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# 8 Nitrogen and Carbon Isotopic Tracers of the Source and Transformation of Particles in the Deep Sea

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## 8.1 INTRODUCTION

The formation of particulate organic matter (POM) in surface waters and its subsequent removal to depth is a principal control on the distribution of inorganic carbon and other biogeochemically-significant species in the ocean (see Fowler and Knauer, 1986, and this volume for reviews). Though it is generally accepted that large, fast sinking particles are the principal form in which organic matter is transported into the ocean's interior, major issues remain regarding the processes controlling their production and transformation.

In an ever growing body of literature, natural variations in  $^{15}\text{N}/^{14}\text{N}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios have been employed as useful natural tracers for testing hypotheses regarding the biogeochemical cycles of nitrogen and carbon in the marine environment. Isotopic signals are produced when transformation processes cause isotopic discrimination between substrate and product. Their use is particularly important on the time and space scales of the deep sea in which important transformations are both difficult to directly probe and observe. Use of isotopic data involves either recognition of ratios characteristic of specific organic matter sources or transformations or exploitation of temporal or spatial variations as 'natural' tracer experiments in which an isotopic signal propagates from one organic pool to another and from the surface into the ocean's interior.

Since in theory any transformation process can alter isotopic ratios (e.g., photosynthesis, trophic transfer, decomposition), it is possible that interpretations of data could be hopelessly ambiguous. Fortunately, a few isolatable processes dominate isotopic signatures in the marine environment and these will be discussed below. The first section is a brief overview of the principles of isotopic fractionation. The following sections discuss changes in isotopic ratio brought about during primary production and during subsequent transformation of organic matter, respectively. The last section summarizes the findings from a recent case study.

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## 8.2 ISOTOPIC FRACTIONATION DURING BIOGEOCHEMICAL REACTIONS

Because natural variations in isotopic ratio are rather small, the 'δ' notation is used in the literature and is defined as:

$$1) \delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} - 1 \times 1000 \text{ (‰)}$$

R refers to the isotopic ratio. For  $\delta^{15}\text{N}$ , atmospheric  $\text{N}_2$  is the standard used for literature values. For  $\delta^{13}\text{C}$ , values are referenced against the PDB standard. The range in  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  is on the order of tens of per mill (‰). By comparison, analytical reproducibility is on the order of  $\pm 0.1$  to  $0.4\%$ . Natural variations in isotopic ratio occur when the specific reaction rates vary for chemical species containing the different isotopes of an element (e.g.,  $^{12}\text{CO}_2$  vs.  $^{13}\text{CO}_2$ ). The fractionation factor is defined as the ratio of these rates:

$$2) \alpha = k/k^* \quad \text{where } * \text{ denotes the heavier isotope.}$$

For ease of comparison fractionation factors are often transformed to the same units as the 'δ' notation:

$$3) \varepsilon = (\alpha - 1) \times 1000$$

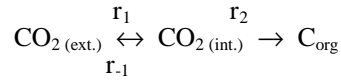
Since reaction rates are usually faster for chemical species containing the lighter isotope,  $\varepsilon$  is usually positive and product pools have lower  $\delta$  values than sources:

$$4) \delta_{\text{product}} = \delta_{\text{source}} - \varepsilon$$

(see Goericke et al., 1994, for an example of an expanded mathematical treatment). As will be seen below actual observed differences in isotopic ratios depend on a number of other factors.

For inorganic reactions,  $\varepsilon$  is a function of reaction conditions, particularly temperature. However, for biogeochemical processes,  $\varepsilon$  is often not only a function of enzyme biochemistry but also organism physiology, and in the literature it usually refers to the net observed fractionation associated with a process that may in reality be the sum of several others. For example, isotopic fractionation during primary production reflects effects occurring during both  $\text{CO}_2$  diffusion across the cell membrane and its subsequent enzymatic fixation into organic matter (e.g., Goericke et al., 1994; O'Leary et al., 1992). On the cellular level, fractionation factors associated with enzymatic reactions where covalent bonds are either broken or formed are usually large compared with those associated with diffusion or active transport of substrates (O'Leary, 1989). For example, RuBP carboxylase

has a value of  $\epsilon$  ranging from 20 to 30‰ (Guy et al., 1986; Roeske and O’Leary, 1984) where diffusion is only on the order of 1‰ (O’Leary, 1984). Consider the simple system:

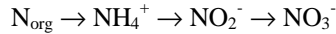


where  $r_1$  is the rate of diffusion into the cell,  $r_{-1}$  is the rate of diffusion out of the cell, and  $r_2$  is the fixation rate of carbon into organic carbon with only this second step producing isotopic fractionation ( $\epsilon_2$ ). Observed fractionation is given by:

$$5) \ \epsilon_{\text{obs.}} = \frac{\epsilon_2 + r_{-1}/r_2}{1 + r_{-1}/r_2}$$

When  $r_{-1}$  is large compared to  $r_2$  (enzyme catalysis limits the overall rate of carbon fixation),  $\epsilon_{\text{obs}}$  approaches  $\epsilon_2$ . At the other extreme, when  $r_1 = r_2$  and  $r_{-1} = 0$  (diffusion limits the overall rate),  $\epsilon_{\text{obs}}$  approaches 0.

This logic can be applied at larger scales. The microbial remineralization of organic nitrogen and its transformation to  $\text{NO}_3^-$  by nitrification involves several steps, some carried out by different bacterial groups, which in oxic, subsurface waters are, for the most part, irreversible:

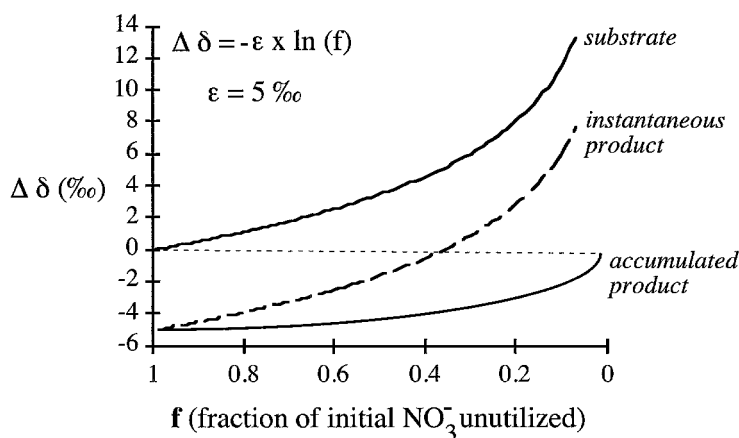


The last two steps are known to have moderate to large values for  $\epsilon$  of 15 to 40‰ (Cifuentes et al., 1989; Horrigan et al., 1990; Miyake and Wada, 1971; Velinsky et al., 1989). However, the first step does not appear to be substantially fractionating (Sweeney and Kaplan, 1980; Velinsky et al., 1991) and since it limits the overall rate,  $\delta^{15}\text{N}$  for newly formed  $\text{NO}_3^-$  should be similar to the  $\delta^{15}\text{N}$  for the organic source under steady state in the deep sea. In fact, little variation has been observed in the  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  outside of denitrification regions, generally ranging from 5 to 6‰ (Liu and Kaplan, 1989), despite large changes in concentration.

In the case of a phytoplankton bloom, in contrast, there are large temporal changes in  $\delta^{15}\text{N}$  of both  $\text{NO}_3^-$  and particulate nitrogen (PN) due to progressive depletion of nutrients and moderate values of  $\epsilon$  associated with  $\text{NO}_3^-$  utilization. Mass balance dictates that the isotopic ratio of substrate increases as a function of depletion as governed by Rayleigh fractionation (Figure 8.1):

$$6) \ \delta^{15}\text{NO}_3^- \text{ (f)} = \delta^{15}\text{NO}_3^- \text{ (f=1)} - \epsilon \times \ln (f)$$

where  $f$  is the fraction of unutilized substrate ( $[\text{NO}_3^-]_{\text{obs.}}/[\text{NO}_3^-]_{\text{initial}}$ ). The  $\delta^{15}\text{N}$  of the PN produced at any instant is given by eq. 4. However, if the system is closed



**Figure 8.1** Expected variation in ‘ $\delta$ ’ value as a function of substrate depletion as predicted by Rayleigh fractionation kinetics.  $f$  is the fraction of unutilized substrate. The change in  $\delta$  for the substrate is given by eq. 6. The change in  $\delta$  for the instantaneous product is given by the combination of eqs. 4 and 6. The change in  $\delta$  for the accumulating product is given by eq. 7.

with respect to the product its observed  $\delta$  as it accumulates is given by the integral of the combination of eqs. 4 and 6 with respect to  $f$  (Figure 8.1):

$$7) \delta^{15}\text{N} - \text{PN}_{(f)} = \delta^{15}\text{NO}_3^-_{(f=1)} + f(1-f) \times \epsilon_u \times \ln(f)$$

In this case, mass balance requires that the  $\delta^{15}\text{N}$  of substrate at  $f = 1$  equals the  $\delta^{15}\text{N}$  of product at  $f = 0$  (Figure 8.1).

### 8.3 SOURCE EFFECTS - $^{15}\text{N}$

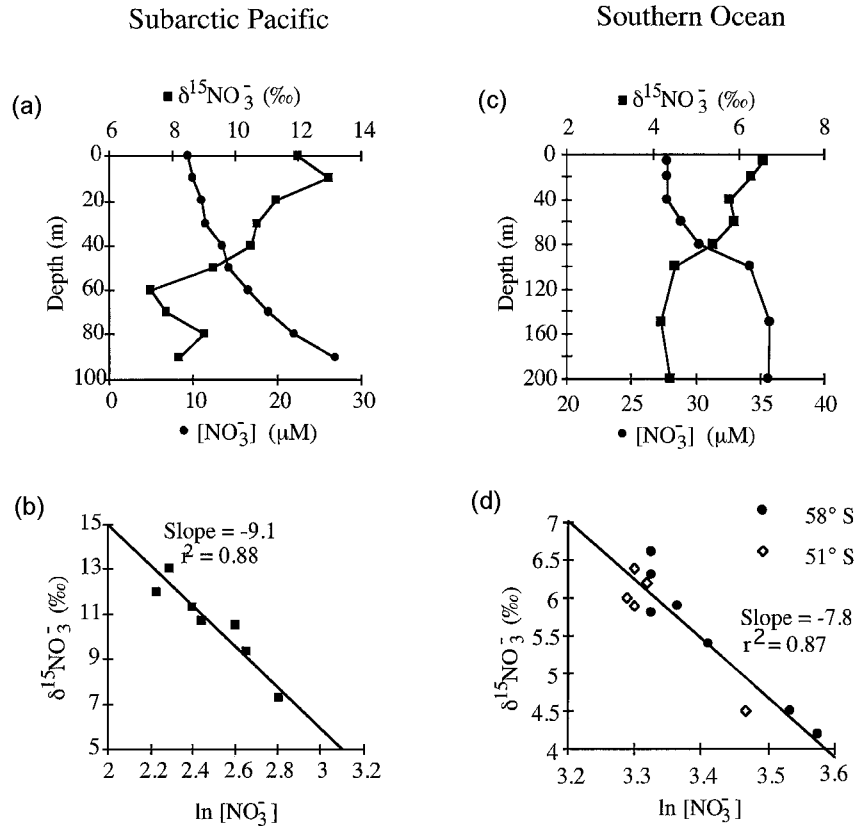
Much of the temporal and regional variation in isotopic variation in POM observed in the marine environment is imparted during primary production, the initial formation of organic matter from inorganic precursors. For nitrogen, utilization of new nitrogen (in contrast to recycled forms) appears to be a critical step. In some settings such as polluted estuaries and anoxic basins (e.g., Black Sea),  $\text{NH}_4^+$  may be the principal new nitrogen source. Rarely, nitrogen fixation from dissolved  $\text{N}_2$  by cyanobacteria makes a major contribution to the fixed N budget. N-fixation occurs with little fractionation so  $\delta^{15}\text{N}$  values for this source are near 0‰ (e.g., Minagawa and Wada, 1986). In the open ocean,  $\text{NO}_3^-$  transported to the surface from below is the predominant form of ‘new’ nitrogen for phytoplankton production. On average, the downward flux of PN from the surface ocean balances the utilization of  $\text{NO}_3^-$  (Eppley and Peterson, 1979). As

there is balance in N fluxes, there must be balance in isotopic composition. In the oligotrophic Sargasso Sea, where  $\text{NO}_3^-$  utilization is complete, the  $\delta^{15}\text{N}$  of sinking PN was shown to be the same as for subsurface  $\text{NO}_3^-$  (Altabet, 1988). As a result, any variations in  $\delta^{15}\text{NO}_3^-$  should be reflected in particulate  $\delta^{15}\text{N}$ .

$\delta^{15}\text{NO}_3^-$  in subsurface waters varies mainly in response to partial removal of  $\text{NO}_3^-$  by denitrification ( $\text{NO}_3^- \rightarrow \text{N}_2$ ) which occurs only under suboxic conditions. Denitrification is strongly fractionating having values for  $\epsilon$  of 20 to 40‰ (Cline and Kaplan, 1975; Liu and Kaplan, 1988; Miyake and Wada, 1971), whereas marine  $\delta^{15}\text{NO}_3^-$  averages 6‰. Values can reach 18‰ in regions such as the Eastern Tropical N. Pacific (ETNP). Subsurface waters from the ETNP flow northward to the S. California Bight where values for  $\delta^{15}\text{NO}_3^-$  are found to be 8 to 9‰ and  $\delta^{15}\text{N}$  for sinking PN is correspondingly about 8‰ (Nelson et al., 1987). As expected in other regions with significant volumes of suboxic water such as the Eastern Tropical S. Pacific and the Arabian Sea, elevated  $\delta^{15}\text{N}$  is also found (Schäfer and Ittekkot, 1993). Substantial decreases in  $\delta^{15}\text{N}$  for sediments in the Arabian Sea during glacial stages has been cited as evidence of climatically driven variations in denitrification in this region (Altabet et al., 1995).

Partial utilization of  $\text{NO}_3^-$  transported to surface waters occurs in large segments of the global ocean either seasonally or perennially. Under these conditions, isotopic fractionation during  $\text{NO}_3^-$  uptake by phytoplankton results in significant  $^{15}\text{N}$  depletion of PN relative  $\text{NO}_3^-$ . In laboratory cultures (Wada and Hattori, 1978; Montoya and McCarthy, 1995)  $\epsilon$  for  $\text{NO}_3^-$  can be as high as 19‰. The earlier study indicated that there was an inverse relationship between  $\epsilon$  and algal growth rate while the latter one showed no change with growth rate but varied instead with species. Diatoms had higher values (9 to 12‰) whereas other forms studied had average  $\epsilon$  values between 1 and 3‰. Field estimates for  $\epsilon$  from the Southern Ocean, Subarctic Pacific, and temperate N. Atlantic fall within the narrow range of 8 to 9‰ (Altabet and Francois, 1994b). However, in the tropical equatorial Pacific,  $\epsilon$  appears to be substantially lower, about 3 to 5‰ (Altabet and Francois, 1994a; Altabet and Francois, manuscript in prep.). This difference may be the result of regional variations in the phytoplankton species responsible for  $\text{NO}_3^-$  depletion. Clearly, more study is required into the factors influencing  $\epsilon$  for  $\text{NO}_3^-$  uptake.

When  $\text{NO}_3^-$  depletion is small, the  $\delta^{15}\text{N}$  of PN should be predicted by eq. 4. In reality, use of recycled N also influences the  $\delta^{15}\text{N}$  of suspended PN and is discussed in the next section. Nevertheless, the lowest values for marine POM (ca. -4 to -5 ‰; Altabet et al., 1991; Altabet and Francois, 1994a) are found where and when there is little depletion of surface ocean  $\text{NO}_3^-$ . As  $\text{NO}_3^-$  is depleted, its  $\delta^{15}\text{N}$  rises as dictated by first-order Rayleigh fractionation kinetics (eq. 6). In near-surface, vertical profiles from the Subarctic Pacific and Southern Ocean,  $\delta^{15}\text{NO}_3^-$  increased with decreasing  $[\text{NO}_3^-]$  toward surface (Altabet and Francois, 1994b; Figure 8.2). The linear relationship between  $\delta^{15}\text{NO}_3^-$  and  $\ln [\text{NO}_3^-]$  predicted by

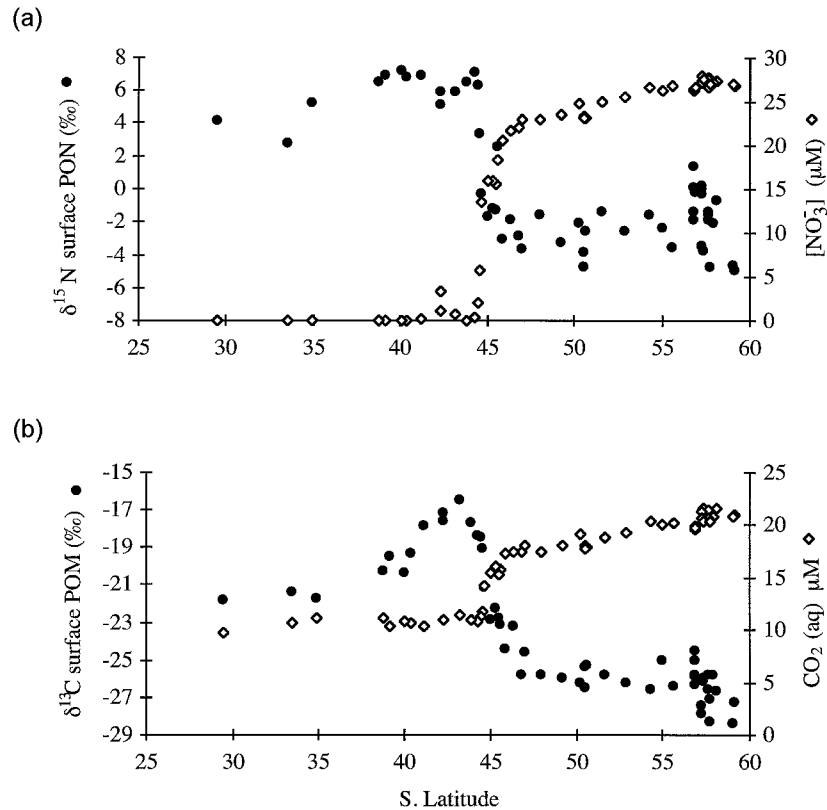


**Figure 8.2** (a) Vertical variations in  $[\text{NO}_3^-]$  and  $\delta^{15}\text{NO}_3^-$  for a site in the central Subarctic Pacific demonstrating isotopic fractionation as function of  $\text{NO}_3^-$  utilization. (b)  $\ln ([\text{NO}_3^-])$  vs.  $\delta^{15}\text{NO}_3^-$  for this data set. According to eq. 6, the slope of the linear regression equals  $-1 \times \epsilon_a$  (9.1‰). (c) Vertical variations in  $[\text{NO}_3^-]$  and  $\delta^{15}\text{NO}_3^-$  for a site in the S.W. Indian Ocean sector of the Southern Ocean showing similar behavior. (d)  $\ln ([\text{NO}_3^-])$  vs.  $\delta^{15}\text{NO}_3^-$  for this data set and another station from the same transect. Calculated  $\epsilon_a = 7.8‰$ .

eq. 5 is observed with the inverse of the slope estimating  $\epsilon$ , in this case showing consistency between the two regions.

Isotopic enrichment in  $\text{NO}_3^-$  by phytoplankton utilization causes the subsequent increase in the  $\delta^{15}\text{N}$  of newly produced PN. Analogous to the vertical variations in  $\delta^{15}\text{NO}_3^-$  with concentration,  $\delta^{15}\text{N}$  values for euphotic zone suspended PN are often lowest at the base of this layer where  $[\text{NO}_3^-]$  is the highest, rising toward surface with decreasing  $[\text{NO}_3^-]$  (Altabet and McCarthy, 1986). Where there are large horizontal gradients in surface  $[\text{NO}_3^-]$ , such as across the northern edge of the Southern Ocean (Figure 8.3a) and the equatorial Pacific (Figure 8.4), there are

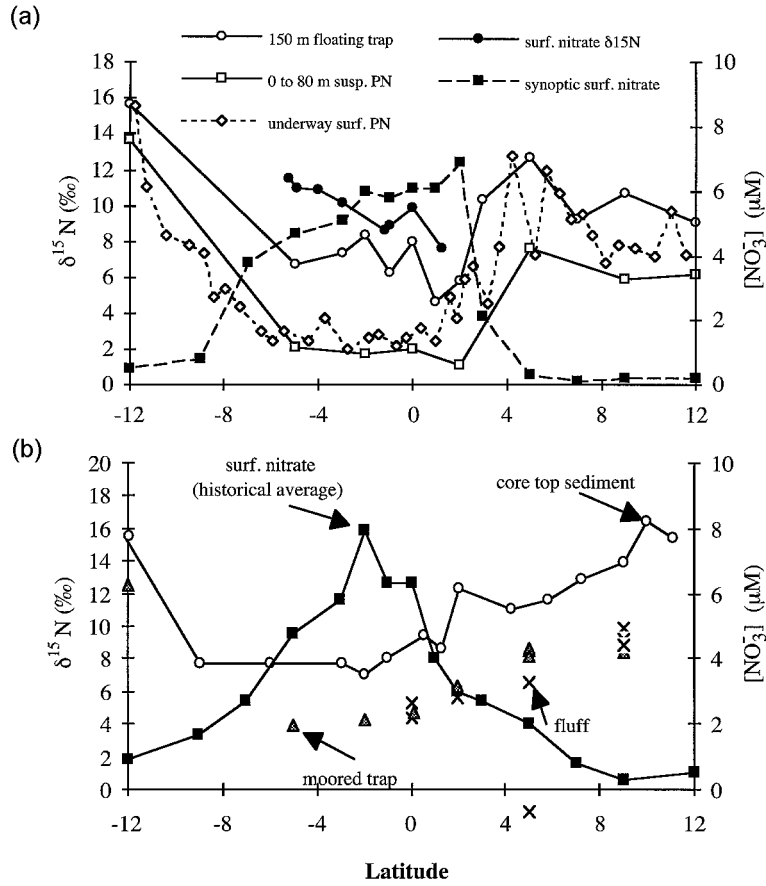
## S.W Indian Ocean Transect



**Figure 8.3** (a) Surface  $[\text{NO}_3^-]$  and  $\delta^{15}\text{N}$  for suspended PN along a transect of the Southern Ocean frontal system (S.W. Indian Ocean sector). The sharp nutrient front at  $45^\circ$  S marks the boundary between subtropical and subpolar water. (b) Surface  $[\text{CO}_2(\text{aq})]$  and  $\delta^{13}\text{C}_{\text{org}}$  for suspended PN along the same transect.

large variations in  $\delta^{15}\text{N}$  of suspended PN inversely correlated with  $[\text{NO}_3^-]$  (Altabet and Francois, 1994b). It is important to note that the  $\delta^{15}\text{N}$  of PN in these regions vary as a function of  $f$  not  $[\text{NO}_3^-]$ . How changes in  $[\text{NO}_3^-]$  reflect  $f$  is highly dependent on the physics of these systems. In the case of the equatorial Pacific, the  $\delta^{15}\text{N}$  of surface  $\text{NO}_3^-$  clearly shows increases with decreasing concentration confirming that latitudinal variations in the  $\delta^{15}\text{N}$  of particles result from partial nutrient utilization (Figure 8.4).

Phytoplankton blooms in which there is substantial drawdown of  $\text{NO}_3^-$  over time result in large temporal/seasonal excursions in particulate  $\delta^{15}\text{N}$ . If the residence



**Figure 8.4** Results for north-south transects of the equatorial Pacific between 135 and 140° W. (a) Comparison of latitudinal variations for synoptic samples collected during the U.S. JGOFS EqPac Fall Survey cruise. Surface concentration and  $\delta^{15}\text{N}$  values for  $\text{NO}_3^-$ , sinking particles collected at 150 m by floating sediment trap, surface suspended particles, and suspended particles averaged over the upper 80 m are shown. (b) Comparison of latitudinal variations in surface  $[\text{NO}_3^-]$  and  $\delta^{15}\text{N}$  values for sediment surface fluff layer, annual average of moored sediment trap collections (880 to 3800 m), and  $\delta^{15}\text{N}$  for core-top sediments.  $\text{NO}_3^-$  data are the historically averaged data of Barber and Chavez (1991).

time of PN in the euphotic zone is short compared to the depletion time of  $\text{NO}_3^-$ , the rise in  $\delta^{15}\text{N}$  with  $f$  will follow more closely eq. 6, otherwise, if PN accumulates in the euphotic zone without any removal, the rise will be more modest and follow eq. 7. The occurrence of this phenomenon is widespread. It has been observed in Gulf Stream warm-core rings (Altabet and McCarthy, 1985), the Sargasso Sea

(Altabet, 1989; Altabet and Deuser, 1985), a coastal Alaska embayment (Goering et al., 1990), mesocosm studies (Nakatsuka et al., 1992), the Arabian Sea (Schäfer and Ittekkot, 1993), the Bay of Bengal (Schäfer and Ittekkot, 1995), the Greenland and Norwegian Seas (Voss et al., 1990) and the temperate N. Atlantic (Altabet et al., 1991). This latter case in which  $\delta^{15}\text{N}$  increased by 13‰ over the course of the bloom will be discussed in greater detail below.

#### 8.4 SOURCE EFFECTS - $^{13}\text{C}$

In contrast to nitrogen isotopes, most of the variation in the  $\delta^{13}\text{C}$  of POM in the ocean results principally from variations in  $\epsilon$  for carbon fixation and not through changes in the isotopic composition of the inorganic source. Dissolved inorganic carbon (DIC) is fairly abundant in the ocean and while it is slightly depleted near-surface due to biological utilization, the corresponding rise in  $\delta^{13}\text{C}$  is only 2 to 3‰ (Kroopnick, 1985). In contrast, marine  $\delta^{13}\text{C}$  values vary by up to 12‰ (-30 vs. -18‰) with lowest values in cold, Antarctic waters and highest values in warm subtropical and tropical waters (Francois et al., 1993; Rau et al., 1982; Rau et al., 1989; Rau et al., 1991; Figure 8.3b). About 3‰ of this change is attributable to temperature dependence of the equilibrium fractionation effect (the difference in  $\epsilon$  for forward and reverse reactions) between  $\text{HCO}_3^-$  and  $\text{CO}_2(\text{aq})$  (Deuser et al., 1968; Mook et al., 1974). While it is  $\text{CO}_2$  that is used by the principal carbon fixing enzyme (RuBP carboxylase), at the typical oceanic pH of 8.2, the bulk of DIC is in the form of  $\text{HCO}_3^-$  which is 8.5 to 11.5‰ enriched in  $^{13}\text{C}$  (as a function of temperature) relative to total DIC. Since  $\delta^{13}\text{C}$  DIC is about 1.5‰,  $\delta^{13}\text{CO}_2$  ranges from -7 to -10‰.

There are alternate carbon fixation pathways employing enzymes such as PEP carboxylase (PEPC) and PEP carboxykinase (PEPCK). While PEPCK has  $\epsilon$  similar for RuBP carboxylase (Arnelle and O'Leary, 1992), the value for PEPC is much less at 2‰ (O'Leary, 1981). Though, at times, measured activities for these enzymes in natural phytoplankton populations can be high (Descolas-Gros and Fontugne, 1988; Descolas-Gros and Fontugne, 1990; Fontugne et al., 1991) and have been cited as the mechanism for variations in marine  $\delta^{13}\text{C}$ , from biochemical considerations they are likely to account for only a very small proportion of total C fixation (Goericke et al., 1994).

Terrestrial carbon (C3 source) has an average  $\delta^{13}\text{C}$  (-27‰) substantially less than what has been considered 'typical' marine  $\delta^{13}\text{C}$  (-22‰) probably as a result of lessened diffusion control of carbon fixation in gas phase ( $\delta^{13}\text{C}$  for atmospheric  $\text{CO}_2$  is higher than for dissolved  $\text{CO}_2$ ). This difference between terrestrial and marine endmembers has been the basis for studies quantifying the importance of terrestrial carbon to marine sediments (Peters et al., 1978). However, most

previous work along these lines ignored the possibility that marine organic carbon could also have low  $\delta^{13}\text{C}$  values.

Given the range in  $\delta^{13}\text{C}$  for marine  $\text{CO}_2(\text{aq})$  and  $\epsilon$  for RuBP carboxylase ( $\epsilon_p$ ),  $\delta^{13}\text{C}$  for POM would thus be expected to vary from -26 to -39‰, substantially lower than observed. It has been pointed out, more recently, that  $\epsilon_p$  is inversely correlated with  $\text{CO}_2(\text{aq})$  which ranges from 9 to 26  $\mu\text{M}$  in surface ocean waters (Popp et al., 1989; Rau et al., 1989).  $\text{CO}_2(\text{aq})$  is a function of total DIC concentration, pH, and temperature, but most of the observed range is the result of changes in the latter (at lower temperatures, the equilibrium between  $\text{HCO}_3^-$  and  $\text{CO}_2$  is pushed toward  $\text{CO}_2$ ). The simplest explanation for the correlation between  $\text{CO}_2(\text{aq})$  and  $\epsilon_p$  is that, at the  $\text{CO}_2$  concentrations found in the ocean, diffusion into phytoplankton cells (which is partially controlled by the  $\text{CO}_2$  concentration gradient across the cell membrane) controls or partially controls the overall rate of C fixation and reduces  $\epsilon_p$  toward the relatively low value for diffusion (about 1‰). For terrestrial plants, Farquhar et al. (1982) developed a model in which  $\epsilon_p$  was a specific function of the external/internal difference in  $[\text{CO}_2]$ . In this model, increasing C fixation rate (equivalent to growth rate) resulted in an increased  $\text{CO}_2$  gradient and lowered  $\epsilon_p$ . Rau et al. (1992) observed during the JGOFS NABE (Joint Global Ocean Flux Study - North Atlantic Bloom Experiment) increasing  $\delta^{13}\text{C}$  with decreasing  $\text{CO}_2$  (due to biological drawdown of DIC). Since the overall correlation showed increased sensitivity in comparison to studies of regional variations, the Farquhar model was used to explain these observations as also resulting from changes during the bloom in 'biological demand' (more precisely growth rate or specific C fixation rate). Other cases of temporal variations in  $\delta^{13}\text{C}$  associated with bloom events have been observed (Goering et al., 1990; Nakatsuka et al., 1992).

A number of physiological parameters influence the degree to which  $\text{CO}_2$  diffusion controls C fixation rate and  $\epsilon_p$ . Francois et al. (1993) modeled the effects of cell surface to volume ratios and found variations in  $\epsilon_p$  just as large as for growth rate. It is therefore likely that there are also substantial variations in  $\epsilon_p$  with species. Fry and Wainright (1991) give evidence that large diatoms (low surface to volume) are relatively enriched in  $\delta^{13}\text{C}$ . Hinga et al. (1994) provide further evidence for the influence of species and pH. The excursion of  $\delta^{13}\text{C}$  to values as high as -16‰ independent of  $[\text{CO}_2(\text{aq})]$  in the region just north of the Subantarctic front in the Southern Ocean is further evidence of the importance of these other factors (Figure 8.3b). Laws et al. (1995) have shown in culture studies that growth rate can be as important as  $[\text{CO}_2(\text{aq})]$  in determining  $\epsilon_p$ .

Much of the recent interest in the relationship between  $\delta^{13}\text{C}_{\text{org}}$  and  $\text{CO}_2(\text{aq})$  is driven by the potential for using sedimentary  $\delta^{13}\text{C}_{\text{org}}$  as a paleobarometer of surface ocean  $\text{pCO}_2$  ( $[\text{CO}_2(\text{aq})]$  is related to  $\text{pCO}_2$  by temperature using Henry's Law). Paleo-reconstruction of  $\text{pCO}_2$  would permit mapping of ocean regions in disequilibrium with the atmosphere and extending the current Vostock ice record for atmospheric  $\text{pCO}_2$  back in time. This information would be critical in under-

standing the links between atmospheric  $p\text{CO}_2$  and climate. However, the validity of such reconstructions depends on the observed correlation between  $\delta^{13}\text{C}_{\text{org}}$  ( $\epsilon_p$ ) and  $\text{CO}_2(\text{aq})$  representing a causal relationship. More investigation into its physiological basis is required and the degree to which other factors such as growth rate and species composition influence  $\delta^{13}\text{C}$  must be better understood to avoid biasing the paleo-records. Diagenetic effects during organic carbon preservation have also not been ruled out, but their possibility has motivated isotopic analyses of purified biomarker compounds retrieved from ancient sediments (Hayes et al., 1989; Jasper and Hayes, 1990; Popp et al., 1989).

## 8.5 TRANSFORMATION EFFECTS - SURFACE OCEAN

Trophic transfer of N results in about a 3.5‰ upward shift in  $\delta^{15}\text{N}$  between the food source and the consuming organism (DeNiro and Epstein, 1981; Fry, 1988; Minagawa and Wada, 1984).  $\delta^{13}\text{C}$  appears to rise a more modest 1‰ amongst heterotrophic organisms but changes between primary producers and herbivores are less clear (DeNiro and Epstein, 1978; Rau et al., 1983). As a result, in any given ecosystem primary producers have the lowest  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values followed by herbivores, etc. The 3.5‰ shift in  $\delta^{15}\text{N}$  evidently reflects the balance in fractionation effects for assimilation and excretion. While zooplankton fecal pellets are consistently enriched in  $^{15}\text{N}$  relative to food source (Altabet and Small, 1990; implying isotopically depleted N is assimilated),  $\epsilon$  associated with the cleavage of amino groups and excretion of  $\text{NH}_4^+$  is evidently large (Checkley and Miller, 1989) resulting in the net retention of  $^{15}\text{N}$  and higher  $\delta^{15}\text{N}$  values. Excreted  $\text{NH}_4^+$  has been shown to be depleted in  $^{15}\text{N}$  by 3‰ relative to zooplankton (Checkley and Miller, 1989).

Trophic effects result in several important patterns of variation in  $\delta^{15}\text{N}$  for the surface ocean. First,  $\delta^{15}\text{N}$  increases with particle size since phytoplankton, particularly in oligotrophic regions, tend to be among the smallest of the plankton (as small as about 0.5  $\mu\text{m}$ ) with larger organisms being at higher trophic levels. Second, larger, fast sinking particles are often aggregates of macrozooplankton fecal matter. Makrozooplankton is often omnivorous so that  $\delta^{15}\text{N}$  of its food sources is higher than  $\delta^{15}\text{N}$  of phytoplankton. Also given that fecal pellets are higher in  $\delta^{15}\text{N}$  than the material consumed, it is not surprising that sinking POM is often enriched by up to 5‰ as compared to suspended POM in the euphotic zone. The difference in  $\delta^{15}\text{N}$  ( $\Delta\delta^{15}\text{N}$ ) between suspended and sinking PN has been proposed as a measure of the number of trophic steps linking primary production to the export of POM from the euphotic zone as sinking particles (Altabet, 1988). In fact, a  $\Delta\delta^{15}\text{N}$  of 0 has been observed during a bloom event, when phytoplankton may be expected to aggregate and sink directly out of the euphotic zone without any trophic transfer (Altabet et al., 1991). In contrast, in the equatorial Pacific,

