Ocean Process Tracers: Nitrogen Isotopes in the Ocean (MS 632)

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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”) 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 0.36765% ±0.00081%. Natural samples exhibit small deviations from the standard ratio, which are expressed in $\delta$-notation (in units of permil, ‰):

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

In this notation, the \( \delta^{15}\text{N} \) of atmospheric \( \text{N}_2 \) 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 dominated by kinetic fractionation associated with the conversions of \( \text{N} \) from one form to another. The kinetic isotope effect, \( \varepsilon \), of a given reaction is defined by the difference in rates with which the two \( \text{N} \) isotopes are converted from reactant to product:

\[ \varepsilon \text{ (‰)} = (^{14}\text{k}^{15}\text{k} - 1)*1000, \]  \text{ equation 2} 

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

**Measurements**

The isotopic analysis of \( \text{N} \) relies on the generation of a stable gas as the analyte for isotope ratio mass spectrometry. On-line combustion to \( \text{N}_2 \) is currently the standard method for the preparation of an \( \text{N} \) sample for isotopic analysis. With “off-the-shelf” technology, a typical sample size requirement is 1-2 \( \mu \text{mol N} \) per analysis. Gas chromatography followed by combustion to \( \text{N}_2 \) is improving as a technique for specific organic compounds, amino acids in particular, although the polarity of many \( \text{N} \) 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 1970’s, the $\delta^{15}N$ of marine nitrate ($\text{NO}_3^-$), nitrite ($\text{NO}_2^-$), and ammonium ($\text{NH}_4^+$) has been analyzed by conversion to ammonia gas and collection of the cationic ammonium form for subsequent conversion to $\text{N}_2$ (often referred to as the ammonia “distillation” and “diffusion” methods). Recently, more sensitive isotope analysis methods have been developed for nitrate and nitrite in which these species are converted to nitrous oxide ($\text{N}_2\text{O}$), followed by isotopic analysis of this gas (the “bacterial” or “denitrifier” method and the “chemical” or “azide” method). The $\text{N}_2\text{O}$-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 ($\text{NH}_4^+$), which can be converted to nitrate and/or nitrite. With respect to dissolved gases, methods of collection and isotopic analysis have been developed for $\text{N}_2$ and $\text{N}_2\text{O}$, with recent progress on isotopomer analysis of $\text{N}_2\text{O}$ (i.e. distinguishing $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ from $^{14}\text{N}^{15}\text{N}^{16}\text{O}$).

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 central parameter, and the $\delta^{15}N$ of the
initial reactant N pool ($\delta^{15}N_{\text{initial}}$) and kinetic isotope effect ($\epsilon$) are the two central isotopic parameters. If a transformation proceeds with a constant isotope effect and if the reactant N pool is not replenished during the transformation process, then the process can be described in terms of Rayleigh fractionation kinetics, which define the isotopic variation of the reactant N pool (equation 3), the instantaneously generated product N (equation 4), and the integrated product N pool (equation 5) as a given reservoir of reactant N is consumed (Figure 1):

$$
\delta^{15}N_{\text{reactant}} = \delta^{15}N_{\text{initial}} - \epsilon \{\ln(f)\} \quad \text{equation 3}
$$

$$
\delta^{15}N_{\text{inst}} = \delta^{15}N_{\text{reactant}} - \epsilon \quad \text{equation 4}
$$

$$
\delta^{15}N_{\text{int}} = \delta^{15}N_{\text{initial}} + \epsilon \{f/(1-f)\} \ln(f) \quad \text{equation 5}
$$

where $f$ is the fraction of the reactant remaining, $\delta^{15}N_{\text{initial}}$ is the $\delta^{15}$N of the initial reactant N pool, and $\epsilon$ is the kinetic isotope effect of the transformation (the above equations being simplified, approximate forms of the full expressions). The Rayleigh model is often used to describe events in the ocean, such as the uptake of nitrate by phytoplankton during a bloom.

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 equations apply to the reactant N pool (equation 6) and the product N pool (equation 7) (Figure 1):

$$
\delta^{15}N_{\text{reactant}} = \delta^{15}N_{\text{initial}} + \epsilon(1 - f) \quad \text{equation 6}
$$

$$
\delta^{15}N_{\text{product}} = \delta^{15}N_{\text{initial}} - \epsilon(f) \quad \text{equation 7}
$$
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

$\text{N}_2$ fixation is the major input of fixed N to the ocean (Figure 2). $\text{N}_2$ fixation is carried out by $\text{N}_2$ fixers, cyanobacteria and other microorganisms able to catalyze the conversion of atmospheric $\text{N}_2$ 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 $\text{N}_2$ fixer, have yielded a $\delta^{15}\text{N}$ of $\sim -2$ to $+0.5\%e$. Taking into account the $\delta^{15}\text{N}$ of dissolved $\text{N}_2$ (0.6‰ in the surface mixed layer), this range in $\delta^{15}\text{N}$ is consistent with, but perhaps less variable than, the range in isotope effects estimated from culture studies of marine and terrestrial $\text{N}_2$ fixers, $\sim 0$ to 4‰ (Table 1). An average $\delta^{15}\text{N}$ of -1‰ has been suggested for the fixed N input to the ocean from $\text{N}_2$ 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 $\delta^{15}\text{N}$ in pristine river systems ranges mostly from 0 to 5‰. However, biological processing along the flow path and in estuaries (in particular, by denitrification; see below) can alter the $\delta^{15}\text{N}$ of the final inputs from terrestrial runoff in complex ways. Anthropogenic inputs often increase the $\delta^{15}\text{N}$ of a system because they encourage denitrification. A wide range in $\delta^{15}\text{N}$ of inorganic ($\sim -16$ to 10‰) and organic
(~ -8 to 1‰) N in atmospheric inputs has been observed, with increasing evidence that at least some of this variability can provide insight into sources and processes. In the face of large uncertainties, a pre-industrial mean $\delta^{15}N$ of 4‰ for terrestrial runoff and -4‰ 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, $^{15}N$, progressively enriching the remaining nitrate pool in $^{15}N$ as nitrate consumption proceeds. Culture studies of denitrifying bacteria suggest (with some exceptions) an isotope effect of ~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 unconsumed nitrate effluxing from the cell back into ambient waters allows the enzyme-level isotope effect to be expressed. Where it occurs in low-oxygen regions of the mid-depth ocean, water column denitrification causes a clear elevation in the $\delta^{15}N$ of nitrate, and it is the reason that global ocean nitrate $\delta^{15}N$ 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 $\delta^{15}N$ of water column nitrate. The high $\delta^{15}N$ 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, yielding an ‘effective’ isotope effect of 3‰ or less in the 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 (from nitrate reduction or ammonium oxidation) oxidizes ammonium to produce N₂ (\(\text{NO}_2^- + \text{NH}_4^+ \rightarrow N_2 + 2\text{H}_2\text{O}\)). This process, which has recently received much attention, 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, remineralization processes are the source of the ammonium, and both are completely consumed in the environment where anammox occurs, then the isotope discrimination would simplify to that of the nitrate reduction by denitrifiers combined 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 conversion of fixed N to N₂ by ‘denitrification’ have inherently included the effect of anammox, in that they regress the nitrate \(\delta^{15}\text{N}\) increase against the total nitrate deficit relative to phosphate.

Internal cycling

\textit{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 (Figure 2). Field-based estimates of the isotope effect of nitrate assimilation range from 4-10‰, 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 enzyme-level isotope effect is expressed by efflux of unconsumed nitrate out of the cell, as appears to be the case with denitrifiers as well. The lower range of isotope effect estimates associated with algal nitrate assimilation than with denitrification suggests proportionally less nitrate efflux by algae, perhaps related to the fact that fixed N is often scarce in the surface ocean. Some studies suggest the degree of efflux and isotope effect of nitrate assimilation may vary with growth conditions; one set of studies of the diatom *Thalassiosira weissflogii* showed a higher isotope effect under light-limited growth than under growth limited by iron or temperature. 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 value is of significance in the application of N isotopes to various questions in the modern and past oceans. Thus, it should be a priority to develop a predictive understanding of its controls.
Other forms of fixed N assimilated by phytoplankton (ammonium, nitrite, and urea) are generated 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 δ¹⁵N of the remaining ammonium pool. Isotope effect estimates based on ammonium concentrations and δ¹⁵N in these environments range from ~6.5-18.5‰ (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 bacteria. Isotopic discrimination may occur at all steps involved in remineralization. Field studies generally suggest that both bacteria and zooplankton preferentially degrade low-δ¹⁵N particulate N to ammonium, yielding residual organic matter relatively high in ¹⁵N. The wide spectrum of reactions involved in organic N degradation and the heterogeneous nature of organic matter (comprised of compounds with distinct δ¹⁵N 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 $\leq 3\%e$.

Culture studies indicate a large isotope effect for the oxidation of ammonium to nitrite, the first step in nitrification (Table 1). Estimates of the isotope effect for marine nitrifiers (~14-19‰) are lower than those for terrestrial nitrifiers (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 nitrifiers (Table 1).

**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), with hypotheses that this isotopic depletion is due to the oxidation of newly fixed N, which, as described above, has a $\delta^{15}N$ of ~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 $\sim 5\%$e, despite large inter-basin differences in nitrate concentration. The lack 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 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 can be elevated to above $15\%$e (Figure 8). The subsurface $\delta^{15}$N maximum occurs in the core of the oxygen minimum and is correlated with the 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 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 (~ -1‰, considering $N_2$ fixation and terrestrial
sources) (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‰ for N loss. That the
modern mean oceanic nitrate $\delta^{15}N$ is ~5‰, 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 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 δ^{18}O and δ^{15}N in nitrate from 1:1 can therefore provide information about the nitrate being added by nitrification, such as whether it derives from newly fixed N.

**Ammonium**

The δ^{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 μM, excluding studies in the open ocean. In estuarine systems, where ammonium can be abundant, its δ^{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, there is likely to be simultaneous oxidation and
assimilation of ammonium. 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.
The isotopes of upper ocean N pools promise to provide an integrative constraint on the
relative rate of nitrification in the upper ocean.

*Dissolved organic nitrogen*

Dissolved organic N (DON) concentrations are significant in the open ocean,
typically $\geq 2 \mu M$ in deep water and $\geq 4 \mu M$ in surface waters. 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
particulate N) (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 6b). 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 (Figure 6a and 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. Other promising avenues include work on separable fractions of the DON pool (e.g., the high molecular weight fraction and its components).

**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). 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 N$_2$O is produced by nitrification and both produced and consumed by denitrification. The marine flux of N$_2$O is perhaps one third of the global flux of this greenhouse gas to the atmosphere; therefore, an understanding of the mechanisms of N$_2$O production and their regulation in the ocean is an important goal. Culture studies indicate that bacterial production of N$_2$O by nitrification and denitrification produces gas depleted in $^{15}$N and $^{18}$O relative to the source material. Consumption of N$_2$O by denitrification leaves the residual gas enriched in $^{15}$N and $^{18}$O, with $\delta^{15}$N of N$_2$O as high as 40‰ measured in the Arabian Sea. In oxygenated waters of the open ocean, nitrification likely dominates N$_2$O production and its isotopic profile. A depth profile in the subtropical North Pacific shows three main features (Figure 11): 1) isotopic equilibrium with atmospheric N$_2$O at the surface, 2) a subsurface $\delta^{15}$N minimum attributed to nitrification, and 3) a broad $\delta^{15}$N maximum in deeper waters probably due to N$_2$O consumption, perhaps in the denitrifying waters of the eastern Pacific margin. In and near
denitrification zones, a strong maximum in the $\delta^{15}$N of N$_2$O is observed, presumably due to isotope fractionation associated with N$_2$O consumption (via reduction to N$_2$).

Particulate N

*Suspended particles*

A typical profile of suspended particles has its lowest $\delta^{15}$N in the surface layer, increasing below the euphotic zone (Figure 12). The $\delta^{15}$N of suspended particles reflects in part the $\delta^{15}$N of nitrate supplied to the surface ocean and, in nutrient-rich surface waters, subsequent fractionation associated with nitrate assimilation. However, the low $\delta^{15}$N in the surface layer is typically lower than what would be expected solely from nitrate assimilation. This low $\delta^{15}$N has two competing explanations: N$_2$ fixation and N recycling. As described earlier, N$_2$ fixation is expected to add fixed N with a $\delta^{15}$N of ~-1‰ to surface waters. The isotopic effect of N recycling originates from heterotrophic processes. Zooplankton appear to release ammonium which has a lower $\delta^{15}$N than their food source, making their tissues and solid wastes ~3‰ higher in $\delta^{15}$N than their food source. The low-$\delta^{15}$N ammonium is consumed by phytoplankton and thus retained in the surface ocean N pool, while the $^{15}$N-enriched particulate N is preferentially exported as sinking particles, leading to a lower $\delta^{15}$N of surface particulate N in regions where recycled N is an important component of the gross N supply to phytoplankton. Low $\delta^{15}$N observed in suspended particulate N from the Antarctic and other high latitude regions 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\textsubscript{2} fixation and N recycling, this question deserves further study.

The $\delta^{15}$N of suspended particles in the subsurface is typically $\sim 6\%$ higher than suspended particles in the surface ocean and $\sim 3\%$ higher than the sinking flux (Figure 12). Since suspended particles in the subsurface are thought to derive from sinking particles, it is inferred that their higher $\delta^{15}$N is the result of isotopic discrimination during degradation and consumption by bacteria. 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 particulate N.

In addition to suspended particles, typically comprised of autotrophic primary producers, isotopic analysis of zooplankton and organisms at higher trophic levels can provide insights into the marine N cycle. The ‘trophic effect’, an observed $\sim 3\%$ increase per trophic level that presumably results from isotopic discrimination during metabolism of N-bearing organic matter, is used widely in foodweb 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 particulate N 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 needed for the sediment column to record the history of surface ocean processes (Figure 7c). 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 7c), 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 particulate N 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 presumed that changes in the “diagenetic offset” have not occurred within any given sediment column. 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.
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 $\delta^{15}N$ of sedimentary N include 1) mean ocean nitrate $\delta^{15}N$, 2) regional subsurface nitrate $^{15}N$ depletion or enrichment relative to the global ocean owing to $N_2$ 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 $\delta^{15}N$ records underlying three environments where a single process or parameter is thought to dominate changes in sinking $\delta^{15}N$. In oligotrophic regions, sediment $\delta^{15}N$ is assumed to reflect the $\delta^{15}N$ of mean ocean nitrate and therefore the global ocean balance of inputs and outputs of fixed N (Figure 13a). In denitrifying regions, sediment $\delta^{15}N$ has been taken to largely reflect changes in regional $^{15}N$ enrichment due to water column denitrification (Figure 13b). In high nutrient regions, sediment $\delta^{15}N$ 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 13c). However, it must be kept in mind that multiple processes may affect the $\delta^{15}N$ of sediments in any given region. For example, sediment $\delta^{15}N$ in a denitrifying zone may respond to changes in the $\delta^{15}N$ of mean ocean nitrate, the amplitude of regional nitrate $\delta^{15}N$ enrichment by water column denitrification in the subsurface, and possible changes in local nitrate consumption by algal assimilation.
Concluding remarks

The study of the N isotopes in the ocean is young relative to those 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.

Further reading


Altabet, M.A., and R. Francois, 1994. The use of nitrogen isotopic ratio for reconstruction of past changes in surface ocean nutrient utilization, in Carbon Cycling in


Keywords: fixed nitrogen, nitrate, ammonium, particulate nitrogen, dissolved organic nitrogen, sediment trap, sediment, nitrogen fixation, nitrification, denitrification, nitrogen budget, isotope fractionation, nutrient, phytoplankton, assimilation
Cross references: 271, 275, 176, 251

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<table>
<thead>
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<th>Process</th>
<th>Isotope effect (ε)</th>
<th>Details</th>
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<td>1.8 - 3.0 ‰</td>
<td><em>Trichodesmium</em> spp.</td>
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<td></td>
<td>- 0.2 ‰</td>
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<tr>
<td></td>
<td>-0.4 - 0.2‰</td>
<td>Western Tropical Atlantic</td>
</tr>
<tr>
<td>Denitrification ($NO_3^- \rightarrow N_2$)</td>
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<td><em>Pseudomonas stutzeri</em> (marine)</td>
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<tr>
<td>Water column</td>
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<td>Sedimentary</td>
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<tr>
<td></td>
<td>$12 - 16 %$</td>
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Figure Captions

**Figure 1.** The $\delta^{15}$N of reactant and product N pools of a single unidirectional reaction as a function of the fraction of the initial reactant supply that is left unconsumed, for two different models of reactant supply and consumption, following the approximate equations given in the text. The Rayleigh model (black lines) applies when a closed pool of reactant N is consumed. The steady state model (grey lines) applies when reactant N is supplied continuously. The same isotopic parameters, an isotope effect ($\epsilon$) of $5\%$ and a $\delta^{15}$N of $5\%$ for the initial reactant supply, are used for both the Rayleigh and steady state models. $\epsilon$ is evident as the isotopic difference between reactant N and its product (the instantaneous product in the case of the Rayleigh model).

**Figure 2.** Marine 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 (NO$_3^-$). Inputs are marine N$_2$ 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 $\delta^{15}$N of nitrate (dark area). Remineralization of newly-fixed N can explain the low $\delta^{15}$N of nitrate in the shallow subsurface, or thermocline, of some regions (light area). Internal cycling is represented with dashed arrows. Nitrate supplied from the deep ocean and thermocline is assimilated in the surface ocean. Particulate N is recycled in the surface ocean, degraded to ammonium (NH$_4^+$) that is subsequently assimilated or solubilized to dissolved organic
nitrogen (DON). 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 $\delta^{15}N$ of particulate suspended and sinking N, dissolved organic N, and thermocline nitrate is taken from the North Atlantic. Question marks indicate the greatest uncertainties, due to variation in the available data and/or insufficient data.

**Figure 3.** Schematic diagram of the processes and pools of N central to the internal cycling of N in the ocean. The isotope effects shown here are based on laboratory studies. Dashed arrows represent assimilation of dissolved species into particulate matter and solid arrows represent remineralization. Complete consumption of the ammonium pool by assimilation in the surface ocean or by nitrification in the ocean interior causes the relatively high isotope effects associated with these processes to have little effect on N isotope dynamics. However, in regions where ammonium assimilation and nitrification co-occur, their isotope effects will impact the $\delta^{15}N$ of their respective products – particulate N and nitrate. The processes surrounding DON production and utilization are not well understood from an isotopic perspective but are thought to play an important role in N cycling.

**Figure 4.** Isotopic fractionation during nitrate ($\text{NO}_3^-$) assimilation by a culture of the marine diatom *Thalassiosira pseudonana*. (A) Time series of $\text{NO}_3^-$ concentration in the culture medium (filled circles), particulate nitrogen (PN) (open circles), and fluorescence
(filled triangles), a measure of phytoplankton biomass; (B) $\delta^{15}$N of PN accumulated over the same time period; (C) $\delta^{15}$N of PN accumulated during log phase of growth plotted versus F, a measure of nitrate utilization. F is $-f/(1-f)\ln f$, where $f$ is the fraction of initial NO$_3^-$ remaining at the time the culture is sampled. $\varepsilon$ is calculated to be 4.5‰ from the slope of the regression in panel C, according to the Rayleigh integrated product equation (see text, equation 5). Dashed lines in B and C represent the initial $\delta^{15}$N of the source NO$_3^-$ (3.8‰). Reprinted with permission from Waser, N.A.D., P.J. Harrison, B. Nielsen, S.E. Calvert, and D.H. Turpin, 1998, *Limnology and Oceanography*, 43: 215 – 224.

**Figure 5.** The instantaneous effect of different marine N cycle processes on nitrate $\delta^{15}$N and concentration, assuming an initial nitrate $\delta^{15}$N of 5‰. The trajectories are for reasonable estimates of the isotope effects, and they depend on the initial nitrate $\delta^{15}$N as well as the relative amplitude of the changes in nitrate concentration (30% for each process in this figure). A solid arrow denotes a process that adds or removes fixed N from the ocean, while a dashed line denotes a component of the internal cycling of oceanic fixed N. The effects of these two types of processes can be distinguished in many cases by their effect on the concentration ratio of nitrate to phosphate in sea water. The actual impact of the different processes on the N isotopes varies with environment. For instance, if phytoplankton completely consume the available nitrate in a given environment, the isotope effect of nitrate uptake plays no major role in the $\delta^{15}$N of the various N pools and fluxes; the effect of nitrate generation by organic matter degradation and nitrification, not shown here, will depend on this dynamic. Similarly, the lack of a large isotope effect for
sedimentary denitrification is due to the fact that nitrate consumption by this process can approach completion within sedimentary pore waters.

**Figure 6.** Depth profiles of (A) [NO$_3^-$] (open circles) and [TON] (total organic N, or DON plus the small pool of particulate N) (open squares) and (B) NO$_3^-$ $\delta^{15}$N (filled circles) and TON $\delta^{15}$N (filled squares) at the Bermuda Atlantic Time-Series Study site in the oligotrophic Sargasso Sea. Low NO$_3^-$ $\delta^{15}$N in the thermocline has been proposed to reflect N$_2$ fixation, while the increase 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- $\delta^{15}$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 (~2.4‰). High nitrate concentrations below 250 m prevent accurate assessment of TON $\delta^{15}$N using published methods. The $\delta^{15}$N of sinking particles collected at 100 m (3.7‰) is indicated by the arrow at top of panel B; surface suspended PN $\delta^{15}$N is -0.2‰ (not shown). Nitrate and TON data are the means of monthly measurements between June 2000 and May 2001. Modified from Knapp, A.H., D.M. Sigman, and F. Lipschultz, 2005, *Global Biogeochemical Cycles*, 19: doi:10.1029/2004GB002320. Sinking and suspended PN $\delta^{15}$N data from Altabet, M.A., 1988, *Deep Sea Research*, 35: 535-554.

**Figure 7.** Nitrate $\delta^{15}$N data from the Southern Ocean show the effect of uptake by phytoplankton. A depth profile of nitrate concentration (A) and $\delta^{15}$N (B) from the Antarctic region of the east Indian Ocean (53.2°S, 115°E) shows a decrease in nitrate
concentration into the surface layer and an associated increase in nitrate $\delta^{15}\text{N}$, both resulting from nitrate uptake by phytoplankton. A meridional transect (C) of nitrate concentration (open circles) and $\delta^{15}\text{N}$ (filled circles) in the surface mixed layer of the Southern Ocean along 115°E shows that nitrate $\delta^{15}\text{N}$ is spatially correlated with variations in the utilization of nitrate by phytoplankton, as reflected by the equatorward decrease in nitrate concentration. Nitrate $\delta^{15}\text{N}$ is lowest where the nitrate concentration is highest (and nitrate utilization is lowest), in Antarctic waters, south of ~51°S in this region. The meridional gradient in nitrate $\delta^{15}\text{N}$ is recorded in bulk sediment $\delta^{15}\text{N}$ along 115°E (C, crosses) by the sinking of particulate N out of the surface ocean. Across the transect, sediment $\delta^{15}\text{N}$ is ~5‰ higher than expectations for and measurements of sinking N $\delta^{15}\text{N}$, probably mainly due to isotopic alteration of this N at the seafloor. Nevertheless, the link between nitrate consumption and sediment $\delta^{15}\text{N}$ provides a possible avenue for paleoceanographic reconstruction of nitrate utilization by phytoplankton. The left axis in C is scaled to 35 $\mu\text{M}$, the nitrate concentration of Upper Circumpolar Deep Water that upwells in the Antarctic (see A). Panels A and B are reprinted from Sigman, D.M., M.A. Altabet, R.H. Michener, D.C. McCorkle, B. Fry, and R.M. Holmes, 1997, *Marine Chemistry*, 57: 227-242. Panel C is modified from Sigman, D.M., M.A. Altabet, D.C. McCorkle, R. François, and G. Fischer, 1999, *Global Biogeochemical Cycles*, 13: 1149-1166, with the sediment data taken from Altabet, M.A. and R. François, 1994, *Global Biogeochemical Cycles*, 8: 103-116.

**Figure 8.** (A) The $\delta^{15}\text{N}$ 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 O₂ concentration < 10 μM where denitrification consumes NO₃⁻ (B, concentration shown in filled squares) and leads to a characteristic NO₃⁻ deficit (B, open squares) relative to phosphate. Measurements indicate enrichment of NO₃⁻ in ¹⁵N and concurrent depletion of N₂ in ¹⁵N, arising from isotope discrimination during denitrification, with the conversion of NO₃⁻ to N₂. ε for denitrification in this environment was estimated to be ~25‰.


**Figure 9.** Simplified global ocean N isotope budget. The y-axis indicates the δ¹⁵N of a given flux or pool. The δ¹⁵N of N from oceanic N₂ fixation, the dominant N input to the ocean, is ~ -1‰ (“N₂ fixation” on the left). At steady state, the total denitrification loss (“denitrification” on the right) must have the same δ¹⁵N as the input. The δ¹⁵N of mean ocean nitrate is ~5‰. Water column denitrification removes nitrate with a low δ¹⁵N (“water column” at lower right), while sedimentary denitrification removes nitrate with a δ¹⁵N similar to the 5‰ of mean ocean nitrate (“sedimentary” at upper right). The need for the flux-weighted δ¹⁵N of the denitrification loss to be ~ -1‰ leads to estimates of partitioning between water column and sedimentary denitrification in which sedimentary denitrification is found to be roughly two-thirds of the total N loss.

**Figure 10.** The δ¹⁸O versus δ¹⁵N in nitrate as it is progressively assimilated by 4 eukaryotic species of marine phytoplankton. Both δ¹⁵N and δ¹⁸O in nitrate increase as nitrate is consumed, and they do so with an O:N ratio for isotopic discrimination (¹⁸ε:¹⁵ε)

**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 panel (A) indicates theoretical saturation with atmospheric N₂O at *in situ* temperatures. 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 panels (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 from Kim and Craig, 1990. Reprinted with permission from Dore, J.E., B.N. Popp, D.M. Karl, and F.J. Sansone, 1998, *Nature*, 396: 63-66.

**Figure 12.** Nitrogen isotopic values of suspended particulate matter and sinking particles (as collected by sediment traps) in the North Atlantic Ocean (31° 50’ N, 64° 10’ W). The profiles of suspended particulate N show the representative depth gradient in δ₁⁵N, with lower δ₁⁵N in the surface ocean than at depth. The δ₁⁵N of the sinking flux shows a decrease with depth. The reason for this decrease, which has now been observed in other regions, is unknown. Reprinted with permission from Altabet, M.A, W.G. Deuser, S. Honjo, and C. Stienen, 1991, *Nature*, 354: 136-139.
Figure 13. Sedimentary $\delta^{15}$N records spanning the past 140 thousand years, which encompasses 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 ($8^\circ30.4\ N, 112^\circ19.9\ E$), where sedimentary $\delta^{15}$N is expected to approximate that of nitrate in the western Pacific thermocline, which, in turn, is hoped to have maintained a constant isotopic relationship with deep ocean nitrate. The small magnitude of variation in $\delta^{15}$N (<1.5‰) and lack of correlation with glacial/interglacial transitions suggests mean ocean nitrate $\delta^{15}$N remained unchanged through shifts in Earth’s climate. (B) Sedimentary $\delta^{15}$N record underlying the Eastern Tropical North Pacific ($22^\circ23.3\ N, 107^\circ04.5\ W$), a major region of denitrification. Interglacials are characterized by high $\delta^{15}$N (8-9‰), with $\delta^{15}$N 2-3‰ lower during glacials. Low $\delta^{15}$N, along with coincident evidence for decreased productivity and enhanced oxygenation of the mid-depth water column, indicates decreased water column denitrification during glacial periods. (C) Sedimentary $\delta^{15}$N record from the high-nitrate Antarctic Zone of the Southern Ocean ($54^\circ55\ S, 73^\circ50\ E$) shows higher $\delta^{15}$N 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 $^{15}$N enrichment suggests reduced nutrient supply from below.

All data shown are of bulk sediment. The sedimentary $\delta^{15}$N record shown in (B) is from a region of high organic matter preservation in the sediments, where bulk sedimentary $\delta^{15}$N correlates well with sinking $\delta^{15}$N. The records in (A) and (C) are from regions where a diagenetically driven difference is observed between sinking and sedimentary N, which
$\delta^{15}N$ (%o vs. air) vs. fraction of reactant remaining
Atmospheric N$_2$ 
$\delta^{15}N = 0\%$ 

Atmospheric precipitation 
$\delta^{15}N = -4\%$ 

Terrestrial runoff 
$\delta^{15}N = 4\%$ 

N$_2$ fixation 
$\delta^{15}N = 2\%$

Dissolved N$_2$ 
$\delta^{15}N = 0.6\%$

Particulate N 
$\delta^{15}N = 0\%$

Recycling 
$\epsilon \leq 3\%$

DON 
$\delta^{15}N = 4\%$

Thermocline NO$_3^-$ 
$\delta^{15}N = 3\%$

Deep NO$_3^-$ 
$\delta^{15}N = 5\%$

Deep water column denitrification 
$\epsilon \approx 25\%$

Terrestrial denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ supply and assimilation 
$\delta^{15}N \approx 5\%$

Sinking 
$\epsilon \leq 3\%$

Remineralization 
$\epsilon \leq 3\%$

Sedimentary denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ 
$\delta^{15}N = 0.6\%$

Particulate N 
$\delta^{15}N = 0\%$

Recycling 
$\epsilon \leq 3\%$

DON 
$\delta^{15}N = 4\%$

Thermocline NO$_3^-$ 
$\delta^{15}N = 3\%$

Deep NO$_3^-$ 
$\delta^{15}N = 5\%$

Deep water column denitrification 
$\epsilon \approx 25\%$

Terrestrial denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ supply and assimilation 
$\delta^{15}N \approx 5\%$

Sinking 
$\epsilon \leq 3\%$

Remineralization 
$\epsilon \leq 3\%$

Sedimentary denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ 
$\delta^{15}N = 0.6\%$

Particulate N 
$\delta^{15}N = 0\%$

Recycling 
$\epsilon \leq 3\%$

DON 
$\delta^{15}N = 4\%$

Thermocline NO$_3^-$ 
$\delta^{15}N = 3\%$

Deep NO$_3^-$ 
$\delta^{15}N = 5\%$

Deep water column denitrification 
$\epsilon \approx 25\%$

Terrestrial denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ supply and assimilation 
$\delta^{15}N \approx 5\%$

Sinking 
$\epsilon \leq 3\%$

Remineralization 
$\epsilon \leq 3\%$

Sedimentary denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ 
$\delta^{15}N = 0.6\%$

Particulate N 
$\delta^{15}N = 0\%$

Recycling 
$\epsilon \leq 3\%$

DON 
$\delta^{15}N = 4\%$

Thermocline NO$_3^-$ 
$\delta^{15}N = 3\%$

Deep NO$_3^-$ 
$\delta^{15}N = 5\%$

Deep water column denitrification 
$\epsilon \approx 25\%$

Terrestrial denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ supply and assimilation 
$\delta^{15}N \approx 5\%$

Sinking 
$\epsilon \leq 3\%$

Remineralization 
$\epsilon \leq 3\%$

Sedimentary denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ 
$\delta^{15}N = 0.6\%$

Particulate N 
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Thermocline NO$_3^-$ 
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Deep NO$_3^-$ 
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Deep water column denitrification 
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Terrestrial denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ supply and assimilation 
$\delta^{15}N \approx 5\%$

Sinking 
$\epsilon \leq 3\%$

Remineralization 
$\epsilon \leq 3\%$

Sedimentary denitrification 
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Recycling 
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Deep water column denitrification 
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Terrestrial denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ supply and assimilation 
$\delta^{15}N \approx 5\%$

Sinking 
$\epsilon \leq 3\%$

Remineralization 
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Sedimentary denitrification 
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Particulate N 
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Recycling 
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DON 
$\delta^{15}N = 4\%$

Thermocline NO$_3^-$ 
$\delta^{15}N = 3\%$

Deep NO$_3^-$ 
$\delta^{15}N = 5\%$

Deep water column denitrification 
$\epsilon \approx 25\%$

Terrestrial denitrification 
$\epsilon \approx 0\%$

Dissolved N$_2$ supply and assimilation 
$\delta^{15}N \approx 5\%$

Sinking 
$\epsilon \leq 3\%$

Remineralization 
$\epsilon \leq 3\%$

Sedimentary denitrification 
$\epsilon \approx 0\%$
Degradation
(ε ≤ 3‰ ?)

Assimilation
(ε_nitrate ~ 5‰)
(ε_nitrite ~ 1‰)
(ε_ammonium ≤ 20‰)
(ε_urea ~ 1‰)

Nitrification
(ε_ammonium oxidation ~ 16‰)
(ε_nitrite oxidation ~ ?)
to ammonium in nature involves a wide spectrum of reactions, making representative laboratory studies difficult. Given the available data, it appears that the net isotope effect of this process is small in most cases, less than 5‰ and probably smaller.

The use of stable isotopes to study nitrification in the field has been limited by low ambient concentrations of ammonium and nitrite in most open ocean environments. Current paradigms suggest that nitrification should be of limited importance for the isotope dynamics of both dissolved and particulate N pools in the open ocean because essentially all ammonium generated from particles is oxidized to nitrite and nitrate before it can be transported into or out of a given environment. However, culture studies indicate a large isotope effect for the oxidation of ammonium to nitrate (as high as 35‰). Given a large isotope effect, even small deviations from this picture of complete ammonium transformation could lead to significant isotopic fractionation of reactants and products. Thus, nitrification has been hypothesized as a cause for observed isotopic depletion of nitrate and nitrous oxide in several open ocean settings. In marine sediments and estuarine waters, where ammonium oxidation is typically incomplete, nitrification plays an important role in N isotope dynamics, generally resulting in 15N enrichment of residual ammonium pool.

### Nitrogen Reservoirs

#### Dissolved N

**Nitrate** Nitrate accounts for most of the fixed N in the ocean. The δ15N of oceanic nitrate varies between ~1 and 20‰, with a mean deep ocean value of ~5‰. Values significantly lower than this have so far been observed only in the upper thermocline of the low latitude oligotrophic ocean, with the hypothesis that this isotopic depletion is due to the oxidation of newly fixed N (Figure 5). Values higher than 5‰ result from fractionation during either assimilative uptake by phytoplankton at the ocean surface or denitrification by bacteria in oxygen-deficient zones of the ocean interior (Figure 5).

In high latitude, nutrient-rich regions, such as the Southern Ocean and the Subarctic Pacific, and regions, such as the California Current and the Equatorial Pacific, there is a strong correlation between the degree of nitrate consumption by phytoplankton and the δ15N of the nitrate remaining in the water (Figure 6).

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**Figure 4** Isotopic fractionation during nitrate (NO₃⁻) assimilation by a culture of the marine diatom Thalassiosira pseudonana. (A) Time series of (●) NO₃⁻ concentration in the culture medium, (○) particulate nitrogen (PN), and (△) fluorescence, a measure of phytoplankton biomass; (B) (●) δ15N of PN accumulated over the same time period; (C) (●) δ15N of PN accumulated during log phase of growth plotted versus F, a measure of nitrate utilization. F is $[-f/(1-f)]\ln f$, where f is the fraction of initial NO₃⁻ remaining at the time the culture is sampled. ε is calculated to be 4.5‰ from the slope of the regression in (C), according to the Rayleigh integrated product equation (see text, eqn [5]). Dashed lines in (B) and (C) represent the initial δ15N of the source NO₃⁻ (3.8‰). (Reproduced (modified) with permission from Waser NAD, Harrison PJ, Nielsen B, Calvert SE and Turpin DH (1998) Limnology and Oceanography 43: 215–224.)
Water column denitrification $\varepsilon \sim 25\%$

Nitrate uptake $\varepsilon \sim 5\%$

Sedimentary denitrification $\varepsilon \sim 0\%$

Newly fixed N added $\delta^{15}N \sim -1\%$

$\delta^{15}\text{NO}_3^-$ (‰ vs. air)

$[\text{NO}_3^-]$ (factor of initial value)
Figure 6

A. [N] (μM)

B. δ¹⁵N (% vs. air)
MS 632 Figure 8
\[
\Delta \delta^{18}\text{O of NO}_3^- (\%_o vs. initial) = \frac{18}{15} \epsilon = 1, 0.9, 1.1
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- T. weissflogii
- T. pseudonana
- T. oceanica
- E. huxleyi
Figure 12: 

- Depth (m) vs. $\delta^{15}N(\%)$
- Sediment trap
- Suspended particles

MS 632 Figure 12