THE USE OF NITROGEN ISOTOPIC RATIO FOR RECONSTRUCTION OF PAST CHANGES IN SURFACE OCEAN NUTRIENT UTILIZATION

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ABSTRACT. Sedimentary $^{15}$N/$^{14}$N ratios can be used as a unique measure of past changes in surface ocean nutrient utilization which in turn is a function of past changes in productivity and nutrient input from deeper waters. Due to isotopic fractionation during nitrate uptake by phytoplankton, partial nutrient utilization produces substantial $^{15}$N enrichment in particulate matter reaching the seafloor. Examples are given from the N. Atlantic, Equatorial Pacific, and Southern Ocean. In the latter two regions large variations in nutrient utilization with latitude are observed which go along with gradients in both near-surface ocean and core top $^{15}$N/$^{14}$N. Thus isotopic signals generated in surface waters are transferred and preserved in sediments. First down core results from the Southern Ocean indicate that only modest increases in nutrient utilization and perhaps productivity occurred in Subantarctic waters during the last glacial maximum.

INTRODUCTION

The availability of nutrients in the surface ocean is an important control on primary production, whose variability over geologic time may have altered major biogeochemical cycles and influenced climate (e.g. Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox and McElroy, 1984; Toggweiler and Sarmiento, 1985). Cd/Ca and $\delta^{13}$C in foraminiferal calcite have separately been used as indicators for surface nutrient concentrations (Boyle, 1988; Keigwin and Boyle, 1989; Labeyrie and Duplessy, 1985; Charles and Fairbanks, 1990). Ge/Si ratios in preserved diatom frustules have been used to reconstruct past changes in surface silicate utilization (Froelich et al., 1989) but now appear to actually be an indicator for changes in oceanic Ge/Si (Froelich, pers. comm.). Despite the importance of fixed nitrogen as a limiting nutrient, means have not been previously available for specific reconstruction of past surface concentrations or utilization.
Natural variations in nitrogen isotopic ratio have been widely used as a contemporary tracer of nitrogen biogeochemistry in the marine environment (see Montoya, this volume for a general review), but paleoceanographic applications have been rather limited (Rau et al., 1987; Altabet and Curry, 1989). It is only recently that sedimentary $^{15}$N/$^{14}$N have been applied as the only recorders available of surface nutrient utilization (Francois et al., 1992; Francois et al., 1993; Calvert et al., 1992; Altabet and Francois, 1993). Findings to date indicate substantial potential for sedimentary $^{15}$N, by detecting the degree of nutrient depletion of overlying surface waters, to make important contributions to our understanding of past changes in surface productivity and its influence on ocean biogeochemistry.

This application of sedimentary $^{15}$N is based on the observation that, in contemporary surface waters, nutrient depletion is strongly related to large changes in the $^{15}$N of particulate organic matter (POM) as a result of isotopic fractionation during phytoplankton utilization of nitrate (e.g. Altabet et al., 1991). Paleoceanographic use, however, hinges in part on the fidelity with which this isotopic signal generated in surface waters is preserved in sediments. Unlike Cd/Ca and calcite $^{13}$C which are carried in mineral phases of marine microfossils, the $^{15}$N signal is carried in organic matter raining down from surface waters. Therefore, $^{15}$N values can potentially be substantially altered by particle decomposition (Saino and Hattori, 1980; Altabet and McCarthy, 1986; Saino and Hattori, 1987; Altabet, 1988) and trophic exchange of nitrogen (DeNiro and Epstein, 1981; Minagawa and Wada, 1984; Fry, 1988). Despite this perspective, recent work summarized below does demonstrate that the surface signal is coherently transferred to and preserved in the sediments of the Southern Ocean and Equatorial Pacific. The following sections also include a brief methodological description, and discussion of the factors influencing generation and magnitude of the surface-ocean signal and its transfer to the seafloor.

MATERIALS AND METHODS

In all the examples given below (Table 1), suspended PN (particulate nitrogen) was collected from near-surface waters by filtering water samples onto precombusted ($450^\circ$ C), Whatman GF/F filters. These filters have been found to have very low blank levels when precombusted, retain particles at small enough sizes to collect the majority of open ocean PN, and are sufficiently robust for convenient handling (Altabet, 1990). Protocols have been designed to minimize contamination from air-born particles (e.g. in-line filter holders were used.

\[ \delta^{15}N (\%o) = \frac{^{15}N/^{14}N_{sample} - ^{15}N/^{14}N_{atm. \ N_2}}{^{15}N/^{14}N_{atm. \ N_2}} \times 1000 \]