OCEAN PROCESS TRACERS: NITROGEN ISOTOPES IN THE OCEAN

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Introduction

Nitrogen has two stable isotopes, \(^{14}\text{N}\) and \(^{15}\text{N}\) (atomic masses of 14 and 15, respectively). \(^{14}\text{N}\) is the more abundant of the two, comprising 99.63% of the nitrogen found in nature. Physical, chemical, and biological processes discriminate between the two isotopes, leading to subtle but measurable differences in the ratio of \(^{15}\text{N}\) to \(^{14}\text{N}\) among different forms of nitrogen found in the marine environment.

Nitrogen is a central component of marine biomass and one of the major nutrients required by all phytoplankton. In this sense, biologically available (or ‘fixed’, i.e., non-N\(_2\)) N is representative of the fundamental patterns of biogeochemical cycling in the ocean. However, N differs from other nutrients in that its oceanic sources and sinks are dominantly internal and biological, with marine N\(_2\) fixation supplying much of the fixed N in the ocean and marine denitrification removing it. The N isotopes provide a means of studying both the input/output budget of oceanic fixed N and its cycling within the ocean. In this overview, we outline the isotope systematics of N cycle processes and their impacts on the isotopic composition of the major N reservoirs in the ocean. This information provides a starting point for considering the wide range of questions in ocean sciences to which the N isotopes can be applied.

Terms and Units

Mass spectrometry can measure precisely the ratio of the N isotopes relative to a N reference containing a constant isotopic ratio. The universal reference for N isotopes is atmospheric N\(_2\), with an \(^{15}\text{N}/^{14}\text{N}\) ratio of 0.367 65% \(\pm\) 0.000 81%. Natural samples exhibit small deviations from the standard ratio, which are expressed in \(\delta\) notation (in units of per mil, \(\%\)):

\[
\delta^{15}\text{N}(\%o) = \left(\frac{{^{15}\text{N}/^{14}\text{N}}_{\text{sample}}}{{^{15}\text{N}/^{14}\text{N}}_{\text{standard}}} - 1\right) \times 1000 \quad [1]
\]

In this notation, the \(\delta^{15}\text{N}\) of atmospheric N\(_2\) is 0\%. Special terms are also used to characterize the amplitude of isotopic fractionation caused by a given process. Isotope fractionation results from both equilibrium processes (‘equilibrium fractionation’) and unidirectional reactions (‘kinetic fractionation’). Nitrogen isotope variations in the ocean are typically dominated by kinetic fractionation associated with the conversions of N from one form to another. The kinetic isotope effect, \(e\), of a given reaction is defined by the ratio of rates with which the two N isotopes are converted from reactant to product:

\[
e(\%) = \left(\frac{k_{^{15}\text{N}}}{k_{^{14}\text{N}}}\right) \times 1000 \quad [2]
\]

where \(k_{^{15}\text{N}}\) and \(k_{^{14}\text{N}}\) are the rate coefficients of the reaction for \(^{14}\text{N}\)- and \(^{15}\text{N}\)-containing reactant, respectively. For \(e \ll 1000\%\), \(e\) is approximated by the difference in \(\delta^{15}\text{N}\) between the reactant and its instantaneous product. That is, if a reaction has an \(e\) of 5\%, then the \(\delta^{15}\text{N}\) of the product N generated at any given time will be \(\sim 5\%\) lower than the \(\delta^{15}\text{N}\) of the reactant N at that time.

Measurements

The isotopic analysis of N relies on the generation of a stable gas as the analyte for isotope ratio mass spectrometry. Online combustion to N\(_2\) is currently the standard method for the preparation of a N sample for isotopic analysis. With ‘off-the-shelf’ technology, a typical sample size requirement is 1–2 \(\mu\)mol N per analysis. Gas chromatography followed by combustion to N\(_2\) is improving as a technique for specific organic compounds, amino acids in particular, although the polarity of many N compounds remains a challenge. Liquid chromatography is also being explored. There are standard methods of collection for most bulk forms of particulate N (PN) in the ocean. Shallow and deep samples of suspended PN are filtered onto glass fiber filters. Sinking PN is collected by sediment traps. Zooplankton can be picked from filtered samples or net tows, and particulates can be separated into size classes. In the case of dissolved forms of N, the species of interest must be converted selectively to a gas or other extractable form for collection. Since the 1970s, the \(\delta^{15}\text{N}\) values of marine nitrate (NO\(_3^–\)), nitrite (NO\(_2^–\)), and ammonium (NH\(_4^+\)) have been...
analyzed by conversion to ammonia gas and collection of the cationic ammonium form for subsequent conversion to N\(_2\) (often referred to as the ammonia ‘distillation’ and ‘diffusion’ methods). Recently, more sensitive isotope analysis methods (requiring only 5–10 nmol of N per analysis) have been developed for nitrate and nitrite in which these species are converted to nitrogen oxide (N\(_2\)O), followed by isotopic analysis of this gas (the ‘bacterial’ or ‘denitrifier’ method and the ‘chemical’ or ‘azide’ method). The N\(_2\)O produced by these methods (or naturally occurring N\(_2\)O) is analyzed by a purge and trap system, followed by gas chromatography and isotope ratio mass spectrometry. The N\(_2\)O-based trap system, followed by gas chromatography and isotope ratio mass spectrometry. The N\(_2\)O-based methods also allow for oxygen isotope analysis of nitrate and nitrite, a measurement not previously possible in seawater. In addition, they provide a cornerstone for isotopic analysis of other dissolved forms of N, such as dissolved organic N (DON) and ammonium (NH\(_4^+\)), which can be converted to nitrate and/or nitrite. With respect to dissolved gases, methods of collection and isotopic analysis have been developed for N\(_2\) and N\(_2\)O, with recent progress on isotopomer analysis of N\(_2\)O (i.e., distinguishing \(^{15}\)N\(^{14}\)N\(^{16}\)O from \(^{14}\)N\(^{15}\)N\(^{16}\)O).

**Models**

Two simple models, the ‘Rayleigh’ model and the ‘steady-state’ model, are frequently used to interpret N isotope data from the ocean. In both of these models, the degree of consumption of the reactant N pool is a key parameter, and the \(\delta^{15}\)N of the initial reactant N pool (\(\delta^{15}\)N\(_{\text{initial}}\); eqn [3]), the instantaneously generated product N (\(\delta^{15}\)N\(_{\text{instantaneous}}\); eqn [4]), and the integrated product N pool (\(\delta^{15}\)N\(_{\text{integrated}}\); eqn [5]) as a given reservoir of reactant N is consumed (Figure 1):

\[
\delta^{15}\text{N}_{\text{reactant}} = \delta^{15}\text{N}_{\text{initial}} - \varepsilon \{\ln(f)\} \quad [3]
\]

\[
\delta^{15}\text{N}_{\text{instantaneous}} = \delta^{15}\text{N}_{\text{reactant}} - \varepsilon \quad [4]
\]

\[
\delta^{15}\text{N}_{\text{integrated}} = \delta^{15}\text{N}_{\text{initial}} + \varepsilon \{(1 - f)\} \ln(f) \quad [5]
\]

where \(f\) is the fraction of the reactant remaining, \(\delta^{15}\text{N}_{\text{initial}}\) is the \(\delta^{15}\)N of the initial reactant N pool, and \(\varepsilon\) is the kinetic isotope effect of the transformation. These equations are simplified, approximate forms of the full expressions. They are typically adequate, but their error is greater for higher consumption (lower \(f\)) and higher \(\varepsilon\). The Rayleigh model is often used to describe events in the ocean, such as the uptake of nitrate by phytoplankton during a bloom in a stratified surface layer.

The end-member alternative to the Rayleigh model is the steady-state model, in which reactant N is continuously supplied and partially consumed, with residual reactant N being exported at a steady-state rate such that the gross supply of reactant N equals the sum of the product N and the residual reactant N exported. In this case, the following approximate expressions apply to the reactant N pool (\(\delta^{15}\)N\(_{\text{reactant}}\); eqn [6]) and the product N pool (\(\delta^{15}\)N\(_{\text{product}}\); eqn [7]) (Figure 1):

\[
\delta^{15}\text{N}_{\text{reactant}} = \delta^{15}\text{N}_{\text{initial}} + \varepsilon (1 - f) \quad [6]
\]

\[
\delta^{15}\text{N}_{\text{product}} = \delta^{15}\text{N}_{\text{initial}} - \varepsilon f \quad [7]
\]

The steady-state model and modified forms of it, such as the more spatially complex ‘reaction–diffusion’ model, are used to quantify uptake processes where supply and uptake are simultaneous and relatively time-invariant, such as in the consumption
of nitrate by denitrification in the ocean interior or in sediments.

**Processes**

**Inputs**

N₂ fixation is the major input of fixed N to the ocean (Figure 2). N₂ fixation is carried out by N₂ fixers, cyanobacteria and other microorganisms able to convert N₂ into biomass N. Subsequent remineralization of this biomass supplies new N to the dissolved fixed N pools in the surface and subsurface ocean. Field collections of Trichodesmium colonies, the best-known genus of open ocean N₂ fixer, have yielded a δ¹⁵N of c. −2‰ to +0.5‰. Taking into account the δ¹⁵N of dissolved N₂ (0.6‰ in the surface mixed layer), this range in δ¹⁵N is consistent with, but perhaps less variable than, the range in isotope effects estimated from culture studies of marine and terrestrial N₂ fixers, ~0–4‰ (Table 1). An average δ¹⁵N of −1‰ has been suggested for the fixed N input to the ocean from N₂ fixation.

Other inputs of fixed N to the marine environment include terrestrial runoff and atmospheric precipitation, the N isotopic compositions of which are poorly constrained (Figure 2). Dissolved and particulate δ¹⁵N in pristine river systems ranges mostly from 0‰ to 5‰. However, biological processes along the flow path and in estuaries (in particular, by denitrification; see below) can alter the δ¹⁵N of the final inputs from terrestrial runoff in complex ways. Anthropogenic inputs often increase the δ¹⁵N of a system because they encourage denitrification. In atmospheric inputs, a wide range in the δ¹⁵N of inorganic (c. −16‰ to 10‰) and organic (c. −8‰ to 1‰) N has been observed, with increasing evidence that at least some of this variability can provide

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**Figure 2** Processes affecting the distribution of nitrogen isotopes in the sea. The inputs and outputs (solid arrows) control the ocean’s inventory of fixed N, the majority of which is in the form of nitrate (NO₃⁻). Inputs are marine N₂ fixation in the surface ocean, terrestrial runoff, and atmospheric precipitation. Outputs indicated are sedimentary and water column denitrification. As discussed in the text, water-column denitrification in low-oxygen regions of the ocean interior leads to elevated δ¹⁵N of nitrate (dark area). Remineralization of newly fixed N can explain the low δ¹⁵N of nitrate in the shallow subsurface, or thermocline, of low-latitude regions (light area). Internal cycling is represented with dashed arrows. Nitrate supplied from the deep ocean and thermocline is assimilated in the surface ocean. PN is recycled in the surface ocean, degraded to ammonium (NH₄⁺) that is subsequently assimilated; the role of DON in this recycling is not yet clear. Sinking and remineralization (via degradation and nitrification, see text) returns N from the particulate pool to nitrate. For simplicity, possible nitrification in the surface ocean is not shown. The isotope fractionation associated with nitrification in the ocean interior is also excluded because this process generally goes to completion (see text). The δ¹⁵N of particulate suspended and sinking N, DON, and thermocline nitrate is taken from the subtropical North Atlantic. Question marks indicate the greatest uncertainties, due to variation in the available data and/or insufficient data.
insight into sources and processes. In the face of large uncertainties, a preindustrial mean \( \delta^{15}N \) of 4% for terrestrial runoff and \(-2\%\) for atmospheric precipitation has been suggested by some workers.

**Outputs**

Denitrification, the bacterial reduction of nitrate to N\(_2\), is the major mechanism of fixed N loss from the ocean, occurring both in the water column and in sediments when the oxygen concentration is low \((<5 \mu M)\) (Figure 2). Denitrification strongly discriminates against the heavier isotope, \(^{15}\text{N}\), progressively enriching the remaining nitrate pool in \( ^{15}\text{N} \) as nitrate consumption proceeds. Culture studies of denitrifying bacteria suggest \((\text{with some exceptions})\) an isotope effect of \( \sim 20-30\%\), a range supported by water column estimates (Table 1). The isotopic discrimination during denitrification likely takes place as nitrate is reduced intracellularly to nitrite by the dissimilatory form of the enzyme nitrate reductase, such that un consumed, \(^{15}\text{N}\)-enriched nitrate effluxing from the cell back into ambient waters allows the enzyme-level isotope effect to be expressed at the environmental scale. Where it occurs in low-oxygen regions of the mid-depth ocean, water column denitrification causes a clear elevation in the \( ^{15}\text{N} \) of nitrate, and it is the reason that global ocean nitrate \( ^{15}\text{N} \) is higher than that of the N source from N\(_2\) fixation, the dominant input.

In contrast to water-column denitrification, denitrification in sediments leads to little increase in the \( ^{15}\text{N} \) of water-column nitrate. The high \( ^{15}\text{N} \) of nitrate within the pore waters of actively denitrifying sediments demonstrates that isotopic discrimination occurs at the scale of the organism. However, expression of the organism-scale isotope effect at the scale of sediment/water exchange is minimized by nearly complete consumption of the nitrate at the site of denitrification within sediment pore waters, which prevents \( ^{15}\text{N} \)-enriched residual nitrate from evading to the overlying water column, yielding an ‘effective’ isotope effect of \( 3\% \) or less in most sedimentary environments studied so far (Table 1).

Another mechanism of fixed N loss that occurs in sediments and the water column is anaerobic ammonium oxidation, or ‘anammox’, in which nitrite \((\text{from nitrate reduction or ammonium oxidation})\) is used to oxidize ammonium to N\(_2\) \((\text{NO}_2^- + \text{NH}_4^+ \rightarrow \text{N}_2 + 2\text{H}_2\text{O})\). This process has unknown effects on isotope distributions in the ocean. The effects of anammox on N isotopes must depend on the organism-scale isotope effects, the sources of nitrite and ammonium substrates for the reaction, and the degree to which these substrates are consumed. For instance, if nitrate reduction by denitrifiers is the source of the nitrite,

<table>
<thead>
<tr>
<th>Process</th>
<th>Isotope effect (%)</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2) fixation (N(_2)→PN)</td>
<td>1.8–3.0%</td>
<td>( \text{Trichodesmium spp.} )</td>
</tr>
<tr>
<td></td>
<td>(-0.2%)</td>
<td>Western Tropical North Pacific</td>
</tr>
<tr>
<td></td>
<td>(-0.4–0.2%)</td>
<td>Western Tropical Atlantic</td>
</tr>
<tr>
<td>Denitrification (NO(_3^-)→N(_2))</td>
<td>5–30%</td>
<td>( \text{Pseudomonas stutzeri (marine)} )</td>
</tr>
<tr>
<td></td>
<td>18–28%</td>
<td>( \text{Paracoccus denitrificans (terrestrial)} )</td>
</tr>
<tr>
<td>Water column</td>
<td>( \leq 3% )</td>
<td>Coastal sites, eastern N. Pacific margin, and deep Bering Sea</td>
</tr>
<tr>
<td>Sedimentary</td>
<td>5–17%</td>
<td>( \text{Thalassiosira weissflogii} )</td>
</tr>
<tr>
<td></td>
<td>5–6%</td>
<td>Coastal Antarctic</td>
</tr>
<tr>
<td></td>
<td>5–9%</td>
<td>Open Antarctic and Subantarctic</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>Subarctic Pacific</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>Equatorial Pacific</td>
</tr>
<tr>
<td>NO(_3^-) assimilation (NO(_3^-)→PN)</td>
<td>20%</td>
<td>( \text{Thalassiosira pseudonana} )</td>
</tr>
<tr>
<td></td>
<td>8–27%</td>
<td>( \text{Skeletonema costatum} )</td>
</tr>
<tr>
<td></td>
<td>4–27%</td>
<td>Bacterial assemblage</td>
</tr>
<tr>
<td></td>
<td>6.5–8%</td>
<td>Chesapeake Bay</td>
</tr>
<tr>
<td></td>
<td>9%</td>
<td>Delaware Estuary</td>
</tr>
<tr>
<td></td>
<td>18.5%</td>
<td>Scheldt Esturary</td>
</tr>
<tr>
<td>NH(_4^+) assimilation (NH(_4^+)→PN)</td>
<td>14%</td>
<td>( \text{Nitrosomonas marina (marine)} )</td>
</tr>
<tr>
<td></td>
<td>19%</td>
<td>( \text{Nitrosomonas C-113a (marine)} )</td>
</tr>
<tr>
<td></td>
<td>35–38%</td>
<td>( \text{Nitrosomonas europaea (terrestrial)} )</td>
</tr>
<tr>
<td></td>
<td>12–16%</td>
<td>Chesapeake Bay</td>
</tr>
<tr>
<td>Nitrification</td>
<td>Unknown</td>
<td></td>
</tr>
</tbody>
</table>
remineralization processes are the source of the ammonium, and both the nitrite and ammonium are completely consumed in the environment where anammox occurs, then the isotope discrimination would simplify to that of the nitrate reduction by denitrifiers averaged with any isotope discrimination during the remineralization that produces the needed ammonium. It should be noted that many water-column-derived isotope effect estimates for ‘denitrification’ have inherently included the effect of anammox, in that they regress the nitrate $\delta^{15}N$ increase against the total nitrate deficit relative to phosphate, and ammonium is not observed to accumulate.

**Internal Cycling**

The fluxes associated with internal cycling are neither sources nor sinks of fixed N but affect the distributions of N species and isotopes in the ocean.

**N assimilation** In the surface ocean, phytoplankton assimilate fixed N (nitrate and ammonium, as well as nitrite, urea, and other organic N compounds) (Figure 3). Culture studies indicate that different forms of fixed N are assimilated with distinct isotope effects, although these isotope effects may vary with physiological conditions. For all studied forms, phytoplankton preferentially consume $^{14}N$ relative to $^{15}N$ (Figures 3 and 4). Nitrate is the deep-water source of fixed N for phytoplankton growth, and the degree of its consumption varies across the surface ocean. The isotope effect of nitrate assimilation therefore has a major impact on the isotopic distributions of all N forms in the ocean. Field-based estimates of the isotope effect of nitrate assimilation range from 4% to 10%, with most estimates closer to 5–8% (Table 1). Culture-based estimates are more variable. Physiological studies suggest that isotopic fractionation associated with nitrate assimilation is imparted by the intracellular assimilatory nitrate reductase enzyme, which has an estimated intrinsic isotope effect of 15–30%.

The isotope effect of nitrate assimilation is an integrative characteristic of...
the upper ocean biota that can be measured without perturbing the system, and its magnitude is of broad significance in the application of N isotopes to various questions in the modern and past oceans. Thus, it is a priority to develop a predictive understanding of its controls.

Other forms of fixed N assimilated by phytoplankton (ammonium, nitrite, and urea) are produced and nearly completely consumed within the open ocean surface mixed layer (Figure 3). Culture studies suggest an isotope effect for ammonium assimilation of up to $20\%$, decreasing as ammonium concentration decreases, and minimal isotope effects ($<1\%$) for assimilation of nitrite and urea. In estuaries, where ammonium can accumulate in the shallow subsurface and be entrained into the surface layer, ammonium assimilation causes a clear increase in the $\delta^{15}N$ of the remaining ammonium pool. Isotope effect estimates based on ammonium concentrations and $\delta^{15}N$ in these environments range from $6.5\%$ to $18.5\%$ (Table 1).

Remineralization The return of organic N to nitrate occurs in two steps, the degradation of organic N to ammonium and the bacterial oxidation of ammonium to nitrate, or ‘nitrification’ (Figure 3). Nitrification itself occurs in two steps, the oxidation of ammonium to nitrite and the oxidation of nitrite to nitrate, mediated by distinct groups of microorganisms. Isotopic discrimination may occur at all steps involved in remineralization. Field studies generally suggest that both bacteria and zooplankton preferentially degrade low-$\delta^{15}N$ PN to ammonium, yielding residual organic matter relatively high in $^{15}N$. The wide spectrum of reactions involved in organic N degradation and the heterogeneous nature of organic matter (comprised of compounds with distinct $\delta^{15}N$ that degrade at various rates) make quantifying the isotope effect associated with degradation difficult. A few laboratory studies have quantified the isotope effects of individual processes such as thermal peptide bond cleavage, bacterial amino acid uptake and transamination, and zooplankton ammonium release. Laboratory studies attempting to mimic degradation as a whole suggest a net isotope effect of $\leq 3\%$.

Culture studies indicate a large isotope effect for the conversion of ammonium to nitrite, the first step in nitrification (Table 1). Estimates of the isotope effect for marine ammonia-oxidizing bacteria ($14–19\%$) are lower than those for terrestrial
ammonia-oxidizing bacteria (as high as ~38%), possibly due to phylogenetic differences. The isotope effect of nitrification estimated from ammonium concentration and $\delta^{15}N$ measurements in the Chesapeake Bay is 12–16‰, similar to the culture results for marine ammonia-oxidizing bacteria (Table 1). Thus far, no culture-based information is available regarding isotope effects for ammonia-oxidizing crenarchaea or nitrite-oxidizing bacteria.

Nitrogen Reservoirs

Dissolved N

Nitrate Nitrate accounts for most of the fixed N in the ocean. The $\delta^{15}N$ of deep ocean nitrate is typically ~5‰. Regionally, the $\delta^{15}N$ of nitrate varies between 2‰ and 20‰ due to the effects of N$_2$ fixation, nitrate assimilation, and denitrification (Figure 5). Nitrate $\delta^{15}N$ significantly lower than deep-ocean nitrate has been observed in the upper thermocline of the low-latitude oligotrophic ocean (Figure 6). This $^{15}N$ depletion is most likely due to the oxidation of newly fixed N, which, as described above, has a $\delta^{15}N$ of c. −1‰. Values higher than 5‰ result from discrimination associated with nitrate assimilation by phytoplankton at the ocean surface (Figure 7) or denitrification in oxygen-deficient zones of the ocean interior (Figure 8).

Nitrate assimilation by phytoplankton leads to elevated $\delta^{15}N$ of nitrate in regions of the ocean where nitrate is incompletely consumed in surface waters, such as the high-latitude, nutrient-rich regions of the Southern Ocean and the subarctic Pacific, and the low-latitude upwelling regions of the California Current and the Equatorial Pacific. In the surface waters of these regions, there is a strong correlation between the degree of nitrate consumption by phytoplankton and the $\delta^{15}N$ of the nitrate remaining in the water (Figure 7). However, while nitrate assimilation elevates the $\delta^{15}N$ of nitrate in the surface ocean and causes modest $^{15}N$ enrichment in some newly formed thermocline waters, it does not appear to affect greatly the $\delta^{15}N$ of nitrate in the deep ocean. Below 2.5–3.0-km depth in the ocean, nitrate $\delta^{15}N$ is relatively constant at ~5‰, despite large inter-basin differences in nitrate concentration. The minimal degree of isotopic variation in the nitrate of the deep ocean is due to the fact that, in most surface waters, the nitrate supply from below is almost completely consumed by phytoplankton, such that the organic N exported from the surface ocean converges on the $\delta^{15}N$ of the nitrate supply. Because the sinking flux $\delta^{15}N$ is close to that of the nitrate supplied from the ocean interior, remineralization of the sinking flux in the ocean interior does not alter greatly the $\delta^{15}N$ of deep nitrate. In this respect, the oceanic cycling of N isotopes differs markedly from that of the carbon isotopes.

Because water-column denitrification occurs in the subsurface and because it consumes only a fraction of the nitrate plus nitrite available, its isotope effect is more completely expressed in the $\delta^{15}N$ of subsurface nitrate. In denitrifying regions of the water column, the $\delta^{15}N$ of nitrate in the subsurface is commonly elevated to 15‰ or higher (Figure 8). The subsurface $\delta^{15}N$ maximum occurs in the core of the oxygen minimum and is correlated with the estimated degree of nitrate consumption by water-column denitrification.

Denitrification, both in the water column and sediments, exerts a direct control on the $\delta^{15}N$ of mean
When the ocean N budget is at steady state, the $\delta^{15}N$ of the fixed N removed (through water-column and sedimentary denitrification) will equal the $\delta^{15}N$ of the fixed N added (c. $-1\%o$, approximating N$_2$ fixation as the sole source) (Figure 9). If denitrification with an isotope effect of 20–30% were occurring homogenously in the ocean water column and responsible for all fixed N loss, the $\delta^{15}N$ of mean oceanic nitrate would be 19–29% to achieve a $\delta^{15}N$–1% for N loss. That the modern mean oceanic nitrate $\delta^{15}N$ is $\sim 5\%o$ but higher than that of thermocline nitrate at Bermuda ($\sim 2.5\%o$). High nitrate concentrations below 250m prevent accurate assessment of TON $\delta^{15}N$ using published methods (see text). The $\delta^{15}N$ of sinking particles collected at 100 m (3.7%) is indicated by the arrow at top of (b); surface suspended PN $\delta^{15}N$ is c. $-0.2\%o$ (not shown). Nitrate and TON data are the means of monthly measurements between June 2000 and May 2001. Modified from Knapp AH, Sigman DM, and Lipschutz F (2005) N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic time-series study site. Global Biogeochemical Cycles 19: GB1018 (doi:10.1029/2004GB002320). Sinking and suspended PN $\delta^{15}N$ data from Altabet MA (1988) Variations in nitrogen isotopic composition between sinking and suspended particles: Implications for nitrogen cycling and particle transformation in the open ocean. Deep Sea Research 35: 535–554.

**Figure 6** Depth profiles of (a) [NO$_3^-$] (open circles) and TON (total organic N, or DON plus the small pool of PN) (open squares) and (b) nitrate $\delta^{15}N$ (filled circles) and TON $\delta^{15}N$ (filled squares) at the Bermuda Atlantic Time-Series Study site in the oligotrophic Sargasso Sea. Low nitrate $\delta^{15}N$ in the thermocline has been proposed to reflect N$_2$ fixation at the surface, the N from which sinks and is remineralized at depth. The increase in nitrate $\delta^{15}N$ above 200 m reflects fractionation associated with nitrate assimilation. [TON] increases slightly into the surface layer while TON $\delta^{15}N$ decreases, suggesting a possible source of low-$^{15}N$ DON in the surface. The $\delta^{15}N$ of the TON pool is lower than that of mean ocean nitrate and deep nitrate at Bermuda (5%) but higher than that of thermocline nitrate at Bermuda ($\sim 2.5\%o$). High nitrate concentrations below 250m prevent accurate assessment of TON $\delta^{15}N$ using published methods (see text). The $\delta^{15}N$ of sinking particles collected at 100 m (3.7%) is indicated by the arrow at top of (b); surface suspended PN $\delta^{15}N$ is c. $-0.2\%o$ (not shown). Nitrate and TON data are the means of monthly measurements between June 2000 and May 2001. Modified from Knapp AH, Sigman DM, and Lipschutz F (2005) N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic time-series study site. Global Biogeochemical Cycles 19: GB1018 (doi:10.1029/2004GB002320). Sinking and suspended PN $\delta^{15}N$ data from Altabet MA (1988) Variations in nitrogen isotopic composition between sinking and suspended particles: Implications for nitrogen cycling and particle transformation in the open ocean. Deep Sea Research 35: 535–554.

Deep ocean nitrate. When the ocean N budget is at steady state, the $\delta^{15}N$ of the fixed N removed (through water-column and sedimentary denitrification) will equal the $\delta^{15}N$ of the fixed N added (c. $-1\%o$, approximating N$_2$ fixation as the sole source) (Figure 9). If denitrification with an isotope effect of 20–30% were occurring homogenously in the ocean water column and responsible for all fixed N loss, the $\delta^{15}N$ of mean oceanic nitrate would be 19–29% to achieve a $\delta^{15}N$ of $-1\%$o for N loss. That the modern mean oceanic nitrate $\delta^{15}N$ is $\sim 5\%o$, much lower than 19–29%, reflects at least two factors: (1) the importance of sedimentary denitrification, which appears to express a minimal isotope effect; and (2) the localized nature of water-column denitrification. With regard to the second, because denitrification consumes a significant fraction of the ambient nitrate in the ocean’s suboxic zones and elevates its $\delta^{15}N$ above that of the mean ocean (Figures 5 and 8), the $\delta^{15}N$ of nitrate being removed by water column denitrification is higher than if the substrate for denitrification had the mean ocean $\delta^{15}N$. Much as with sedimentary denitrification, this reduces the expression of the organism-level isotope effect of water column denitrification and thus lowers the mean $\delta^{15}N$ of nitrate required to achieve an isotope balance between inputs and outputs. With these considerations, one study estimates that water-column denitrification is responsible for 30% of fixed N loss from the modern ocean, with sedimentary denitrification responsible for the remainder. Still, this isotope-based budget for marine fixed N remains uncertain.

One limitation of using the N isotopes to investigate N cycling in the ocean is their inability to separate co-occurring processes with competing N isotopic signatures, such as denitrification/N$_2$ fixation and nitrate assimilation/nitrification. Coupled analysis of N and O isotopes in nitrate promises to disentangle such otherwise overprinting processes. Culture studies have demonstrated that the two most important nitrate-consuming processes, nitrate assimilation and denitrification, fractionate the N and O in nitrate with a ratio close to 1:1 (Figure 10). Deviations in the ratio of $\delta^{18}O$ and $\delta^{15}N$ in nitrate from 1:1 can therefore provide information about the nitrate being added by nitrification, such as if it derives from newly fixed N or if there is otherwise undetected nitrate cycling within a water parcel.
Nitrite is an intermediate in oxidative and reductive processes such as nitrification and denitrification. It also serves as a substrate for anammox and can be assimilated by phytoplankton. Only when these processes become uncoupled, such as at the base of the euphotic zone and in oxygen minimum zones, does nitrite accumulate to significant levels (0.1–10 μM). In some oxygen-deficient
regions of the water column in the eastern tropical North Pacific, eastern tropical South Pacific, and the Arabian Sea, nitrite can represent as much of nitrate as 0.2–0.4. Measurements indicate enrichment of NO$_3^-$ in $^{15}$N and concurrent depletion of N$_2$ in $^{15}$N, arising from isotope discrimination during denitrification, with the conversion of NO$_3^-$ to N$_2$. For denitrification in this environment, a enrichment of nitrogen was estimated to be $\sim -25\%$. Modified from Brandes JA, Devol AH, Yoshinari T, Jayakumar DA, and Naqvi SWA (1998) Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles. *Limnology and Oceanography* 43: 1680–1689.

**Figure 8** (a) The $\delta^{15}$N of NO$_3^-$ (filled circles) and N$_2$ (open circles) in water column profiles through an intense denitrification zone in the eastern tropical North Pacific (22°N, 107°W). The shaded interval indicates the depth range with dissolved O$_2$ concentration $<10$ μM where denitrification is encouraged (b, concentration shown in filled squares) and leads to a characteristic NO$_3^-$ deficit (b, open squares) relative to phosphate. Measurements indicate enrichment of NO$_3^-$ in $^{15}$N and concurrent depletion of N$_2$ in $^{15}$N, arising from isotope discrimination during denitrification, with the conversion of NO$_3^-$ to N$_2$. For denitrification in this environment, an enrichment of nitrogen was estimated to be $\sim -25\%$. Modified from Brandes JA, Devol AH, Yoshinari T, Jayakumar DA, and Naqvi SWA (1998) Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles. *Limnology and Oceanography* 43: 1680–1689.

**Figure 9** Simplified global ocean N isotope budget. The y-axis indicates the $\delta^{15}$N of a given flux or pool. The $\delta^{15}$N of N from oceanic N$_2$ fixation, the dominant N input to the ocean, is c. $-1\%$ (‘N$_2$ fixation’ on the left). At steady state, the total denitrification loss (‘denitrification’ on the right) must have the same $\delta^{15}$N as the input. The $\delta^{15}$N of mean ocean nitrate is $\sim 5\%$. Water column denitrification removes nitrate with a low $\delta^{15}$N (‘water column’ at lower right), while sedimentary denitrification removes nitrate with a $\delta^{15}$N similar to that of mean ocean nitrate (‘sedimentary’ at upper right). The need for the flux-weighted $\delta^{15}$N of the denitrification loss to be c. $-1\%$ leads to estimates of partitioning between water-column and sedimentary denitrification in which sedimentary denitrification is found to drive the greater part of the total N loss.

**Figure 10** The $\delta^{18}$O vs. $\delta^{15}$N in nitrate as it is progressively assimilated by four eukaryotic species of marine phytoplankton. Both $\delta^{15}$N and $\delta^{18}$O in nitrate increase as nitrate is consumed, and they do so with an O:N ratio for isotopic discrimination ($^{18}$O:$^{15}$N) of $\sim 1$. Dashed lines show slopes of 1.1 and 0.9 for comparison. Modified from Granger J, Sigman DM, Needoba JA, and Harrison PJ (2004) Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton. *Limnology and Oceanography* 49: 1763–1773.
as 25% of the pool of nitrogen oxides (NO$_3^-$ + NO$_2^-$).

The $\delta^{15}$N of nitrite is expected to reflect the balance of isotopic fractionation during nitrite production and consumption processes. In the eastern tropical North Pacific, the $\delta^{15}$N of nitrite is very low ($-18\%$ to $-7\%$). This $\delta^{15}$N is $\sim 30\%$ lower than the nitrate in the same environment and is lower than expected from denitrification alone, given the known isotope effects for nitrate and nitrite reduction. The meaning of this low $\delta^{15}$N is still not well understood but likely points to other processes acting on the NO$_2^-$ pool. In these regions, nitrite can represent a significant reservoir of N that is depleted in $^{15}$N. Until recently, the two species nitrate and nitrite have typically been combined in isotopic analysis, such that the presence of low $\delta^{15}$N nitrite may have masked some of the $^{15}$N enrichment of nitrate in the oxygen-deficient zone.

Ammonium The $\delta^{15}$N of ammonium reflects the production of ammonium by the degradation of organic N and its consumption by nitrification, ammonium assimilation, and perhaps anammox (Figure 3). Analytical constraints have limited isotopic studies of ammonium to environments with ammonium concentrations greater than 1 $\mu$M, excluding studies in the open ocean. In estuarine systems, where ammonium can be abundant, its $\delta^{15}$N is often high (commonly higher than $+10\%$, with one observation of $+70\%$) and it increases as the ammonium concentration decreases along transects from riverine to marine waters, due to discrimination associated with ammonium consumption by nitrification and/or ammonium assimilation.

In the open ocean interior, below the depth of algal assimilation, essentially all ammonium generated from particles is oxidized to nitrite and then nitrate before it can be transported into or out of a given region. Thus, nitrification should be of limited importance for the isotope dynamics of both particulate and dissolved N once the former has sunk out of the upper ocean. In the open ocean surface mixed layer, it is generally assumed that ammonium generated by remineralization is quickly and entirely assimilated by plankton, in which case the isotope effect associated with its consumption would not play an important role in N isotope dynamics of the open ocean. However, in at least some regions of the upper ocean, ammonium oxidation and assimilation are likely to co-occur. If the isotope effect of ammonium oxidation is greater than that of ammonium assimilation, low-$\delta^{15}$N N will preferentially be routed to the nitrate pool by oxidation and high-$\delta^{15}$N N will be routed back to the PN pool by assimilation. If the isotope effect of oxidation is less than that of assimilation, the opposite will occur. Thus, with better constraints on the isotope effects of ammonium-consuming processes, the isotopes of upper ocean N pools promise to provide an integrative constraint on the relative rate of nitrification in the upper ocean, especially when paired with the O isotopes of nitrate (see above).

Dissolved organic nitrogen DON concentrations are significant in the open ocean, typically $\geq 4$ $\mu$M in surface waters, decreasing to $\sim 2$ $\mu$M in deep water. Fluxes associated with the DON pool are among the least constrained terms in the modern marine N budget and may be important. Studies to date of bulk DON have been in the subtropical ocean, where DON is by far the dominant N pool in the surface ocean. In the surface mixed layer at the Bermuda Atlantic Time-series site in the Sargasso Sea, the concentration and $\delta^{15}$N of TON are $\sim 4$ $\mu$M and $\sim 4\%$ (TON being total organic N, or DON plus the small pool of PN) (Figure 6). This $\delta^{15}$N is similar to or slightly higher than the shallow subsurface nitrate that is entrained into the euphotic zone during wintertime vertical mixing (Figure 6(b)). Minimal gradients in the concentration and $\delta^{15}$N of DON in this region of the upper ocean hinder reconstruction of fluxes of DON or the $\delta^{15}$N of those fluxes. There is a weak increase in the concentration of TON into the surface layer and an accompanying decrease in its $\delta^{15}$N (Figures 6(a) and 6(b)). Thus, there may be an input of low-$\delta^{15}$N N into the surface DON pool, which is remineralized at depth, but this requires further validation. Progress on DON $\delta^{15}$N dynamics would be aided by a method to remove nitrate from samples without compromising the DON pool, which would make subsurface waters and high-nitrate surface waters more accessible to study. Ongoing work on separable fractions of the DON pool (e.g., the high-molecular-weight fraction and its components) is also promising.

Dissolved gases Dissolved N$_2$ in equilibrium with atmospheric N$_2$ at the surface has a $\delta^{15}$N of 0.6%. The isotopic composition of dissolved N$_2$ does not vary greatly in ocean profiles, except in zones of denitrification. Production of low-$\delta^{15}$N N$_2$ in denitrification zones results in measured N$_2$ $\delta^{15}$N as low as 0.2% (Figure 8(a)). Since N$_2$ is the main product of denitrification, its $\delta^{15}$N provides a test of the nitrate-based estimates of the isotope effect for this process.
Dissolved N₂O is produced by nitrification and is both produced and consumed by denitrification. The marine flux of N₂O is perhaps one-third of the global flux of this greenhouse gas to the atmosphere; therefore, an understanding of the mechanisms of N₂O production and their regulation in the ocean is an important goal. Culture studies indicate that bacterial production of N₂O by nitrification and denitrification produces gas depleted in ¹⁵N and ¹⁸O relative to the source material. Consumption of N₂O by denitrification leaves the residual gas enriched in ¹⁵N and ¹⁸O, with δ¹⁵N of N₂O as high as 40‰ measured in the Arabian Sea. In oxygenated waters of the open ocean, nitrification likely dominates N₂O production and its isotopic profile. A depth profile in the subtropical North Pacific shows three main features (Figure 11): (1) isotopic equilibrium with atmospheric N₂O at the surface; (2) a subsurface δ¹⁵N minimum attributed to nitrification; and (3) a broad δ¹³N maximum in deeper waters probably due to N₂O consumption, perhaps in the denitrifying waters of the eastern Pacific margin. In and near denitrification zones, a strong maximum in the δ¹⁵N of N₂O is observed, presumably due to isotope fractionation associated with N₂O consumption (via reduction to N₂).

**Particulate N**

**Suspended particles** A typical profile of suspended particles has its lowest δ¹⁵N in the surface layer, increasing below the euphotic zone (Figure 12). The δ¹⁵N of suspended particles reflects in part the δ¹⁵N of nitrate supplied to the surface ocean and, in nutrient-rich surface waters, isotope discrimination associated with its incomplete assimilation. However, the low δ¹⁵N in the surface layer is typically lower than what would be expected solely from nitrate assimilation. This low δ¹⁵N has two competing explanations: N₂ fixation and N recycling. As described earlier, N₂ fixation is expected to add fixed N with a δ¹⁵N of c. −1‰ to surface waters. The isotopic effect of N recycling originates from heterotrophic processes. Zooplankton appear to release ammonium which has a lower δ¹⁵N than their food source, making their tissues and solid wastes ~3‰ higher in δ¹⁵N than their food source. The low-δ¹⁵N ammonium is consumed by phytoplankton and thus retained in the surface ocean N pool, while the ¹⁵N-enriched PN is preferentially exported as sinking particles, leading to a lower δ¹⁵N of surface PN in regions where recycled N is an important component of the gross N supply to phytoplankton. Low δ¹⁵N observed in

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**Figure 11** Depth profiles of (a) N₂O concentration and (b) δ¹⁵N and (c) δ¹⁸O of N₂O at station ALOHA in the subtropical North Pacific (22° 45' N, 158° W) during four separate cruises. The solid line in (a) indicates theoretical saturation with atmospheric N₂O at in situ temperatures and salinities. The minima in δ¹⁵N and δ¹⁸O around 200 m are thought to be due to significant in situ production of N₂O from nitrification. The broad isotopic maxima at depth are likely due to N₂O consumption, perhaps in the denitrifying waters along the eastern Pacific margin. The filled squares at the top of (b) and (c) represent measurements of δ¹⁵N and δ¹⁸O of atmospheric N₂O during the Hawaii Ocean Time-series 76 cruise, and arrows indicate the range of historical measurements as of the late 1980s. Reprinted from Dore JE, Popp BN, Karl DM, and Sansone FJ (1998) A large source of atmospheric nitrous oxide from subtropical North Pacific surface waters. Nature 396: 63–66.
Nitrogen isotopic values of suspended particulate matter and sinking particles (as collected by sediment traps) in the subtropical North Atlantic Ocean near BATS (31° 50′ N, 64° 10′ W; see Figure 6). The profiles of suspended PN show the representative depth gradient in $\delta^{15}N$, with lower $\delta^{15}N$ in the surface ocean than at depth. The $\delta^{15}N$ of the sinking flux shows a decrease with depth, which has also been observed in other regions. Reprinted from Altabet MA, Deuser WG, Honjo S, and Stienen C (1991) Seasonal and depth-related changes in the source regions. Reprinted from Nature 354: 136–139.

![Figure 12](image)

Suspended PN from the Antarctic and other high-latitude regions, beyond what is expected from isotope discrimination during nitrate assimilation, is unlikely to be due to $N_2$ fixation and thus likely reflects N recycling. In the low-latitude, low-nutrient ocean surface, such as the Sargasso Sea and western tropical Pacific, the relative importance of $N_2$ fixation and N recycling in producing low-$\delta^{15}N$ surface particles is uncertain. Because of its implications for the rates of $N_2$ fixation and N recycling, this question deserves further study.

The $\delta^{15}N$ of suspended particles in the subsurface is typically ~6‰ higher than suspended particles in the surface ocean and ~3‰ higher than the sinking flux (Figure 12). The $\delta^{15}N$ of deep particles is consistent with the inference that deep particles are the breakdown products of material exported from the surface, and that bacteria preferentially remineralize low-$\delta^{15}N$ PN.

Isotopic analysis of zooplankton and organisms at higher trophic levels can provide insights into the marine N cycle. The ‘trophic effect’, an observed ~3‰ increase in $\delta^{15}N$ per trophic level that presumably results from isotope discrimination during metabolism of N-bearing organic matter, is used widely in food-web studies. N isotopic analysis of specific amino acids within organisms and organic matter promises new insights, as some amino acids increase in $\delta^{15}N$ with trophic level while others preserve the $\delta^{15}N$ of the food source.

**Sinking PN and sedimentary N** Because vertical sinking is an important mode of N export from the surface ocean, the $\delta^{15}N$ of the sinking flux is one of the most valuable N isotopic constraints on modern ocean processes. Combined with other isotopic data, sinking flux $\delta^{15}N$ data can provide information on the routes and mechanisms of nitrate supply and can be used to constrain other sources of N to the surface. The sinking flux also transfers the isotopic signal from the surface ocean to the seafloor, providing the link through which the sediment column records the history of surface ocean processes (Figure 7(c)). Sinking particles collected in depth arrays of sediment traps often show a modest decrease in $\delta^{15}N$ with depth (Figure 12). This trend runs contrary to our expectations for the isotopic change of particulate matter as it degrades, and it currently lacks a compelling explanation.

There is generally a good correlation between the $\delta^{15}N$ of surface sediments and sinking particulate $\delta^{15}N$ from the overlying water column. In regions of the ocean where a relatively large fraction of the organic rain is preserved in the sediment column, as occurs along continental margins, this correlation is excellent. In open ocean sediments where only a very small fraction of N is preserved, spatial patterns in the $\delta^{15}N$ of sediment core tops mirror those in the water column above (Figure 7(c)), but a significant $^{15}N$ enrichment (of ~2–5‰) is observed in the sediment N relative to sinking particles. Upon burial, reactions in the shallow sediment column known collectively as ‘diagenesis’ can cause a clear increase in the $\delta^{15}N$ of PN as it is incorporated into the sediment mixed layer. While some studies have found that sedimentary diagenesis has not greatly affected the paleoceanographic information provided by specific sedimentary records, it cannot be assumed that changes in the ‘diagenetic offset’ are unimportant. To address concerns regarding alteration of both sinking and sedimentary bulk $\delta^{15}N$, studies are increasingly focusing on isolating specific N components, the $\delta^{15}N$ of which is insensitive to diagenesis, such as N bound within the mineral matrix of microfossils, or that does not change in $\delta^{15}N$ as it is degraded, such as chlorophyll degradation products.

**N isotopes in the sedimentary record** The isotopes of sedimentary N are used to investigate past changes in the marine N budget and the internal cycling of N.
within the ocean. The processes and parameters reflected by the δ¹⁵N of sedimentary N include (1) mean ocean nitrate δ¹⁵N, (2) regional subsurface nitrate ¹⁵N depletion or enrichment relative to the global ocean owing to N₂ fixation or denitrification, (3) regional isotope dynamics associated with partial nitrate consumption in surface waters, and (4) possible direct contribution of newly fixed N to sinking PN. Paleoceanographers have focused on sediment δ¹⁵N records underlying three environments where a single process or parameter is thought to dominate changes in sinking δ¹⁵N. In oligotrophic regions, sediment δ¹⁵N is assumed to reflect the δ¹⁵N of mean ocean nitrate and therefore the global ocean balance of inputs and outputs of fixed N (Figure 13(a)). In denitrifying regions, sediment δ¹⁵N has been taken to largely reflect changes in regional ¹⁵N enrichment due to water column denitrification (Figure 13(b)). In high-nutrient regions, sediment δ¹⁵N primarily records the degree of nitrate consumption by algal assimilation, providing insight into changes in balance between gross nitrate supply to surface waters and export of organic N from the surface (Figure 13(c)). However, it must be kept in mind that multiple processes may affect the δ¹⁵N of sediments in any given region. For example, even in low-nutrient regions far from denitrification zones, the sediment δ¹⁵N record may record changes not

Figure 13  Sedimentary δ¹⁵N records spanning the past 140 ky, which encompass recent ice ages (shaded, marine oxygen isotope stages 2, 4, and 6, with 2 and 6 being the most extreme) and interglacials (stages 1, 3, and 5, with 1 and 5 being the most extreme). (a) Sediment record underlying the oligotrophic South China Sea (8° 30.4 N, 112° 19.9 E), where sedimentary δ¹⁵N is expected to track, with some offset, the δ¹⁵N of nitrate in the western Pacific thermocline. The western Pacific thermocline nitrate, in turn, is assumed to have maintained a constant isotopic relationship with deep ocean nitrate. The small magnitude of variation in δ¹⁵N (<1.5‰) and lack of correlation with glacial/interglacial transitions suggest that mean ocean nitrate δ¹⁵N remained unchanged through shifts in Earth’s climate. (b) Sedimentary δ¹⁵N record underlying the eastern tropical North Pacific (22° 23.3 N, 107° 04.5 W), a major region of denitrification. Interglacials are characterized by high δ¹⁵N (8–9‰), with δ¹⁵N 2–3‰ lower during glacial periods. Low δ¹⁵N, along with coincident evidence for decreased productivity and higher oxygen content in the mid-depth water-column, indicates decreased water column denitrification during glacial periods. (c) Sedimentary δ¹⁵N record from the high-nitrate Antarctic Zone of the Southern Ocean (54° 55 S, 73° 50 E) shows higher δ¹⁵N during the period spanning glacial stages 2–4, suggesting greater algal utilization of nitrate in the surface ocean. Coupled with evidence of lower glacial productivity, the glacial ¹⁵N enrichment suggests reduced nutrient supply from below. All data shown are of bulk sediment. The sedimentary δ¹⁵N record shown in (b) is from a region of high organic matter preservation in the sediments, where bulk sedimentary δ¹⁵N correlates well with sinking δ¹⁵N. The records in (a) and (c) are from regions where a diagenetically driven difference is observed between sinking and sedimentary N, which introduces uncertainties in interpretation. (a) Core 17961 from Kienast M (2000) Unchanged nitrogen isotopic composition of organic matter in the South China Sea during the last climatic cycle: Global implications. *Paleoceanography* 15: 244–253. (b) Core NH8P from Ganeshram RS, Pederson TF, Calvert SE, and Murray JW (1995) Evidence from nitrogen isotopes for large changes in glacial–interglacial oceanic nutrient inventories. *Nature* 376: 755–758. (c) Core MD84-552 from François R, Altabet MA, Yu E-F, et al. (1997) Contribution of Southern Ocean surface-water stratification to low atmospheric CO₂ concentrations during the last glacial period. *Nature* 389: 929–935.
only in mean ocean nitrate $\delta^{15}$N but also in the $\delta^{15}$N of nitrate imported from subpolar regions and in the isotopic imprint of N$_2$ fixation.

**Concluding Remarks**

The study of the N isotopes in the ocean is young relative to that of the other light isotopes (e.g., carbon, oxygen, and sulfur), with much of the work to date developing the methods needed to measure different forms of oceanic N and establishing the isotope systematics of N cycle processes that are necessary to interpret observed patterns. Over the previous decades, the N isotopes have had perhaps their greatest impact on foodweb studies and in paleoceanographic work. In the case of the latter, this reflects the ability of the N isotopes to provide basic constraints on environmental conditions when there are few other indicators available. Recent and ongoing method development is greatly improving our ability to measure diverse N pools in the ocean. This is yielding a new generation of N isotope studies that promise to provide geochemical estimates for the rates and distributions of N fluxes in the modern ocean, complementing instantaneous ‘bottle’ measurements of these fluxes as well as other geochemical approaches. Fundamental aspects of the oceanic N cycle are still poorly understood, and the N isotopes provide an important tool for their study.

**See also**

Nitrogen Cycle, Redfield Ratio, Sedimentary Record, Reconstruction of Productivity from the.

**Further Reading**


Biographical Sketch

Daniel Sigman is a professor in the Department of Geosciences at Princeton University. He received a bachelor’s degree in geology from Stanford University and a PhD in marine geology and geophysics from the Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography. Sigman studies the cycles of biologically important elements and their interaction with changing environmental conditions through the course of Earth history. His current research activities include the development and application of stable isotope methods by which to track the marine nitrogen cycle, today and in the past, and the construction of simple geochemical models for paleoceanographic studies.

Kristen Karsh is a PhD student in the Department of Geosciences at Princeton University and the Institute of Antarctic and Southern ocean studies at the University of Tasmania, Australia. She received her bachelor’s degree in geology and geophysics from Yale University and her master’s degree in Antarctic and Southern Ocean studies from the University of Tasmania. She was the recipient of a Fulbright Award to study nitrogen isotope biogeochemistry in the Southern Ocean. Her current research focuses on the physiological and environmental controls on nitrogen isotope fractionation by marine phytoplankton.

Karen Casciotti is an associate scientist in the Marine Chemistry and Geochemistry Department at the Woods Hole Oceanographic Institution. She received a bachelor’s degree in environmental engineering science at the California Institute of Technology, a master’s degree in oceanography from the University of California at San Diego’s Scripps Institution of Oceanography, and a PhD in geosciences from Princeton University. Her current research focuses on microbial diversity and nitrogen cycle biogeochemistry, with an emphasis on using nitrogen and oxygen isotopes to understand how nitrogen is cycled in oceanic suboxic zones. She has participated in 10 research cruises in the Pacific, Indian, and Southern Oceans. In addition, she co-teaches introduction to isotope chemistry at the Woods Hole Oceanographic Institution.