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## 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. This is known as isotopic fractionation, and it leads 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  $\text{N}_2$  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 internal cycling and input/output budget of oceanic fixed N, yielding information on both its representative and unique aspects. This overview outlines 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 standard containing a constant isotopic ratio. The universal reference

standard for N isotopes is atmospheric  $\text{N}_2$ , with a  $^{15}\text{N}/^{14}\text{N}$  ratio of  $0.36765\% \pm 0.00081\%$ . Natural samples exhibit small deviations from the standard ratio, which are expressed in  $\delta$ -notation (in units of per mil, ‰):

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

In this notation, the  $\delta^{15}\text{N}$  of atmospheric  $\text{N}_2$  is 0‰.

Special terms are also used to characterize the amplitude of isotopic fractionation caused by a given process. Isotope fractionation occurs both in 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 N from one form to another. The kinetic effect,  $\varepsilon$ , of a given reaction is defined by the difference in rates with which the two N isotopes are converted from reactant into product. For instance, if a reaction has an  $\varepsilon$  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.

$$\varepsilon(\text{‰}) = ({}^{14}k/{}^{15}k - 1) \times 1000, \quad [2]$$

where  ${}^{14}k$  and  ${}^{15}k$  are the rate coefficients of the reaction for  $^{14}\text{N}$ - and  $^{15}\text{N}$ -containing reactant, respectively. For  $\varepsilon \ll 1000\%$ ,  $\varepsilon$  is approximated by the difference in  $\delta^{15}\text{N}$  between the reactant and its instantaneous product.

### Measurements

The isotopic analysis of N relies on the generation of a stable gas, typically  $\text{N}_2$ , as the analyte for isotope ratio mass spectrometry. On-line combustion to  $\text{N}_2$  is the standard method for the preparation of a N sample for isotopic analysis. With current 'off-the-shelf' technology, a typical sample size requirement is 1–4  $\mu\text{mol}$  N per analysis. 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 into a gas or other extractable form for collection. Standard methods exist for nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) at concentrations above 2–3  $\mu\text{M}$ , based on conversion into ammonia gas and collection of the cationic ammonium form for subsequent conversion into  $\text{N}_2$ . The concentration requirement allows for nitrate isotopic studies in much of the ocean but rules out the low-nutrient waters of the low- and mid-latitude surface ocean. Given the concentration range of ammonium in marine waters, the concentration requirement for ammonium isotopic analysis is much more restrictive, typically limiting studies to estuaries and sediments. With respect to dissolved gases, methods of collection and isotopic analysis have been developed for  $\text{N}_2$  and nitrous oxide ( $\text{N}_2\text{O}$ ), although there are relatively few oceanic data for either.

## Models

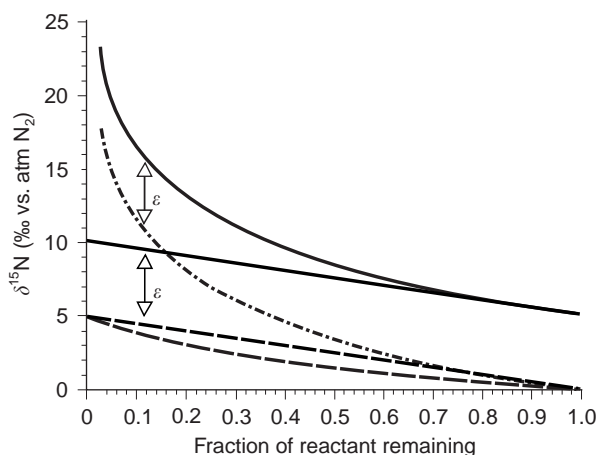
Two simple models, the ‘Rayleigh’ model and the ‘steady state’ model, are frequently used to interpret N isotope data from the ocean. In both of these models, the degree of consumption of the reactant N pool is a central parameter, and the  $\delta^{15}\text{N}$  of the initial reactant N pool ( $\delta^{15}\text{N}_{\text{initial}}$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

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

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

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

where  $f$  is the fraction of the reactant remaining,  $\delta^{15}\text{N}_{\text{initial}}$  is the  $\delta^{15}\text{N}$  of the initial reactant N pool, and  $\varepsilon$  is the kinetic isotope effect of the transformation. The Rayleigh model is often used to describe



**Figure 1** The  $\delta^{15}\text{N}$  of reactant and product N pools of a single unidirectional reaction as a function of the fraction of the initial reactant supply which is left unconsumed, for two different models of reactant supply and consumption. The Rayleigh model applies when a closed pool of reactant N is consumed. The steady-state model applies when reactant N is supplied continuously. The same isotopic parameters, an isotope effect ( $\varepsilon$ ) of 5‰ and a  $\delta^{15}\text{N}$  of 5‰ for the initial reactant supply, are used for both the Rayleigh and steady-state models.  $\varepsilon$  is evident as the isotopic difference between reactant N and its product (the instantaneous product in the case of the Rayleigh model). —, Rayleigh model: reactant; ---, Rayleigh model: integrated product; - · - ·, Rayleigh model: instantaneous product; — — —, steady-state model: reactant; - - - -, steady-state model: product.

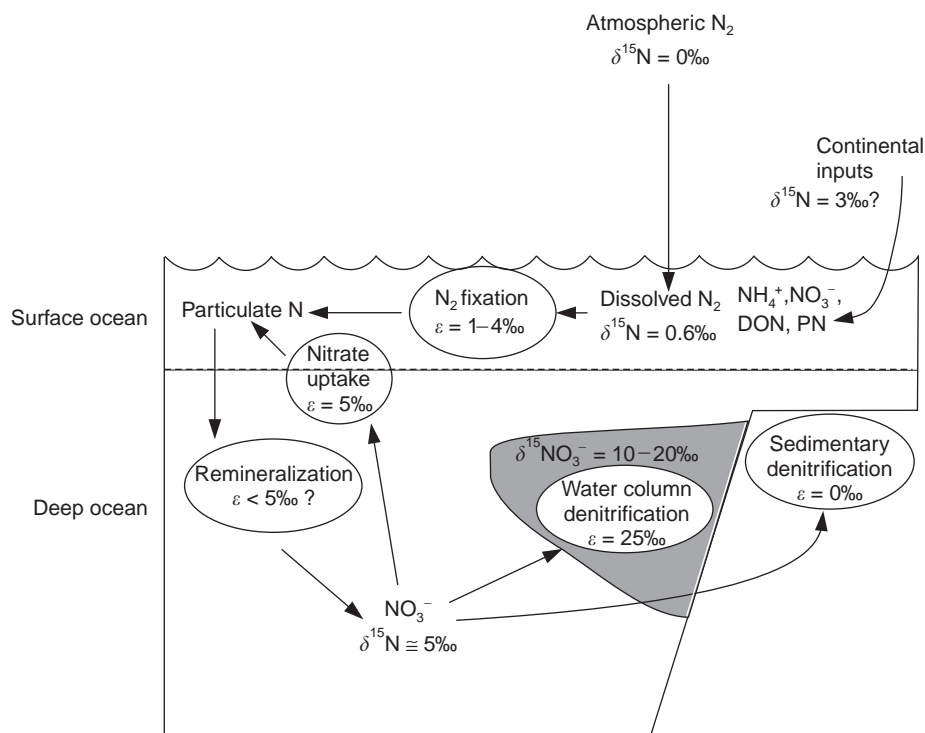
events in the ocean, such as the uptake of nitrate by phytoplankton during a bloom.

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 equations apply to the reactant N pool (eqn [6]) and the product N pool (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-variant, such as in the consumption of nitrate by denitrification in the ocean interior.



**Figure 2** Marine nitrogen isotope budget and processes affecting the distribution of nitrogen isotopes in the sea. Inputs indicated are marine  $N_2$  fixation in the surface ocean and continental inputs. Outputs indicated are sedimentary and water column denitrification. Internal cycling is represented as nitrate uptake in the surface ocean and remineralization at depth. For simplicity, ammonium uptake and regeneration in the surface ocean are not shown. In addition, the isotope fractionation associated with nitrification is excluded because this process typically goes to completion in the oceanic water column (see text). Question marks indicate extreme uncertainty due to wide variations in the available data or insufficient data.

## Processes

### Inputs

Fixed N in the ocean has two major sources: (1) marine  $N_2$  fixation and (2) input from the continents through continental waters and the atmosphere (Figure 2). Of these inputs, only marine  $N_2$

fixation is well characterized with regard to its isotopic effect. Culture studies of  $N_2$  fixers, including *Trichodesmium*, the most well-known genus of open ocean  $N_2$  fixers, have demonstrated that there is only modest fractionation during  $N_2$  fixation (Table 1), such that newly fixed N should have a  $\delta^{15}N$  of  $-4$  to  $-1\text{‰}$  relative to dissolved  $N_2$ . This has been

**Table 1** Representative estimates of isotope effects for N cycle processes

Process	Isotope effect ( $\epsilon$ )	Details
Nitrification ( $NH_4^+ \rightarrow NO_2^-$ )	$35\text{‰}$ $15\text{‰}$	<i>Nitrosomonas europaea</i> Chesapeake Bay
Denitrification ( $NO_3^- \rightarrow N_2$ )	$28\text{‰}$ $20\text{--}30\text{‰}$ $13\text{--}21\text{‰}$ $20\text{--}30\text{‰}$	<i>Paracoccus denitrificans</i> <i>Pseudomonas stutzeri</i> <i>Pseudomonas denitrificans</i> Eastern Tropical North Pacific
Nitrogen fixation ( $N_2 \rightarrow NH_4^+$ )	$\sim 0\text{‰}$ $\sim 0\text{‰}$	<i>Trichodesmium</i> sp. <i>Azotobacter vinlandii</i>
$NH_4^+$ assimilation ( $NH_4^+ \rightarrow PN$ )	$20\text{‰}$ $20\text{‰}$ $6.5\text{--}8.0\text{‰}$ $9.1\text{‰}$	<i>Skeletonema costatum</i> Mixed culture Chesapeake Bay Delaware Estuary
$NO_3^-$ assimilation ( $NO_3^- \rightarrow PN$ )	$5\text{‰}$ $4\text{--}6\text{‰}$ $5\text{‰}$	<i>Thalassiosira pseudonana</i> Antarctic/Subantarctic Subarctic Pacific

confirmed by field collections of *Trichodesmium* colonies, which typically give  $\delta^{15}\text{N}$  values in the range of  $-1$  to  $0\text{‰}$ , compared with a  $\delta^{15}\text{N}$  of  $\sim 0.6\text{‰}$  for dissolved  $\text{N}_2$ .

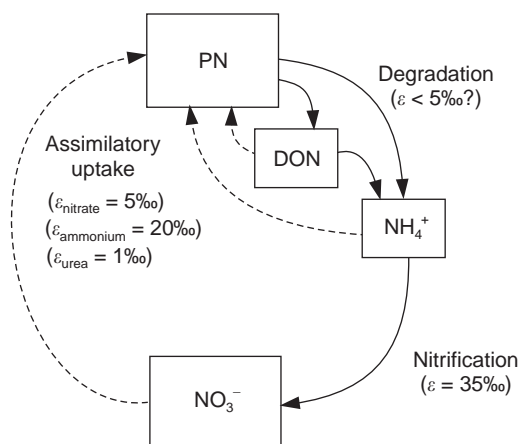
The N isotopic composition of the continental N input to the ocean is the least well-characterized aspect of the marine N isotope budget.  $\text{N}_2$  fixation is the fundamental source of terrestrial N. Moreover, anthropogenic fixed N introduced as fertilizer has a  $\delta^{15}\text{N}$  of  $0\text{--}3\text{‰}$ . Therefore, it is generally reasoned that the N input from continents is low in  $\delta^{15}\text{N}$ , and some measurements in estuarine and coastal settings support this view. However, measurements in terrestrial and freshwater systems as well as in atmospheric deposition indicate that the other processes alter the  $\delta^{15}\text{N}$  of terrestrial fixed N *en route* to the ocean, with measurements of different N pools ranging between  $-20\text{‰}$  and  $+15\text{‰}$ . In the face of large uncertainties, a mean  $\delta^{15}\text{N}$  of  $3\text{‰}$  for the continental input of fixed N to the ocean has been suggested by some workers.

### Outputs

Denitrification, the bacterial reduction of nitrate to  $\text{N}_2$ , is the major mechanism of fixed N loss from the ocean; it occurs both in the water column and in sediments when the oxygen concentration is low,  $< 5\mu\text{M}$  (Figure 2). Culture-based studies suggest that the isotope effect of denitrification is  $\sim 20\text{--}30\text{‰}$  (Table 1). The  $\delta^{15}\text{N}$  of nitrate in oceanic waters clearly reflects the occurrence of water column denitrification, indicating an isotope effect similar to the culture-based estimate. However, the observed isotopic effect of denitrification may be reduced from the inherent isotope effect when denitrification becomes limited by the rate of nitrate supply to the denitrifying bacteria. This appears to occur in at least some ocean margin sediments, where denitrification completely consumes the nitrate that is supplied by diffusion through sediment pore waters, resulting in an 'effective' isotope effect close to  $0\text{‰}$ .

### Internal Cycling (Figure 3)

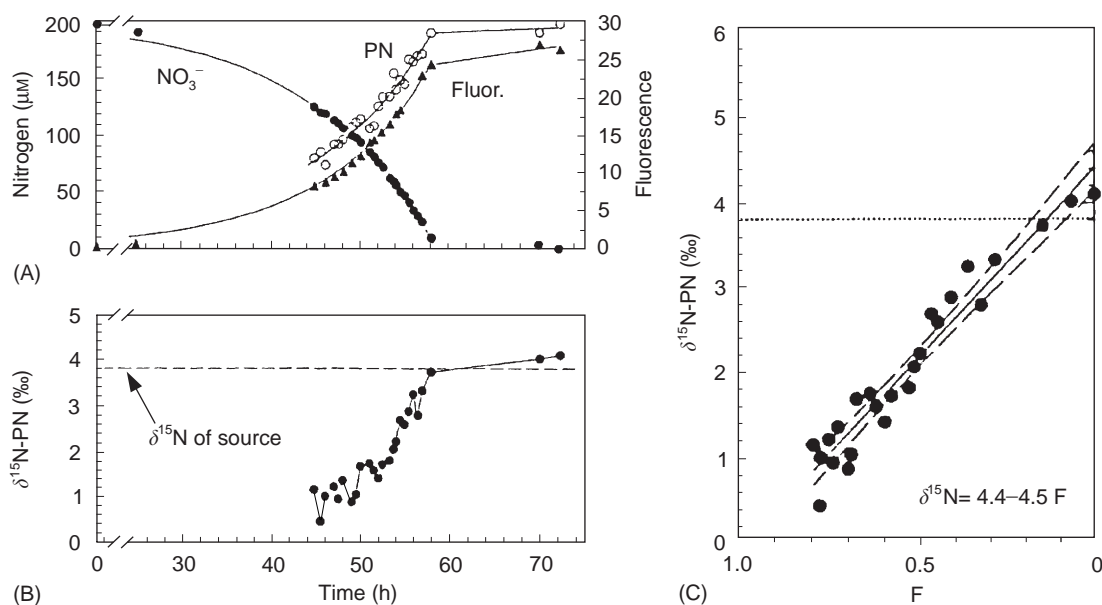
**N assimilation** When phytoplankton take up fixed N for assimilation, they preferentially consume  $^{14}\text{N}$  relative to  $^{15}\text{N}$ . Culture studies indicate that different forms of fixed N are assimilated with distinct isotope effects although these isotope effects may vary with physiological conditions (Table 1). In one culture study of the diatom *Thalassiosira pseudonana*, the isotope effects of nitrate, nitrite, ammonium, and urea were estimated to be  $4.5\text{‰}$ ,  $0.9\text{‰}$ ,  $20\text{‰}$ , and  $0.8\text{‰}$ , respectively (Figure 4).



**Figure 3** Schematic diagram of the processes and pools of N central to the internal cycling of N in the ocean. The isotope effects given here are based on laboratory studies. Dashed arrows represent assimilation of dissolved species into particulate matter and solid arrows represent remineralization. The processes surrounding dissolved organic nitrogen (DON) production and utilization are not well understood from an isotopic perspective but are thought to play an important role in N cycling.

Since nitrite, ammonium, and urea each occur at low concentration in ocean water, their consumption by phytoplankton in the surface ocean is essentially complete. In the case of complete consumption, the product N converges on the  $\delta^{15}\text{N}$  of the initial N source (Figure 1), rendering the isotope effect unimportant to the isotopic composition of assimilated N. However, in some regions of the ocean surface, the consumption of nitrate is incomplete, either permanently or temporarily. Thus, despite the larger isotope effect of ammonium uptake, the isotope effect of nitrate uptake appears to be the most significant for isotopic variations in the open ocean. Each isotope effect is significant as a constraint on the physiological mechanisms of N assimilation.

**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). Isotopic fractionation can occur at both steps. Much of our evidence for isotopic fractionation during degradation to ammonium comes from field studies of particulate N, which suggest that both bacteria and zooplankton preferentially degrade low- $\delta^{15}\text{N}$  particulate N. A few laboratory studies have quantified the isotope effects of processes such as thermal peptide bond cleavage, bacterial amino acid uptake and transamination, and zooplankton ammonium release. However, organic N degradation



**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, (○) particulate nitrogen (PN), and (▲) fluorescence, a measure of phytoplankton biomass; (B) (●)  $\delta^{15}\text{N}$  of PN accumulated over the same time period; (C) (●)  $\delta^{15}\text{N}$  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  $\text{NO}_3^-$  remaining at the time the culture is sampled.  $\epsilon$  is calculated to be  $4.5\text{‰}$  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  $\delta^{15}\text{N}$  of the source  $\text{NO}_3^-$  ( $3.8\text{‰}$ ). (Reproduced (modified) with permission from Waser NAD, Harrison PJ, Nielsen B, Calvert SE and Turpin DH (1998) *Limnology and Oceanography* 43: 215–224.)

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  $5\text{‰}$  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  $35\text{‰}$ ). 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

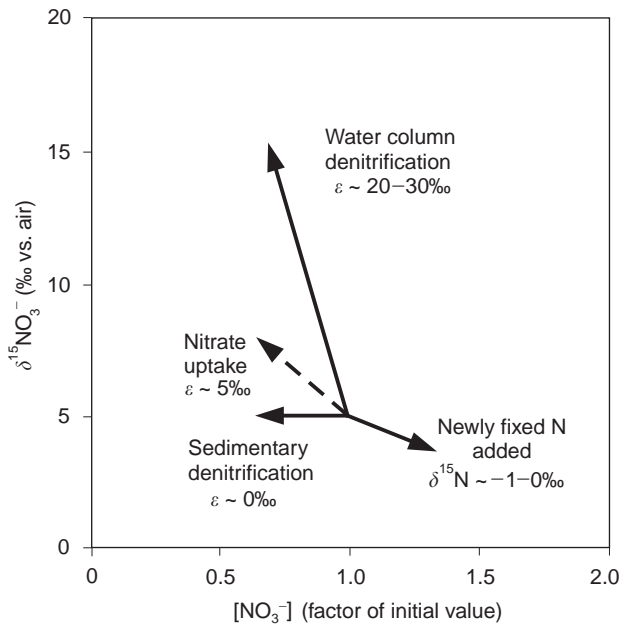
resulting in  $^{15}\text{N}$  enrichment of residual ammonium pool.

## Nitrogen Reservoirs

### Dissolved N

**Nitrate** Nitrate accounts for most of the fixed N in the ocean. The  $\delta^{15}\text{N}$  of oceanic nitrate varies between  $\sim 1$  and  $20\text{‰}$ , with a mean deep ocean value of  $\sim 5\text{‰}$ . 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  $5\text{‰}$  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  $\delta^{15}\text{N}$  of the nitrate remaining in the water (Figure 6). However, although nitrate assimilation has a strong effect on the  $\delta^{15}\text{N}$  of nitrate



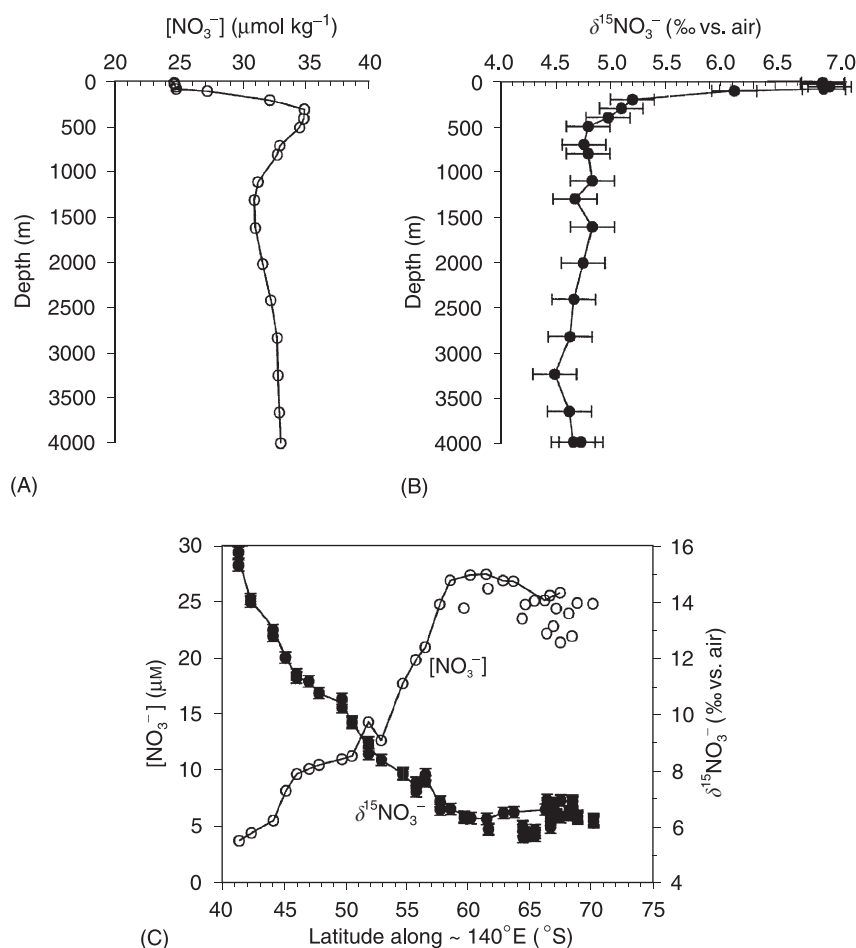
**Figure 5** The instantaneous effect of different marine N cycle processes on nitrate  $\delta^{15}\text{N}$  and concentration, assuming an initial nitrate  $\delta^{15}\text{N}$  of 5‰. The trajectories are for reasonable estimates of the inherent isotope effects, and they depend on the initial nitrate  $\delta^{15}\text{N}$  as well as the relative amplitude of the changes in nitrate concentration (30% for each process in this figure). Solid arrows denote processes which add or remove 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 available nitrate in a given environment the isotope effect of nitrate uptake plays no major role in the  $\delta^{15}\text{N}$  of the various N pools and fluxes. Similarly, the lack of an isotope for sedimentary denitrification is due to the fact that nitrate consumption by this process can approach completion within sedimentary pore waters.

in the upper ocean, it does not appear to affect greatly the  $\delta^{15}\text{N}$  of nitrate in the deep ocean. Below  $\sim 2.5\text{--}3.0\text{ km}$  depth in the ocean, nitrate  $\delta^{15}\text{N}$  is relatively constant at  $\sim 5\text{‰}$ , despite large interbasin 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. As a result of this complete consumption, the organic N exported from the surface ocean converges on the  $\delta^{15}\text{N}$  of the nitrate supply. Because the sinking flux  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  of deep nitrate. In this respect, the oceanic cycling of the N isotopes differs markedly from that of the carbon isotopes.

Because the cycle of nitrate uptake and organic N oxidation has little effect on the  $\delta^{15}\text{N}$  of deep nitrate, the  $\delta^{15}\text{N}$  of nitrate in the ocean interior provides an excellent indicator of other processes, denitrification in particular. In regions of denitrification, the  $\delta^{15}\text{N}$  of nitrate in the subsurface is elevated to above 15‰ (Figure 7). The subsurface  $\delta^{15}\text{N}$  maximum occurs in the core of the oxygen minimum and is strongly correlated with the degree of nitrate consumption by denitrification. This isotopic signal has a number of current and potential applications in one study of the marine N cycle.

One example involves the  $\delta^{15}\text{N}$  of mean oceanic nitrate (Figure 2). If we assume that the mean  $\delta^{15}\text{N}$  of N input to the ocean (by oceanic  $\text{N}_2$  fixation and continental inputs) is close to 0‰, then the  $\delta^{15}\text{N}$  of the output by denitrification should converge on 0‰ to achieve a steady state. If denitrification occurred as a homogeneous process throughout the ocean, the  $\delta^{15}\text{N}$  of mean ocean nitrate, rather than being 5‰, would be set at 20–30‰ so that denitrification (with an inherent isotope effect of 20–30‰) would remove nitrate with a  $\delta^{15}\text{N}$  of 0‰. However, water column denitrification is localized in regions such as the Eastern Tropical North Pacific and the Arabian Sea. Because intensive denitrification leads to higher nitrate  $\delta^{15}\text{N}$  in these regions (Figure 7), the  $\delta^{15}\text{N}$  of nitrate being removed by denitrification is higher than if the substrate for denitrification had the mean ocean  $\delta^{15}\text{N}$  value. This provides a partial explanation for the fact that mean ocean nitrate  $\delta^{15}\text{N}$  is much less than 20‰. In addition, the low  $\delta^{15}\text{N}$  of mean ocean nitrate is partially due to the importance of sedimentary denitrification, with its isotope effect of  $\sim 0\text{‰}$ , as a mechanism of nitrate loss from the global ocean (Figure 2). Quantifying the roles that these processes play in setting the  $\delta^{15}\text{N}$  of mean ocean nitrate may yield a robust estimate of the environments and relative rates of denitrification on a global basis.

**Ammonium** In some estuarine systems, ammonium concentrations are high enough for isotopic analysis. In these environments, ammonium  $\delta^{15}\text{N}$  are typically high, ranging from +10‰ to +29‰ in the Scheldt estuary, +10‰ to +17‰ in Chesapeake Bay, and +10‰ to +40‰ in the Delaware estuary. In each case, ammonium  $\delta^{15}\text{N}$  increases as the ammonium concentration decreases along transects from riverine to marine waters, indicating fractionation during ammonium consumption by either nitrification or assimilative ammonium uptake, with inverse gradients in ammonium and nitrate concentrations indicating where intense nitrification occurs. Interestingly,



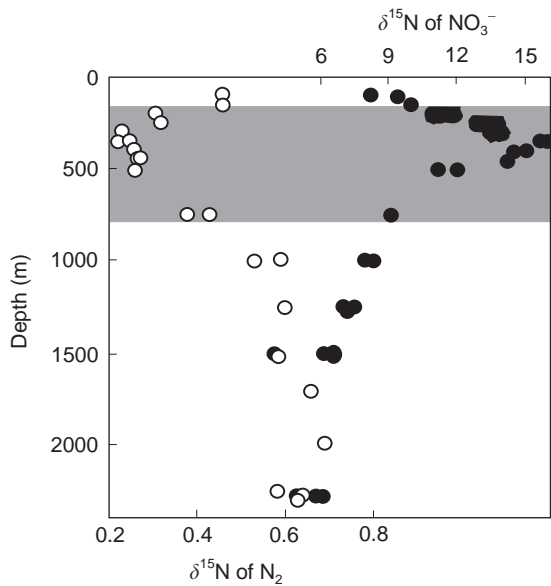
**Figure 6** Nitrate  $\delta^{15}\text{N}$  data from the Southern Ocean show the effect of uptake by phytoplankton. Depth profiles of nitrate concentration (A) and  $\delta^{15}\text{N}$  (B) from the Antarctic region of the east Indian Ocean ( $53.2^\circ\text{S}$ ,  $115^\circ\text{E}$ ) show a decrease 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 and  $\delta^{15}\text{N}$  in surface waters of the Southern Ocean, Pacific sector ( $\sim 140^\circ\text{E}$ ), shows that nitrate  $\delta^{15}\text{N}$  is spatially correlated with variations in the utilization of nitrate by phytoplankton, as indicated 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  $57^\circ\text{S}$  in this region. (Reproduced with permission from (A, B) Sigman DM, Altabet MA, Michener RH *et al.* (1997) *Marine Chemistry* 57: 227–242; (C) Sigman DM, Altabet MA, McCorkle DC, Francois R and Fischer G (2000) *Global Biogeochemical Cycles* 13: 1149–1166).

the isotope effect for nitrification estimated from ammonium concentration and  $\delta^{15}\text{N}$  measurements in the Chesapeake Bay is 12–17‰, roughly half the amplitude of the culture-based estimate from a terrestrial nitrifier (Table 1).

As mentioned, ammonium concentrations rarely rise above  $1 \mu\text{M}$  in open ocean environments, so that we lack the appropriate methods to measure its isotopic signature. Because it is a reactive intermediate that does not accumulate, it is typically assumed to play a secondary role in the N isotope dynamics of the open ocean. Nevertheless, when appropriate methods are developed for this analysis, the results may provide insight into organic N breakdown and

N recycling, which are currently somewhat ‘invisible’ processes. Methodological limitations have also restricted isotopic measurements of dissolved organic N (DON). Unlike ammonium, DON concentrations are significant in the open ocean, typically  $\geq 2 \mu\text{M}$  in deep water and  $\geq 4 \mu\text{M}$  in surface waters, raising the possibility that DON transport represents a significant flux of fixed N in open ocean environments. As a result, DON fluxes may be important to the isotope dynamics of all N pools and the conclusions that are drawn from them.

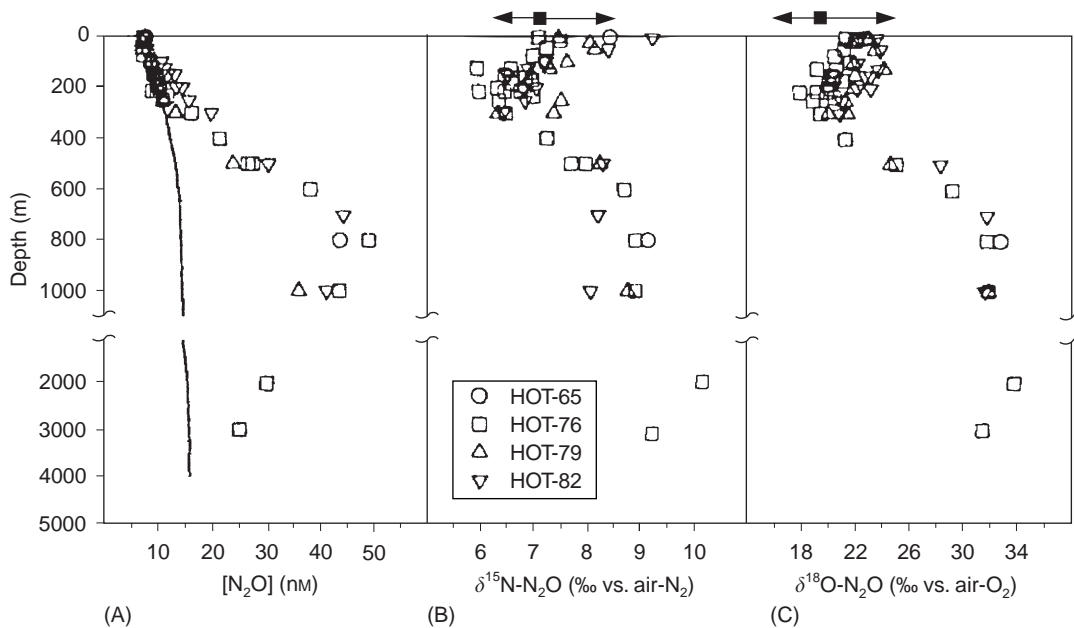
**Dissolved gases** Dissolved  $\text{N}_2$  in equilibrium with atmospheric  $\text{N}_2$  at the surface has a  $\delta^{15}\text{N}$  of



**Figure 7** The  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  (●) and  $\text{N}_2$  (○) 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  $\text{O}_2$  concentration  $< 10 \mu\text{M}$ . Measurements indicate enrichment of  $\text{NO}_3^-$  in  $^{15}\text{N}$  and concurrent depletion of  $\text{N}_2$  in  $^{15}\text{N}$ , arising from isotopic fractionation in the conversion of  $\text{NO}_3^-$  into  $\text{N}_2$ . Using the Rayleigh model (eqn [3]),  $\epsilon$  for denitrification in this environment was estimated to be 25‰, in the range of values reported for denitrification by laboratory cultures. (Reproduced with permission from Brandes JA, Devol AH, Yoshinari T, Jayakumar DA and Naqvi SWA (1998) *Limnology and Oceanography* 43: 1680-1689.)

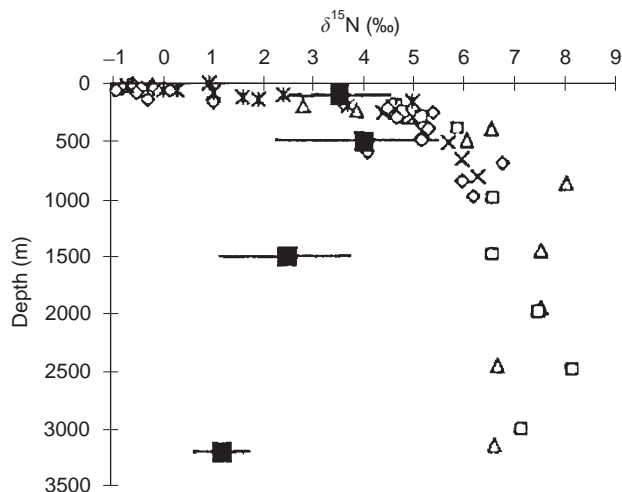
$\sim 0.6\text{‰}$ . The isotopic composition of dissolved  $\text{N}_2$  does not vary greatly in ocean profiles, except in zones of denitrification, where low- $\delta^{15}\text{N}$   $\text{N}_2$  is produced, resulting in measured  $\delta^{15}\text{N}_2$  as low as 0.2‰ (Figure 7). Since  $\text{N}_2$  is the main product of identification,  $\delta^{15}\text{N}_2$  measurements provide a test of the nitrate-based estimates of the isotope effect for this process.

Depth profiles of the  $\delta^{15}\text{N}$  of dissolved  $\text{N}_2\text{O}$  have been generated for several different environments. A profile of  $\delta^{15}\text{N}_2\text{O}$  in the open ocean typically has three main features (Figure 8): (1) isotopic equilibrium with atmospheric  $\text{N}_2\text{O}$  at the surface; (2) a subsurface  $\delta^{15}\text{N}$  minimum; and (3) a broad  $\delta^{15}\text{N}$  maximum in deeper waters coinciding with the  $\text{N}_2\text{O}$  concentration maximum. The observed variations in  $\delta^{15}\text{N}_2\text{O}$  are not yet well-understood.  $\text{N}_2\text{O}$  in the open ocean is generally believed to be a product of nitrification, for which there is only one published measurement of the  $\text{N}_2\text{O}$  isotope effect. Potential explanations for the  $\delta^{15}\text{N}_2\text{O}$  depth variations involve fractionation during consumption of  $\text{N}_2\text{O}$  by denitrifiers, variations in the isotope effect of nitrification, or variations in the  $\delta^{15}\text{N}$  of the substrates for  $\text{N}_2\text{O}$  production by nitrifiers. In denitrification zones, a strong maximum in  $\delta^{15}\text{N}_2\text{O}$  is observed where intense denitrification causes net consumption of  $\text{N}_2\text{O}$  in the water column. In the Arabian Sea,  $\delta^{15}\text{N}_2\text{O}$  has been measured to be as high as 40‰.



**Figure 8** Vertical profiles of (A)  $\text{N}_2\text{O}$  concentration, (B)  $\delta^{15}\text{N}$ , and (C)  $\delta^{18}\text{O}$  of  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  at *in situ* temperatures. The minima in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  around 200m are thought to be due to significant *in situ* production of  $\text{N}_2\text{O}$  from nitrification. The broad isotopic maxima at depth are not well understood. The solid squares at the top of (B) and (C) represent measurements of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of atmospheric  $\text{N}_2\text{O}$  during HOT 76, and arrows indicate the range of historical measurements. (Reproduced with permission from Dore JE, Popp BN, Karl DM and Sansone FJ 1998 *Nature* 396: 63-66.)





**Figure 9** Nitrogen isotopic values of suspended particulate matter ( $\Delta$ ,  $\diamond$ ,  $\square$ ,  $\times$ ,  $\otimes$ ) and sinking particles (as collected by sediment traps,  $\blacksquare$ ) in the North Atlantic Ocean ( $31^{\circ}50' \text{ N}$ ,  $64^{\circ}10' \text{ W}$ ). The profiles of suspended particulate N show the representative depth gradient in  $\delta^{15}\text{N}$ , with lower  $\delta^{15}\text{N}$  in the surface ocean than at depth. The  $\delta^{15}\text{N}$  of the sinking flux shows a decrease with depth. The reason for this decrease, which has also been observed in other regions, is unknown. (Reproduced with permission from Altabet MA, Deuser WG, Honjo S and Stienen C 1991 *Nature* 354: 136–139.)

It has been hypothesized that this extreme  $^{15}\text{N}$  enrichment results from fractionation during  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$  continued isotopic study of dissolved  $\text{N}_2\text{O}$  may greatly improve our understanding of its sources and sinks.

### Particulate N

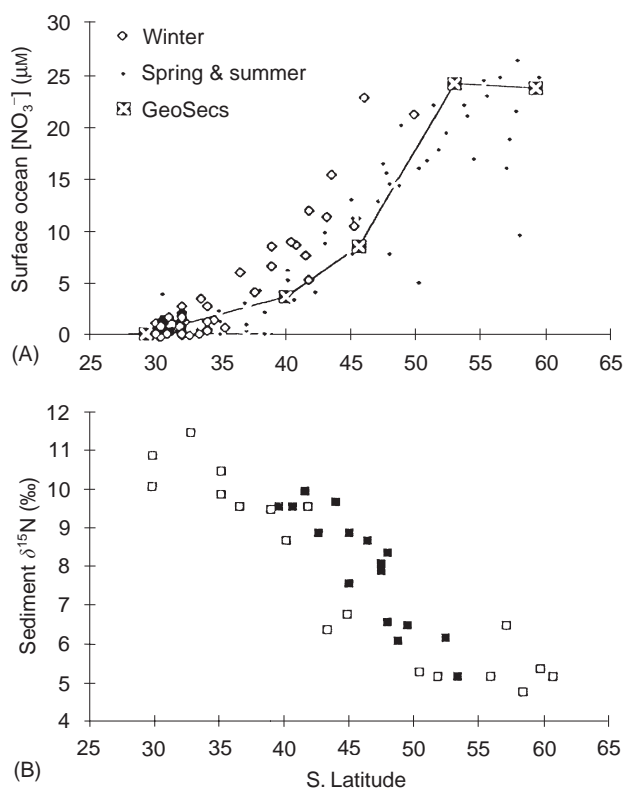
**Suspended particles** A typical profile of suspended particles has its lowest  $\delta^{15}\text{N}$  values in the surface layer, increasing below the euphotic zone (Figure 9). Surface particulate N is low in  $\delta^{15}\text{N}$  not only with respect to deeper particles but also relative to the  $\delta^{15}\text{N}$  that would be expected from uptake of the nitrate supply. The low  $\delta^{15}\text{N}$  values of surface particles have two competing explanations:  $\text{N}_2$  fixation and  $\text{N}_2$  recycling. As described earlier,  $\text{N}_2$  fixation is expected to add fixed N with a  $\delta^{15}\text{N}$  of  $\sim -1$  to  $0\text{‰}$  to surface waters. The isotopic effect of N recycling originates from heterotrophic processes. Zooplankton appear to release ammonium which has a lower  $\delta^{15}\text{N}$  than their food source, making their tissues and solid wastes  $\sim 3\text{‰}$  higher in  $\delta^{15}\text{N}$  than their food source. The low- $\delta^{15}\text{N}$  ammonium is consumed by phytoplankton and thus retained in the surface ocean N pool, while the  $^{15}\text{N}$ -enriched particulate N is preferentially exported as sinking particles, leading to a lower  $\delta^{15}\text{N}$  of surface particulate N in regions where recycled N is an important

component of the gross N supply to phytoplankton. Low  $\delta^{15}\text{N}$  values observed in suspended particulate N from the Antarctic and other high latitude regions cannot be attributed to  $\text{N}_2$  fixation and thus are most likely due to N recycling. In the low-latitude, low-nutrient ocean surface, such as the Sargasso Sea and western tropical Pacific, the relative importance of  $\text{N}_2$  fixation and N recycling in producing low- $\delta^{15}\text{N}$  surface particles is uncertain. Because of its implications for the rates of  $\text{N}_2$  fixation and  $\text{N}_2$  recycling, this question deserves further study.

The  $\delta^{15}\text{N}$  of suspended particles in the subsurface is typically  $6\text{‰}$  higher than suspended particles in the surface ocean and roughly  $3\text{‰}$  higher than the sinking flux. Since suspended particles in the subsurface are thought to derive from sinking particles, it is inferred that their higher  $\delta^{15}\text{N}$  is the result of isotopic fractionation during degradation and consumption by bacteria. Put another way, the  $\delta^{15}\text{N}$  of deep particles is consistent with our inferences that (1) deep particles are the breakdown products of material exported from the surface, and (2) bacteria preferentially remineralize low- $\delta^{15}\text{N}$  particulate N.

**Sinking particulate N and sedimentary N** Because vertical sinking is an important mode of N export from the surface ocean, the  $\delta^{15}\text{N}$  of the sinking flux is one of the most valuable N isotopic constraints on modern ocean processes. Combined with other isotopic data, sinking flux  $\delta^{15}\text{N}$  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 of surface ocean processes to the seafloor, providing the link needed for the sediment column to record the history of surface ocean processes. For instance, isotopic fractionation during nitrate uptake by phytoplankton leads to a strong spatial correlation between nitrate utilization and the  $\delta^{15}\text{N}$  of the particulate N sinking out of nutrient-rich regions. The sinking flux transfers this upper ocean signal to the seafloor, where it is archived in the sediments (Figure 10). This allows for reconstruction of the history of nitrate utilization in nutrient-rich environments such as the Southern Ocean, the Subarctic Pacific, and the equatorial upwelling zones. As a second example, the elevated  $\delta^{15}\text{N}$  of nitrate in regions of denitrification is reflected in the  $\delta^{15}\text{N}$  of the sinking flux, providing the basis for paleoceanographic reconstruction of the strength of regional denitrification.

One of the major concerns in paleoceanographic work involves isotopic changes in particulate N as it sinks through the water column and is buried in sediments. Depth arrays of sediment traps



**Figure 10** Latitudinal variations in surface nitrate concentration (A) and surface sediment  $\delta^{15}\text{N}$  (B) in the east Indian sector of the Southern Ocean. These data indicate that the latitudinal gradient in nitrate utilization by phytoplankton that is recorded in nitrate  $\delta^{15}\text{N}$  (see **Figure 6**) is also recorded in the sediments because of the sinking of particulate N out of the surface ocean. This provides the basis for the paleoceanographic reconstruction of nitrate utilization by phytoplankton. The two data sets in (B) are from two different longitudes (■, East Branch; □, West Branch). (Reproduced from Altabet MA and Francois R 1994 *Global Biogeochemical Cycles* 8: 103–116.)

sometimes show a modest decrease in  $\delta^{15}\text{N}$  with depth (**Figure 9**). This trend runs contrary to our expectations for the isotopic change of particulate matter as it degrades and lacks a good explanation.

Reactions in the shallow sediment column can cause a clear increase in the  $\delta^{15}\text{N}$  of particulate N as it is incorporated into the sedimentary record. The amplitude of this increase depends on the environment, varying between  $\sim 0\text{‰}$  in sediments where a relatively large fraction of the organic rain is preserved into the sediment column, to 2–5‰ in open ocean sediments where only a very small fraction of the N is preserved. Although studies have shown that sedimentary diagenesis has not greatly affected the paleoceanographic information provided by specific sedimentary records, it cannot be presumed that major changes in the ‘diagenetic offset’ have not occurred within any given record. Thus, some recent work has focused on isolating

sedimentary N which is invulnerable to reactions at the seafloor, such as N bound with the mineral matrix of microfossils, or which does not change in  $\delta^{15}\text{N}$  as it is degraded, such as chlorophyll degradation products.

## Concluding Remarks

The study of N isotopes is relatively young, with much of the work to date developing the isotope systematics necessary to study the oceanic N cycle. Nevertheless, important insights into the N cycle have already been gained. Some of the most dramatic contributions have been in the use of sedimentary N isotopes to reconstruct the history of aspects of the oceanic N cycle, such as the assimilative uptake of nitrate by phytoplankton in the ocean surface and the consumption of fixed N by denitrification in low-oxygen regions of the ocean interior. Isotopic studies designed to improve our understanding of the modern N cycle have been hampered in some cases by missing information on important N pools and fluxes. As these hurdles are overcome, the study of N isotopes is entering a new phase of broader application to modern oceanographic questions. In the coming years, the N isotopes promise to provide constraints on a range of topics, such as the physical circulation of the ocean interior, the environments of denitrification, the transport of nutrients in the ocean surface and the rates of  $\text{N}_2$  fixation. Fundamental aspects of the oceanic N cycle are 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.**

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## NOBLE GASES AND THE CRYOSPHERE

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### Introduction

Ice formation and melting strongly influence a wide range of water properties and processes, such as dissolved gas concentrations, exchange of gases between the atmosphere and the ocean, and dense water formation. As water freezes, salt and gases dissolved in the water are expelled from the growing ice lattice and become concentrated in the residual water. As a result of the increased salt content, this residual water becomes more dense than underlying waters and sinks to a level of neutral buoyancy, carrying with it the dissolved gas load. Dense water formation is one of the primary mechanisms by which atmospheric and surface water properties are transported into the interior and deep ocean, and observation of the effects of this process can answer fundamental questions about ocean circulation and the ocean–atmosphere cycling of biogeochemically important gases such as oxygen and carbon dioxide. Because it is not possible to determine exactly when and where dense water formation will occur, it is not an easy process to observe directly, and thus information about the rates of dense water formation and circulation is obtained largely through the observation of tracers. However, when dense water formation is triggered by ice formation, interaction of surface water properties with the ice and the lack of full equilibration between the atmosphere and the water beneath the growing ice can significantly modify the concentrations of the tracers in ways that are not yet fully understood. Consequently, the

information provided by tracers in these ice formation areas is often ambiguous.

A suite of three noble gases, helium, neon, and argon, have the potential to be excellent tracers in the marine cryosphere, providing new information about the interactions of dissolved gases and ice, the cycling of gases between the atmosphere and ocean, and mixing and circulation pathways in high latitude regions of the world's oceans and marginal seas. The physical chemistry properties of these three gases span a wide range of values, and these differences cause them to respond to varying degrees to physical processes such as ice formation and melting or the transfer of gas between the water and air. By observing the changes of the three tracers as they respond to these processes, it is possible to quantify the effect the process has on the gases as a function of the physical chemistry of the gases. Subsequently, this 'template' of behavior can be used to determine the physical response of any gas to the process, using known information about the physical chemistry of the gas. Although this tracer technique is still being developed, results from laboratory experiments and field programs have demonstrated the exciting potential of the noble gases to provide unique, quantitative information on a range of processes that it is not possible to obtain using conventional tracers.

### Noble Gases in the Marine Environment

The noble gases are naturally occurring gases found in the atmosphere. **Table 1** shows the abundance of the noble gases in the atmosphere as a percentage of the total air composition, and the concentrations