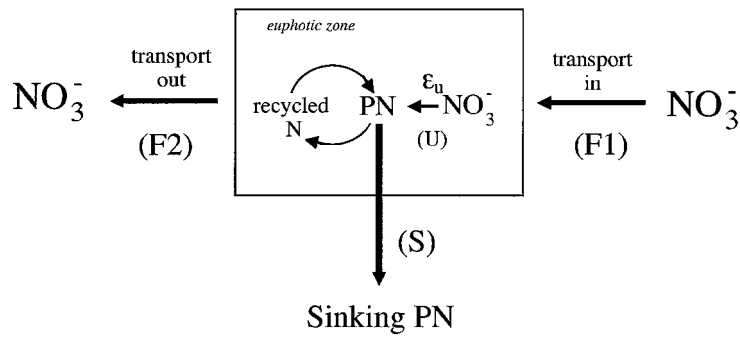


where extensive recycling of N is thought to inhibit nitrate uptake, $\Delta\delta^{15}\text{N}$ is as high as 6‰ (Figure 8.4a). $\Delta\delta^{15}\text{N}$ may thus be related to the efficiency of nutrient recycling in the euphotic zone (f-ratio). The larger the number of trophic steps the greater the proportion of nitrogen supplied to phytoplankton in the form of NH_4^+ (or urea) recycled by consumers.

Though at first counter-intuitive, the need for balance between new nitrogen (NO_3^-) utilized by phytoplankton and the export of sinking PN from the euphotic zone requires that the $\delta^{15}\text{N}$ of utilized NO_3^- equals on average the $\delta^{15}\text{N}$ of sinking PN (Figure 8.5). This is important in that it is the isotopic composition of sinking PN, not euphotic zone suspended PN, which records the isotopic imprint of denitrification and partial utilization of NO_3^- on $\delta^{15}\text{NO}_3^-$. This observation is an important prerequisite for the use of sedimentary PN (which is derived from the sinking PN reaching the seafloor) as a record of past changes in either denitrification or surface ocean nutrient utilization. It follows that when there is substantial recycling of nitrogen in the euphotic zone, the $\delta^{15}\text{N}$ of suspended PN decreases as a result of increasing utilization by phytoplankton of NH_4^+ depleted



$$F1 = F2 + S$$

$$F1 \times \delta^{15}\text{N}_{F1} = (F2 \times \delta^{15}\text{N}_{F2}) + (S \times \delta^{15}\text{N}_S)$$

$$\delta^{15}\text{N}_{F2} - \delta^{15}\text{N}_{F1} = -\epsilon_U \times \ln(F2/F1)$$

Figure 8.5 Schematic of major nitrogen fluxes in the surface ocean pertinent for determining N isotopic ratios. The most important terms are the input of new NO_3^- and any subsequent export of the unutilized fraction, fractionation during uptake into suspended PN, and the removal of sinking PN. Recycling does not influence the overall nitrogen balance. Corresponding equations for nitrogen and nitrogen isotopic balance are shown.

in ^{15}N . This makes sense when it is realized that the production of ^{15}N depleted NH_4^+ and its subsequent imprint on the phytoplankton (in open ocean waters NH_4^+ rarely accumulates but instead is immediately taken up) balances the ^{15}N enrichment of higher trophic levels. As a result, values for suspended PN in oligotrophic waters (f for $\text{NO}_3^- = 0$) approaching 0‰ or less should not necessarily be interpreted as reflecting large inputs from nitrogen fixation (which has an isotopic composition similar to atmospheric N_2 ; Minagawa and Wada, 1986), but are likely to be caused by N-recycling. The low values for suspended PN in the equatorial Pacific (Figure 8.4a) are another example of this phenomenon.

8.6 TRANSFORMATION EFFECTS - WATER COLUMN AND SEDIMENT SURFACE

Below the euphotic zone and in the ocean's interior there is a net heterotrophic destruction of organic matter and remineralization to inorganic constituents (DIC and NO_3^-). In principle, isotopic fractionation can accompany this process resulting in modification of the isotopic composition of the residual POM. The ubiquitous increase in the $\delta^{15}\text{N}$ of small, suspended particles with depth below the euphotic zone correlated with decreasing concentration has often been cited as evidence for isotopic fractionation during the destruction of PN (Altabet and McCarthy, 1986; Saino and Hattori, 1980; Saino and Hattori, 1985). Alternatively, it has been suggested that the increase in $\delta^{15}\text{N}$ reflects contributions to the suspended PN pool from the fragmentation of large, fast sinking particles (Altabet, 1988). Large, fast sinking particles show, in contrast, no increase in $\delta^{15}\text{N}$ with depth and below 1000 m often decrease in $\delta^{15}\text{N}$ when overall fluxes are low (Altabet et al., 1991). Sedimentary $\delta^{15}\text{N}$ does appear to be enriched by several ‰ compared to $\delta^{15}\text{N}$ of sinking particles (Altabet and Francois, 1994a; Figure 8.4b). $\delta^{13}\text{C}_{\text{org}}$ for sinking particles also shows little vertical variation, but suspended $\delta^{13}\text{C}$ appears to decrease with depth (Eadie and Jeffrey, 1973; Jeffrey et al., 1983). Sedimentary $\delta^{13}\text{C}$, in contrast, is higher by up to 4‰ as compared to sinking particles in the few studies made (Fischer, 1991). Together these observations appear to present a confusing picture of diagenetic effects on $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$.

If there are diagenetic effects on isotopic composition there are two types of mechanisms that could be responsible. In the first, there is isotopic fractionation during organic N and C remineralization on a molecular scale; released N or C has a lower isotopic ratio than their precursors thereby isotopically enriching the residual. Significant isotopic fractionation has been shown to occur during acid hydrolysis (abiotic) of simple peptides (Silfer et al., 1992), with preferential releases of amino acids containing the lighter isotope. During biological remineralization, though, fractionation effects appear to be rather small. NH_4^+ extracted from organic-rich nearshore sediments (still containing a large fraction of labile

PON) with KCl was $1 \pm 0.4\%$ ($n = 5$) heavier than bulk sediment $\delta^{15}\text{N}$ (Altabet and Christensen, unpublished), suggesting a small fractionation effect during bacterial decay of organic matter. A similar relationship between sedimentary PN and NH_4^+ has been found in the S. California Bight (Sweeney and Kaplan, 1980), Framvaren Fjord, and Great Marsh Delaware (Velinsky et al., 1991). Similarly, respired CO_2 has $\delta^{13}\text{C}$ values only slightly lower than the source organic matter (DeNiro and Epstein, 1978). Another piece of evidence against a significant molecular isotope fractionation during diagenesis is the lack of increases in the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of sinking particles with depth despite large decreases in N flux (Altabet, 1989; Altabet et al., 1991). In this case, though, these observations could be explained if the decrease in flux with depth was brought about by ingestion of large particles by metazoans instead of microbial remineralization.

Alternatively, there may be selective removal/preservation of different organic components that vary in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$. In this case, mass balance dictates the residual POM changes accordingly. Due to fractionation along biosynthetic pathways, major biochemical classes vary substantially in isotopic ratio (e.g., Degens et al., 1968; Macko et al., 1987). The best example of this is the observation that lipids are depleted in ^{13}C relative to proteins and carbohydrates. The decrease in $\delta^{13}\text{C}$ for POC with depth has been attributed to the selective preservation of lipids. Organic nitrogen in living biomass is found chiefly in the form of amino acids and proteins, but Macko (1987) has found in bacteria that $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ for individual amino acids can vary by up to 12‰ and 26‰, respectively, mostly as a result of fractionation during transamination. In the water column, though, amino acid distribution pattern does not change markedly with depth (e.g., Haake et al., 1992).

Regarding the sediments, a consensus has developed that almost all labile material is removed shortly after deposition in the deep sea (Martin et al., 1991). Since $\delta^{15}\text{N}$ values for seafloor 'fluff' material are similar to sediment trap values but lower than the top layers of consolidated sediment (Altabet et al., in prep.; Figure 8.4b), the shift in $\delta^{15}\text{N}$ observed appears to happen during this process. Protection of surviving material could occur via the formation of high molecular weight refractory organic matter during humification. In the case of nitrogen, amino acids in proteins and peptides are the dominant forms of N in living organisms, but they account for less than 50% in sinking PN (Ittekkot et al., 1984; Haake et al., 1992; Haake et al., 1993) and less than 10% in surficial deep-sea sediments (Mopper and Degens, 1972; Whelan, 1977). A similar trend is found for organic carbon identifiable as proteins, carbohydrates or lipids. The survival of refractory biomass components with distinct isotopic composition may indeed account for the apparent diagenetic shifts in the isotopic composition of deep-sea sediments.

Selective preservation could also occur as a result of the close association of specific organic pools with mineral phases which protect them from bacterial degradation (Altabet and Curry, 1989; Shemesh et al., 1993). In fact, all the amino

acids present in deep-sea sediments may be in association with minerals (Müller and Suess, 1977). In general, all organic matter in deep-sea sediments may have been preserved by adsorption to surfaces (Keil et al., 1994). Also significant are the organic templates of calcareous and siliceous skeletons produced during biomineralization (King, 1975; King, 1977) which may account for a significant fraction of total organic matter in some deep-sea sediments (e.g., Froelich, 1980).

The view that emerges is that diagenetic shifts in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ are likely to be caused by selective removal of particulate components which vary in isotopic ratio. However, explicit evidence is needed for the mechanisms accounting for the upward shifts in $\delta^{15}\text{N}$ with apparent diagenesis of suspended particles in the water column and between sinking particles and the sediments.

8.7 THE JGOFS NORTH ATLANTIC BLOOM EXPERIMENT - A CASE STUDY

In 1989, the JGOFS NABE program studied a spring phytoplankton bloom in the N.E. Atlantic Ocean. Intense biological activity produced large changes in surface water biogeochemical properties. NO_3^- decreased in concentration from 6 μM to near 0 (Figure 8.6a) over the course of the bloom and DIC (ΣCO_2) concentrations correspondingly decreased from 2093 to 2040 μM (Chipman et al., 1993). $\text{CO}_2(\text{aq})$ decreased from 13 to 10 μM in response to the drop in DIC since there was little change in surface temperature during the bloom (Figure 8.6c). Consistent with previous observations discussed above there were substantial increases in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ for near-surface suspended and sinking POM (Figures 8.6b and d).

8.7.1 NEAR-SURFACE TIME-SERIES SIGNALS IN $\delta^{15}\text{N}$ AND $\delta^{13}\text{C}$

Hypothetically, seasonal variations in $\delta^{15}\text{N}$ may be roughly divided into three phases; pre-bloom, bloom, and post-bloom. During the pre-bloom period, euphotic zone NO_3^- is not yet significantly depleted and $\delta^{15}\text{N}$ for POM produced at this time would be expected to be a function of the $\delta^{15}\text{N}$ value for NO_3^- and the fractionation factor (ϵ_u , if there is little recycling of ^{15}N nitrogen during the early stage of the bloom). NO_3^- prior to depletion should have $\delta^{15}\text{N}$ values between 5 and 6‰ since deepwater NO_3^- (in regions uninfluenced by water column denitrification) has been found to be fairly homogenous in $\delta^{15}\text{N}$ within this range (Liu and Kaplan, 1989). With $\delta^{15}\text{NO}_3^- = 5$ to 6‰ and $\delta^{15}\text{N}_{\text{POM}} = -3$, ϵ_u is 8 to 9‰ (also see Altabet et al., 1991). Similar values for ϵ_u have been found for the Subarctic Pacific and the Southern Ocean (Figure 8.2) and are consistent with recent laboratory determinations of ϵ_u for diatoms which dominated the early portion of the bloom.

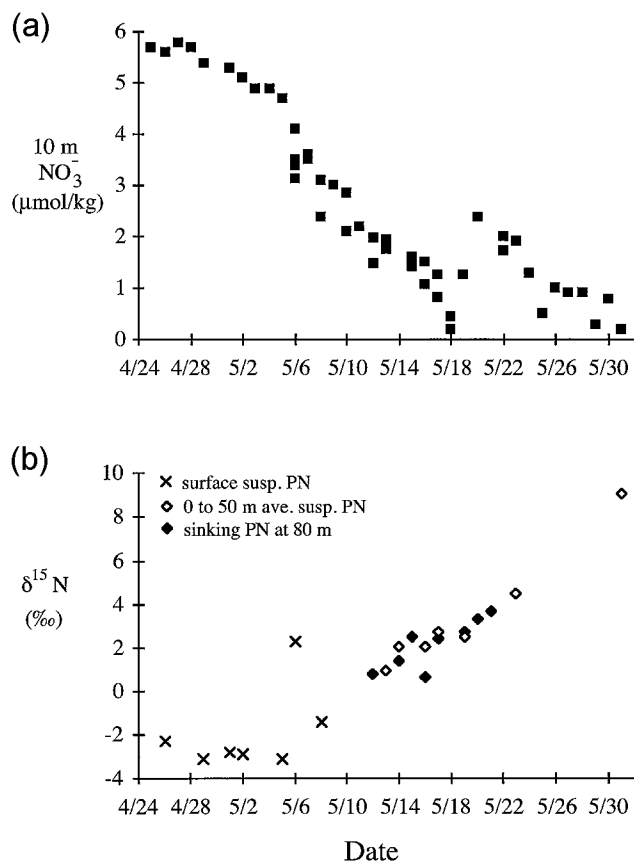


Figure 8.6 Time-series variations in near-surface properties during the JGOFS N. Atlantic Bloom Experiment (NABE). (a) NO_3^- concentration at 10 m. (b) $\delta^{15}\text{N}$ of suspended and sinking PN. Values for suspended PN averaged over the upper 50 m (nominal depth of euphotic zone) are weighted by PN concentration. (c) Surface ΣCO_2 (Chipman et al., 1993) and $\text{CO}_2(\text{aq})$ concentrations. (d) $\delta^{13}\text{C}$ of suspended and sinking POC. Values for suspended POC averaged over the upper 50 m (nominal depth of euphotic zone) are weighted by POC concentration. Where indicated, surface suspended POC $\delta^{13}\text{C}$ data are from Rau et al. (1992).

During the bloom phase, significant biological depletion of euphotic zone NO_3^- occurs and $\delta^{15}\text{NO}_3^-$ increases according to eq. 6. The actual temporal response in bulk $\delta^{15}\text{N}_{\text{POM}}$ depends strongly on its residence time in the euphotic zone. Plotting predicted $\delta^{15}\text{N}$ shows that observations lie in between those predicted by the instantaneous (zero residence time) and accumulated (infinite residence time) product equations; eqs. 6 and 7 (Figure 8.7). Predictions for $\delta^{15}\text{N}_{\text{POM}}$ and PN

