *336*, 922–925, doi:10.1126/science.1219424.

Sachs, J., and D. Repeta (1999), Oligotrophy and nitrogen fixation during eastern Mediteranean sapropel events, *Science*, *286*, 2485–2488, doi:10.1126/science.286.5449.2485.

Sarnthein, M. (2003a), Age model of sediment core GIK16772-1, http://doi.pangaea.de/10.1594/PANGAEA.134239, PANGAEA, Network for Geol. and Environ. Data, Germany.

Sarnthein, M. (2003b), Age model of sediment core GIK16772-2, http://doi.pangaea.de/10.1594/PANGAEA.134249, PANGAEA, Network for Geol. and Environ. Data, Germany.

Schubert, C. J., and S. E. Calvert (2001), Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: Implications for nutrient utilization and organic matter composition, *Deep Sea Res., Part I*, *48*, 789–810, doi:10.1016/S0967-0637(00)00069-8.

Shemesh, A., S. A. Macko, C. D. Charles, and G. H. Rau (1993), Isotopic Evidence for Reduced Productivity in the Glacial Southern-Ocean, *Science*, *262*(5132), 407–410, doi:10.1126/science.262.5132.407.

Sigman, D. M., M. A. Altabet, R. Francois, D. C. McCorkle, and J.-F. Gaillard (1999), The isotopic composition of diatom-bound nitrogen in Southern Ocean sediments, *Paleoceanography*, *14*, 118–134, doi:10.1029/1998PA900018.

Sigman, D. M., K. L. Karsh, and K. L. Casciotti (2009), Nitrogen isotopes in the ocean, in *Encyclopedia of Ocean Sciences*, 2nd ed., edited by J. H. Steele et al., pp. 40–54, Academic, London, doi:10.1016/B978-012374473-9.00632-9.

Sigman, D. M., M. P. Hain, and G. H. Haug (2010), The polar ocean and glacial cycles in atmospheric CO$_2$ concentration, *Nature*, *466*, 47–55, doi:10.1038/nature09149.

Silverberg, N., A. Martinez, S. Aguiñiga, J. D. Carriquiry, N. Rombero, E. Shumilin, and S. Cota (2004), Contrasts in sedimentation flux below the southern California Current in late 1996 and during the El Niño event of 1997–1998, *Estuarine Coastal Shelf Sci.*, *59*, 575–587, doi:10.1016/j.ecss.2003.11.003.

Sirocko, F., C.-D. Garbe-Schönberg, and C. W. Devey (2000), Processes controlling trace element geochemistry of Arabian Sea sediments during the last 25,000 years, *Global Planet. Change*, *26*, 217–303, doi:10.1016/S0921-8181(00)00046-1.

Somes, C. J., A. Schmittner, E. D. Galbraith, M. F. Lehmann, M. A. Altabet, J. P. Montoya, R. M. Letelier, A. Mix, A. Bourbonnais, and M. Eby (2010), Simulating the global distribution of nitrogen isotopes in the ocean, *Global Biogeochem. Cycles*, *24*, GB4019, doi:10.1029/2009GB003767.

Struck, U., F. Pollehne, E. Bauerfeind, and B. v. Bodungen (2004), Sources of nitrogen for the vertical particle flux in Gotland Sea (Baltic Proper)–results from sediment trap studies, *J. Mar. Syst.*, *45*, 91–101, doi:10.1016/j.jmarsys.2003.11.012.

Thunell, R., C. Pride, E. Tappa, and F. Muller-Karger (1994), Biogenic silica fluxes and accumulation rates in the Gulf of California, *Geology*, *22*, 303–306, doi:10.1130/0091-7613(1994)022<0303:BSFAAR>2.3.CO;2.

Thunell, R. C., D. M. Sigman, F. Muller-Karger, Y. Astor, and R. Varela (2004), Nitrogen isotope dynamics of the Cariaco Basin, Venezuela, *Global Biogeochem. Cycles*, *18*, GB3001, doi:10.1029/2003GB002185.

Velinsky, D. J., and M. L. Fogel (1999), Cycling of dissolved and particulate nitrogen and carbon in the Framvaren Fjord, Norway: Stable isotopic variations, *Mar. Chem.*, *67*, 161–180, doi:10.1016/S0304-4203(99)00057-2.

Velinsky, D. J., M. L. Fogel, J. F. Todd, and B. M. Tebo (1991), Isotopic fractionation of dissolved ammonium at the oxygen-hydrogen sulfide interface in anoxic waters, *Geophys. Res. Lett.*, *18*, 649–652, doi:10.1029/91GL00344.

Wang, P., L. Wang, Y. Bian, and Z. Jian (1995), Late Quaternary paleoceanography of the South China Sea: Surface circulation and carbonate cycles, *Mar. Geol.*, *127*, 145–165, doi:10.1016/0025-3227(95)00008-M.