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Nitrogen isotope dynamics of the Cariaco Basin, Venezuela

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[1] We report $^{15}\text{N}/^{14}\text{N}$ measurements of water column nitrate and ammonium, sinking particles, and sediments from the Cariaco Basin, an anoxic marine basin off the coast of Venezuela. Water column denitrification occurring in the basin has only a very small isotopic imprint on nitrate in the basin because nitrate consumption is nearly complete in the actively denitrifying water near the oxic/anoxic interface (~ 275 m). Being free of a large denitrification signal, the $\delta^{15}\text{N}$ of shallow thermocline nitrate is $\sim 3.5\text{‰}$, significantly lower than the mean deep ocean nitrate $\delta^{15}\text{N}$ of 5‰ . This may be due to the nitrification of newly fixed N, whether it occurs within the basin or in open Atlantic waters that flow into the Cariaco over the sill. The $^{15}\text{N}/^{14}\text{N}$ of the sinking flux in the deepest trap (~ 1250 m) is similar to that of thermocline nitrate, as expected given the complete consumption of nitrate in the surface layer. Moreover, the $^{15}\text{N}/^{14}\text{N}$ of the seafloor sediment is similar to that of the sinking flux, as is common in environments of high export production, low O_2 , and good organic matter preservation. Thus the modern Cariaco Basin records the $^{15}\text{N}/^{14}\text{N}$ of the thermocline nitrate, which, in turn, may record the input of newly fixed N to the upper ocean, be it local or more regional in origin.

INDEX TERMS: 1615 Global Change: Biogeochemical processes (4805); 4802 Oceanography: Biological and Chemical: Anoxic environments; 4870 Oceanography: Biological and Chemical: Stable isotopes; **KEYWORDS:** Cariaco Basin, denitrification, nitrogen isotopes

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1. Introduction

[2] Biologically available (or “fixed”) nitrogen is the proximate limiting nutrient for primary productivity in most of the open ocean. In recent budgets of oceanic fixed nitrogen, N_2 fixation ($\text{N}_2 \rightarrow \text{N}_{\text{org}}$) is the dominant input and denitrification ($\text{NO}_3^- \rightarrow \text{N}_2$) is the dominant output. The current state of the oceanic fixed N budget is highly uncertain, and it is not clear whether the fixed N reservoir is changing or at steady state [Brandes and Devol, 2002; Codispoti, 1995; Codispoti et al., 2001; Gruber and Sarmiento, 1997]. The effective sensitivities of the budget also are poorly understood. Redfield argued that N_2 fixers regulate the oceanic nitrate reservoir to match the phosphate reservoir [Redfield et al., 1963]. Being competitive in P-bearing, N-deplete systems, they should add N more quickly when the oceanic nitrate reservoir drops below the N/P ratio required by phytoplankton (the 16/1 “Redfield

ratio”). However, other environmental parameters, such as iron availability, may have an equivalent or greater role than the availability of nitrate versus phosphate in determining the success of the N_2 fixers and thus the rate of N_2 fixation [Falkowski, 1997], and the global mean N/P of phytoplankton may vary in space and time [Klausmeier et al., 2004]. It is also conceivable that denitrification regulates the size of the oceanic nitrate reservoir [Toggweiler and Carson, 1995], through the requirement of suboxia for denitrification to occur [Cline and Richards, 1972; Codispoti et al., 2001]. As the nitrate reservoir grows, the oxygen content of the ocean interior should drop due to enhanced productivity (ignoring for the moment limitation by phosphate). This would increase the expanse of suboxic denitrifying environments, leading to more rapid nitrate loss. Solving the riddle of whether and how the oceanic N reservoir is regulated might involve reductionist studies of the central organisms and enzymes [e.g., Berman-Frank et al., 2001; Kustka et al., 2002, 2003], observations of the modern ocean on regional and global scales [e.g., Deutsch et al., 2001; Gruber and Sarmiento, 1997; Karl et al., 1997; Sanudo-Wilhelmy et al., 2001], or paleoceanographic efforts to reconstruct past responses of the N cycle to external forcings [e.g., Altabet et al., 1995; Ganeshram et al., 1995]. In the case of the latter two approaches, the global ocean may be studied, but isolated marine environments, such as the Cariaco Basin, may also provide critical test cases [Haug et al., 1998].

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[3] The stable isotopes of nitrate provide insight into the oceanic fixed N budget and may play a critical role in revealing the sensitivities of the oceanic N budget. Most of the deep ocean (>2 km) is roughly constant in nitrate $\delta^{15}\text{N}$, at $\sim 5\%$ relative to atmospheric N_2 [Liu and Kaplan, 1989; Sigman *et al.*, 2000] ($\delta^{15}\text{N}_{\text{sample}} = ((^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference}} - 1) \times 1000\%$, where the $^{15}\text{N}/^{14}\text{N}$ reference is N_2 in air). Little fractionation occurs during N_2 fixation, resulting in newly fixed N with a $\delta^{15}\text{N}$ of $\sim -2-0\%$ relative to atmospheric N_2 [Carpenter *et al.*, 1997; Delwiche *et al.*, 1979; Hoering and Ford, 1960]. Inputs of newly fixed N may explain the observation of low nitrate $\delta^{15}\text{N}$ in the shallow subtropical thermocline [Karl *et al.*, 2002; Liu *et al.*, 1996]. Denitrification preferentially consumes $^{14}\text{NO}_3^-$, with an organism-level isotope effect of $\sim 20-30\%$ [Barford *et al.*, 1999], so its occurrence leads to a marked increase in nitrate $\delta^{15}\text{N}$ in oceanic regions of suboxia [Altabet *et al.*, 1999; Brandes *et al.*, 1998; Cline and Kaplan, 1975; Liu and Kaplan, 1989; Voss *et al.*, 2001].

[4] The ^{15}N enrichment of oceanic nitrate by water column denitrification is thought to be the fundamental reason that the $^{15}\text{N}/^{14}\text{N}$ of mean ocean nitrate is higher than that of atmospheric N_2 [Brandes and Devol, 2002]. However, we must then ask why mean ocean nitrate is not more enriched in ^{15}N than it is. If we assume that the $\delta^{15}\text{N}$ of N input to the ocean (by oceanic 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 homogenous process throughout the ocean water column, the $\delta^{15}\text{N}$ of mean ocean nitrate, rather than being 5% , should be $20-30\%$, so that denitrification (with an isotope effect of $20-30\%$) would remove nitrate with a $\delta^{15}\text{N}$ of 0% . The low $\delta^{15}\text{N}$ of mean ocean nitrate (5%) relative to the isotope effect of denitrification ($20-30\%$) must hold information on the environments of denitrification and their exchange with the nitrate reservoir of the global ocean.

[5] Work by Brandes and Devol [1997, 2002] suggests that denitrification within sediment pore waters provides an answer to this puzzle. From isotopic analyses of nitrate from benthic chamber deployments, these authors observed that sedimentary denitrification in the highly reactive sediments of Puget Sound occurs with an isotope effect of $\sim 0\%$, presumably due to diffusion-limitation of denitrification. This basic observation has subsequently been replicated in a range of sedimentary environments [Brandes and Devol, 2002; Sigman *et al.*, 2001, 2003]. Thus Brandes and Devol [2002] posit that the low $\delta^{15}\text{N}$ of oceanic nitrate (5% rather than $20-30\%$) is due to the importance of sedimentary denitrification as a mechanism of nitrate loss from the global ocean.

[6] The isotope fractionation during nitrate assimilation by phytoplankton has received a great deal of attention as a potential tool to reconstruct the nutrient status of the surface ocean in the past [Altabet and Francois, 1994], and the $\delta^{15}\text{N}$ of nitrate in nutrient-rich surface environments shows a clear and consistent imprint of this process [Sigman *et al.*, 1999]. However, the cycle of nitrate uptake and organic N oxidation has only modest effects on the $\delta^{15}\text{N}$ of subsurface

nitrate [Sigman *et al.*, 2000]. As a result, the $\delta^{15}\text{N}$ of nitrate in the ocean subsurface is relatively sensitive to the terms of the whole-ocean fixed N budget, in particular, N_2 fixation and denitrification. Moreover, for most of the low-latitude ocean, the subsurface nitrate brought into the euphotic zone is completely consumed by phytoplankton, so that sinking particle $\delta^{15}\text{N}$ should be similar to that of the subsurface nitrate [Altabet, 1988]. Even in upwelling regions, the nitrate brought to the surface is eventually completely consumed [Altabet *et al.*, 1999]. Thus there is some hope that the organic N accumulating in deep sea sediments may provide a record of subsurface nitrate $\delta^{15}\text{N}$ and thus of past regional and global changes in the oceanic N budget.

[7] The Cariaco Basin provides a unique opportunity to study the history of N cycle processes. The Cariaco Basin is anoxic below ~ 275 m, resulting in sediments that are laminated and rich in organic matter [Hughen *et al.*, 1996; Peterson *et al.*, 1991]. Thus Cariaco Basin sediments might be free of the isotopic alteration of sedimentary N that appears to be associated with diagenesis in oxic sedimentary environments with low rates of organic matter burial [Altabet *et al.*, 1999]. Moreover, the major nutrients are completely consumed in the surface waters of the central part of the basin over the course of a year, so that the annually integrated sinking flux $\delta^{15}\text{N}$ should record only two parameters: (1) the isotopic composition of nitrate upwelled to the surface and (2) any fixation of N_2 by phytoplankton in the Cariaco surface waters.

[8] Here we present results from an ongoing time series sediment trapping and water column chemistry study in the Cariaco Basin. We have collected sinking particles at multiple depths, water column nitrate and ammonium samples, and surface sediments; we report N isotope data for each of these samples types. With these data, we address the following questions: (1) What controls the isotopic composition of nitrate in the Cariaco Basin? (2) What is the relationship between the $\delta^{15}\text{N}$ of subsurface nitrate and that of the sinking flux? (3) What is the relationship between the $\delta^{15}\text{N}$ of the sinking flux and that of the seafloor sediments?

2. Materials and Methods

2.1. Study Area

[9] The Cariaco Basin (Figure 1) is a 1400-m deep depression on the Venezuelan continental shelf that exchanges with the open Atlantic above a shallow (~ 100 m) sill. There are two channels breaching this sill, one in the northeast of 135 m depth (La Tortuga) and a narrower one in the northwest of 146 m depth (Centinela) [Lidz *et al.*, 1969; Richards, 1975]. Owing to slow turnover of basin waters and high surface productivity, decomposition of the sinking material leads to permanent anoxia below about 275 m [Richards, 1975].

[10] The Cariaco Basin undergoes strong seasonal changes in upper ocean conditions due to the migration of the Inter-Tropical Convergence Zone (ITCZ) about the equator [Muller-Karger and Aparicio, 1994]. The ITCZ is in its most southerly position during the Northern Hemisphere winter and spring, at which time rainfall is at a

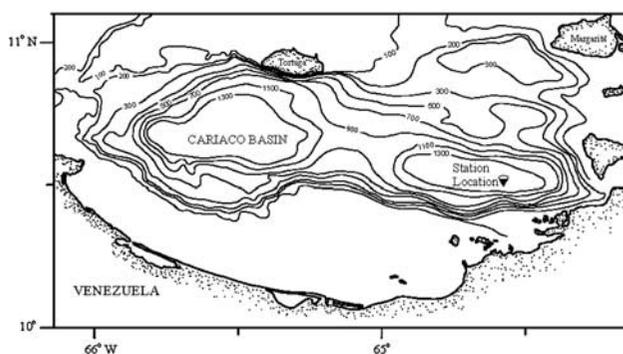


Figure 1. Bathymetric map of the Cariaco Basin showing the location (10.5°N, 64.67°W) of the time series station in the eastern subbasin.

minimum and strong easterly winds cause intense upwelling along the Venezuelan coast. During the summer and early fall, the ITCZ migrates to the north. This leads to an increase in rainfall in the Cariaco Basin, while causing the trade winds to diminish and upwelling to decrease. The relationship between seasonal changes in climatology and the production and flux of organic matter in the Cariaco Basin has been described recently by *Muller-Karger et al.* [2001] and *Goñi et al.* [2003]. Interannual variability of shallow waters of the Cariaco Basin is driven mostly by ENSO [*Enfield and Mayer, 1997*].

2.2. Field Program and Sample Collection

[11] A time series study was initiated in Cariaco Basin in November 1995 with the goal of examining the linkage between physical forcing and vertical carbon flux in a highly productive continental margin setting [*Muller-Karger et al., 2000, 2001*]. This study is based on monthly sampling cruises to a single location (10.5°N, 64.67°W; 1400 m water depth) in the eastern part of the Cariaco Basin (Figure 1) and the continuous measurement of particle fluxes at the same site. Each cruise involves routine hydrographic measurements (temperature, salinity, dissolved oxygen, and light transmission) of the entire water column. Additionally, primary productivity measurements are made at eight depths over the upper 100 m, and water samples are collected for nutrient and chlorophyll concentrations at discrete depths between the surface and 1300 m. A detailed description of the sampling program is provided by *Muller-Karger et al.* [2001].

[12] A single mooring containing four automated sediment traps is used to measure particle fluxes at various depths in the Cariaco Basin water column. The shallowest trap is positioned just above the oxic/anoxic interface (~275 m), with the remaining traps at 450 m, 930 m, and 1250 m. Each trap contains 13 collecting cups, and samples are collected continuously for 2-week intervals. The mooring is recovered and redeployed every 6 months. Here we utilize samples collected from the shallowest and deepest traps over the 4-year time period from November 1996 through October 2000. In addition, surface sediments were collected in May 2000 from four depths (Table 1). Finally,

at the sediment trap sites, four depth profiles of water column samples were collected (May 1997, November 1997, May 2000, and May 2002) for measurement of the $^{15}\text{N}/^{14}\text{N}$ of nitrate, and one of these profiles (May 1997) included waters from below the oxic/anoxic interface, allowing for measurement of the $^{15}\text{N}/^{14}\text{N}$ of ammonium.

2.3. Analytical Methods

[13] Primary production ($\text{mg C m}^{-3} \text{ h}^{-1}$) was measured monthly on samples collected at eight depths (1, 7, 15, 25, 35, 55, 75, and 100 m) using a modified Steeman Nielsen (1952) $\text{NaH}^{14}\text{CO}_3$ uptake assay. Data was integrated for the upper 100 m to produce daily primary productivity estimates ($\text{g C m}^{-2} \text{ d}^{-1}$). The specifics of this sampling and procedure are provided by *Muller-Karger et al.* [2001]. Hydrocasts were performed during each monthly cruise to collect water from 17 depths for nutrient analyses. Nitrate concentrations were determined colorimetrically following the procedures described by *Gordon et al.* [1993]. These analyses were carried out using a Technicon Autoanalyzer II equipped with a colorimeter and interference filters for wavelength selection. Unfortunately, nitrate data is not available for the entire 4-year study period but rather is limited to the period from mid-1997 through the end of 1999. Phosphate concentrations were also determined using standard colorimetric methods [*Strickland and Parsons, 1972*]. With these nutrient data, we were able to calculate N^* , which represents the deviation of the $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$ ratio from the predicted “Redfield” stoichiometry and which is defined here as $[\text{NO}_3^-] - 16^*[\text{PO}_4^{3-}] + 2.9$, in micromolar units [*Deutsch et al., 2001; Gruber and Sarmiento, 1997*].

[14] The $\delta^{15}\text{N}$ of dissolved nitrate was measured by two methods. The first is the “passive ammonia diffusion” method, in which nitrate is quantitatively converted to ammonia under basic conditions, and the ammonia is collected by gas-phase diffusion of ammonia out the seawater sample, through a porous Teflon membrane, and onto an acidified glass fiber disk [*Sigman et al., 1997*]. The acidified disks were combusted by elemental analyzer and the $\delta^{15}\text{N}$ of the resultant N_2 gas analyzed by mass spectrometer, as for the analyses of particulate N described below. The second method of nitrate isotopic analysis, the “denitrifier method,” is the quantitative conversion of nitrate to N_2O by a bacterial denitrifier culture that lacks an active N_2O -reductase, followed by isotopic analysis of the product N_2O by continuous flow isotope ratio mass spectrometry [*Sigman et al., 2001*]. The denitrifier method was used for all profiles but the first (May 1997). To determine the aliquot volumes for isotopic analysis, nitrate concentration was determined in each sam-

Table 1. Nitrogen Isotope Data for Cariaco Basin Surface Sediment Samples

Core Number	Water Depth, m	Latitude, °N	Longitude, °W	$\delta^{15}\text{N}_{\text{sed}}$, ‰
MC-2A	192	10°51.08'	64°44.03'	3.6
GC7-1	366	10°40.72'	64°42.04'	3.5
MC-4A	455	10°38.98'	64°39.66'	3.3
MC-6A	1,380	10°33.31'	64°40.38'	3.3

ple by reduction of nitrate to nitric oxide followed by chemiluminescence detection of nitric oxide [Braman and Hendrix, 1989]. Nitrite was insignificant in all measured samples. This lack of nitrite may reflect actual water column conditions, but it also may have arisen from the preservation of the nitrate in these samples by acid addition, which can cause HNO_2 to be volatilized. The replicate analyses by passive ammonia diffusion and the denitrifier method are consistent with a reproducibility of better than 0.2‰ 1SD, with a tendency toward better precision at higher concentration for both methods.

[15] For water samples collected from below the oxic/anoxic interface in May 1997, there was adequate sample volume to measure the $\delta^{15}\text{N}$ of dissolved ammonium. The passive ammonia diffusion method, excluding the nitrate reduction step, was used for these analyses [Sigman *et al.*, 1997]; the ammonium extracts were analyzed using a Europa Roboprep elemental analyzer on-line with a Finnigan MAT 251 stable isotope mass spectrometer (the system of M. A. Altabet, CMAST), as described in the above reference. The replicate analyses suggest a reproducibility of 0.2‰ 1SD or better.

[16] A buffered formalin solution was placed in each sediment trap sample cup prior to deployment and served as a preservative for the organic matter accumulating in the cups. Samples were stored in sealed containers and kept refrigerated after collection. Whole trap samples were split using a precision rotary splitter and a quarter of each sample was then ground and used for bulk geochemical analyses. A portion of each powdered sample (~25 mg) was treated with a 10% phosphoric acid solution in order to remove all carbonate, rinsed in deionized water, and then dried in a tin capsule. The nitrogen isotope composition of bulk organic matter was determined using a Carlo Erba elemental analyzer interfaced with a VG Optima Stable Isotope Ratio Mass Spectrometer. Urea ($\delta^{15}\text{N} = 0.10\text{‰}$) was used as a working standard. Samples and standards were combusted at 1020°C , with standards spaced approximately every 10 samples. The same analytical procedures were used to determine the nitrogen isotope composition of the surface sediment samples. All of the sediment nitrogen isotope data are reported relative to atmospheric N_2 and have a reproducibility of better than 0.1‰ 1SD.

3. Results

3.1. Primary Production and Nitrate Concentration

[17] Primary productivity in Cariaco Basin is marked by significant seasonal and interannual variability (Figure 2). Annually, the highest production rates occur in the winter-to-spring upwelling season (i.e., January–April) when wind-driven upwelling brings cold, nutrient-bearing water into the photic zone. Lowest production occurs during the Northern Hemisphere summer and fall, when the ITCZ is overhead, the winds are weak, and there is minimal exchange between the warm surface mixed layer and waters below. The highest productivity values ($>5 \text{ mg C m}^{-3} \text{ hr}^{-1}$) are consistently found within the upper 20 m of the water column, with little production occurring below 50 m depth. Depth-integrated (0–100 m) primary production

varied by an order of magnitude over the 4-year study period from a low of $448 \text{ g C m}^{-2} \text{ d}^{-1}$ in October 1999 to a high of $4701 \text{ g C m}^{-2} \text{ d}^{-1}$ in January 1997. The maximum measured values for each year were 4701, 3503, 4140, and $3373 \text{ g C m}^{-2} \text{ d}^{-1}$ for January 1997, March 1998, February 1999, and January 2000, respectively.

[18] The water column maximum in nitrate concentration (10–12 μM) is centered at 125–150 m (Figures 2c and 3). This concentration is significantly higher than is found at similar depths in adjacent open Atlantic waters, probably due both to differences in vertical density structure and the trapping of nutrients within the Cariaco Basin, through the import of Atlantic waters and coastal upwelling. Below this depth, $[\text{NO}_3^-]$ decreases due to denitrification near the oxic/anoxic interface at ~275 m, where $[\text{NO}_3^-]$ is typically near our detection limit (Figure 2c). That denitrification is responsible for this decrease is confirmed by the large decrease in the ratio of $[\text{NO}_3^-]$ -to- $[\text{PO}_4^{3-}]$ or N^* , as well as by N_2/Ar measurements [Richards and Benson, 1961]. Above the 125- to 150-m nutrient maximum, $[\text{NO}_3^-]$ decreases toward the surface. $[\text{NO}_3^-]$ is typically in the range of 4–6 μM at 50 m depth and generally less than 0.5 μM at the surface, suggesting that on an annual basis, there is complete utilization of the nitrate supplied to surface waters.

[19] There is significant seasonal variability in the nitrate concentration of the upper 100 m of the water column in Cariaco Basin (Figure 2). Over the 1998–1999 measurement period, the nitracline shoals significantly during the winter-spring of both years, as well as during June–July of 1998. Nitrate concentrations of 6–8 μM reach depths as shallow as 35 m during these periods. While both winter-time shoalings are also associated with high productivity, the shoaling in July 1998 is not (Figure 2).

3.2. Nitrogen Isotopes

3.2.1. Nitrate

[20] The water column measurements of $\delta^{15}\text{N}$ of dissolved nitrate show similar depth-related patterns for all four sampling periods (Figures 3 and 4). The $\delta^{15}\text{N}$ of nitrate at 125–150 m, the depth of the $[\text{NO}_3^-]$ maximum, is 4 to 4.5‰. This is somewhat lower than the deep ocean mean $\delta^{15}\text{N}$ of ~5‰, but it is higher than the $\delta^{15}\text{N}$ of nitrate at the same depth in the Sargasso Sea near Bermuda [Karl *et al.*, 2002]. An upward decrease in nitrate $\delta^{15}\text{N}$ from this depth into the shallow thermocline is evident in all but the November 1997 samples. However, the upward decrease in nitrate $\delta^{15}\text{N}$ is small compared with the upward decrease observed in thermocline nitrate $\delta^{15}\text{N}$ near Bermuda [Karl *et al.*, 2002]. From the shallow thermocline toward the surface, nitrate $\delta^{15}\text{N}$ increases, albeit variably among the profiles (Figures 3 and 4), presumably due to isotope fractionation associated with nitrate assimilation by phytoplankton.

[21] As described above, nitrate is virtually absent below 300 m in the Cariaco Basin due to its removal by denitrifying bacteria at and below the oxic/suboxic interface. Associated with the downward decrease in $[\text{NO}_3^-]$ toward this interface is an increase in the $\delta^{15}\text{N}$ of nitrate that results from the preferential use of ^{14}N -nitrate in denitrification. For instance, in the profiles from May 2000 and May 2002 (Figure 4), the nitrate $\delta^{15}\text{N}$ increases to over 9‰ just above

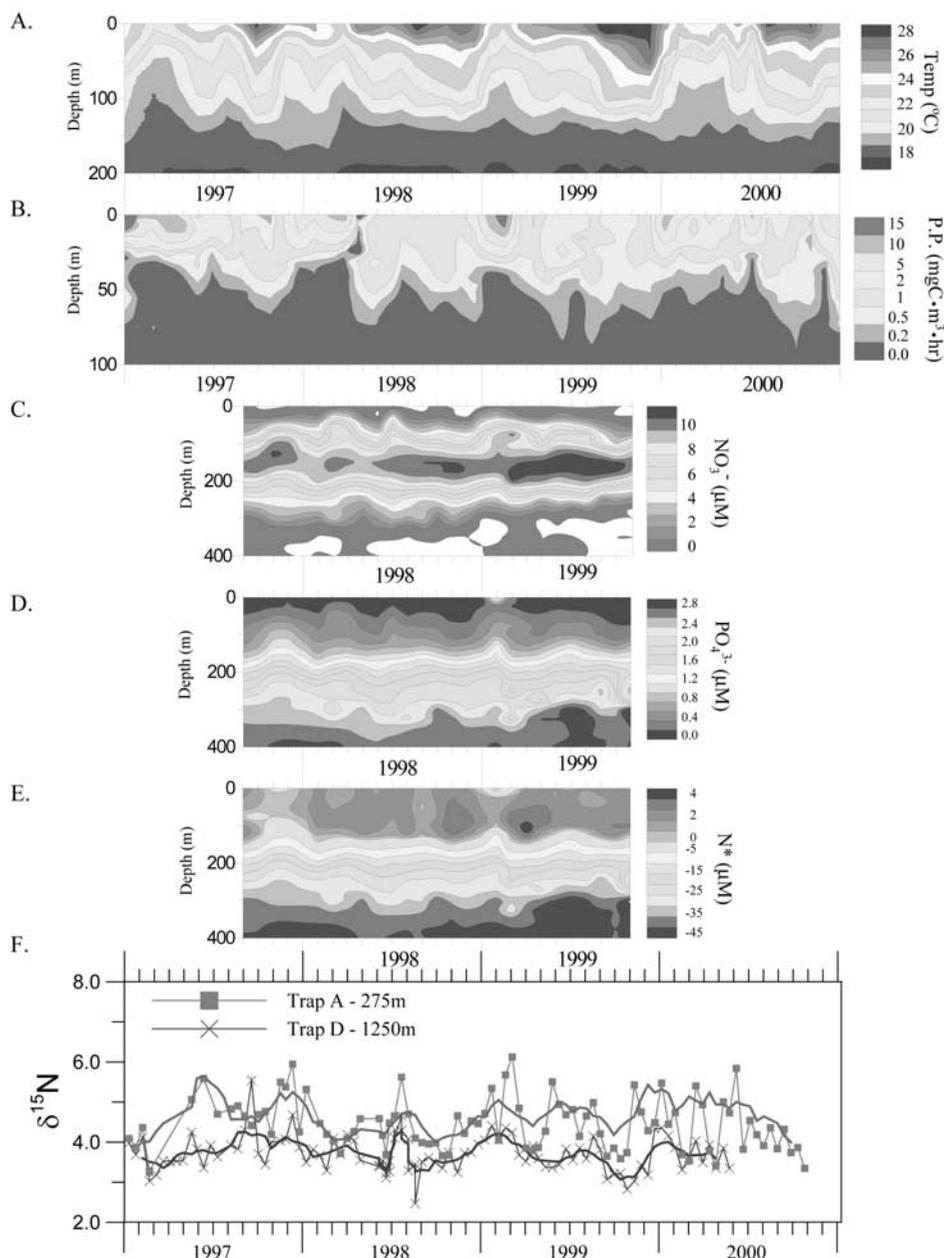


Figure 2. Seasonal variations in (a) temperature, (b) primary productivity, (c) nitrate concentration, (d) phosphate concentration, and (e) N^* (see text) in the upper water column at the Cariaco Basin study location. (f) Seasonal variations in the $\delta^{15}\text{N}$ of sediment trap samples collected at 275 m (trap A) and 1250 m (trap D) at the Cariaco Basin study site. See color version of this figure at back of this issue.

the oxic/anoxic interface (~ 275 m). As described in detail below, this represents a very small degree of isotopic enrichment for the degree of nitrate consumption, when compared with observations from open ocean regions of denitrification, such as the eastern tropical Pacific or the Arabian Sea [Altabet *et al.*, 1999; Brandes *et al.*, 1998; Sigman *et al.*, 2003; Voss *et al.*, 2001]. Because the enrichment is so slight, denitrification in the deep Cariaco Basin has little impact on the $\delta^{15}\text{N}$ of nitrate being upwelled into the surface. Below, we identify the cause of this minimal nitrate ^{15}N enrichment and discuss its implications

for the environmental processes recorded by sediment N isotopic composition in the Cariaco Basin.

3.2.2. Ammonium in the Anoxic Basin Waters

[22] For the profile collected in May of 1997, the concentration of ammonium is $\sim 23 \mu\text{M}$ at 975 m, the deepest sampling point, and decreases upward toward the oxic/anoxic interface, with $5 \mu\text{M}$ at 300 m (Figure 5). The $\delta^{15}\text{N}$ of ammonium is 4.6‰ at 975 m but increases slightly toward the oxic/anoxic interface, with a $\delta^{15}\text{N}$ of $\sim 5.5\text{‰}$ at 300 m (Figure 5). As described below, the $\delta^{15}\text{N}$ of deep ammonium should approach that of the organic matter being

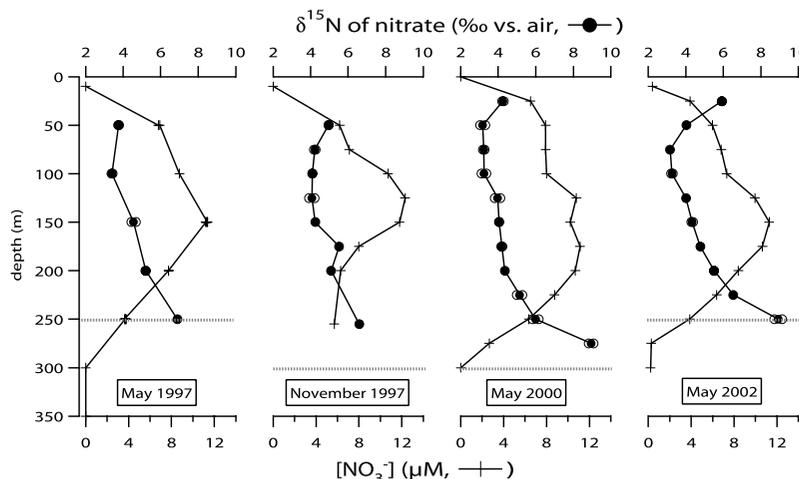


Figure 3. Depth profiles of nitrate $^{15}\text{N}/^{14}\text{N}$ (circles) and concentration (crosses), with samples collected at four separate times. Open circles show individual isotope analyses, and solid circles show the analysis means. The dashed lines show the approximate depth of the oxic/anoxic interface for each sampling period.

degraded in the anoxic basin water and sediments. The increase in ammonium $\delta^{15}\text{N}$ is presumably due to nitrification near the oxic/anoxic interface.

3.2.3. Sinking Particles

[23] Nitrogen isotope analyses were carried out on all samples collected in the shallowest (~275 m) and deepest (~1255 m) sediment traps during the 4-year period from November 1996 through October 2000 (Table 1; Figure 2). All of the $\delta^{15}\text{N}$ measurements for the shallow trap samples fall within a 2.7‰ range (3.3–6.0‰; Figure 2f). The average $\delta^{15}\text{N}$ for these samples over this 4-year period is 4.4‰. Although there is a significant amount of high-frequency variability in the $\delta^{15}\text{N}$ time series from the 275-m trap samples, there is a general trend for the higher values (5–6‰) to occur twice each year, during late fall-winter (November–February) and late spring-summer (May–July). The intervening periods are characterized by a $\delta^{15}\text{N}$ of 3.5–4.0‰.

[24] In almost all cases, the $\delta^{15}\text{N}$ for the samples collected from the 1255-m trap is lower than that for the shallow trap samples from the equivalent sampling period (Figure 2f).

The $\delta^{15}\text{N}$ for most of the deep trap samples fall between 3.0 and 4.5‰, with an average value of 3.7‰. In addition to the absolute values being lower, the range of values recorded in the deeper samples (~1.5‰) is considerably smaller than that determined for the shallow samples (~2.7‰).

3.2.4. Surface Sediments

[25] Surface sediments from four Cariaco Basin cores have a $\delta^{15}\text{N}$ that ranges from 3.3 to 3.6, with an average of 3.4‰ (Table 1). This is approximately 1‰ lower than the average value for the shallow sediment trap samples but quite similar to the average $\delta^{15}\text{N}$ of the deep trap samples and to that of the thermocline nitrate that is mixed into the photic zone. There is a small (0.3‰) but systematic decrease in the surface sediment $\delta^{15}\text{N}$ with increasing water depth.

4. Discussion

4.1. Isotopic Signal of Denitrification

[26] The $\delta^{15}\text{N}$ of nitrate in the Cariaco Basin is remarkable for the very small amplitude of ^{15}N enrichment associated with denitrification near the oxic/anoxic interface

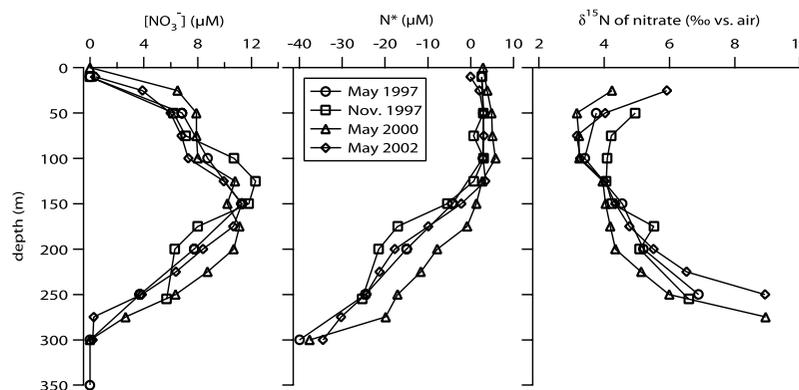


Figure 4. Compilation of the profiles of $[\text{NO}_3^-]$, N^* , and nitrate $^{15}\text{N}/^{14}\text{N}$. See color version of this figure at back of this issue.

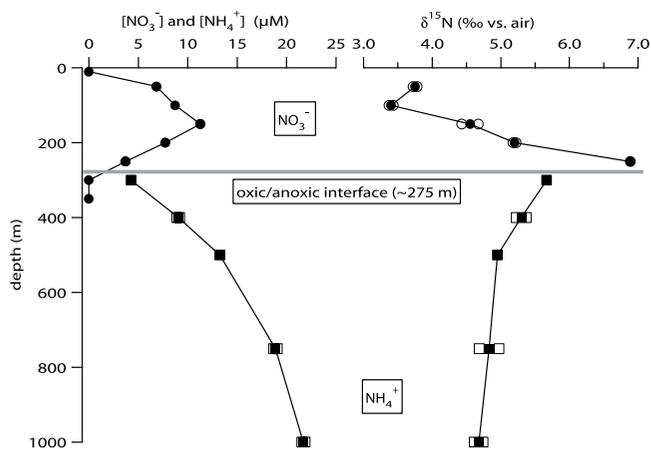


Figure 5. Depth profile of the $\delta^{15}\text{N}$ and concentration of nitrate (circles) and ammonium (squares) for samples collected in May 1997. Open symbols show individual analyses, and solid circles show the analysis means. The typical depth of the oxic/suboxic interface is also indicated (horizontal bar at 275 m). The nitrate data are the same shown in Figures 3 and 4 for May 1997. As with nitrate being consumed by denitrification, the ^{15}N enrichment of ammonium by nitrification near the oxic/suboxic interface is minimal, despite the fact that the isotope effect of ammonium isotope effect of nitrification is relatively large, $\sim 15\text{--}20\text{‰}$ [Casciotti *et al.*, 2003]. As with the nitrate isotopes, this can be explained as the result of nearly complete consumption (oxidation in the case of ammonium) where most of the consumption occurs, at the oxic/suboxic interface.

at ~ 275 m. In other oceanic regions where denitrification occurs in the water column, such as the eastern tropical Pacific or the Arabian Sea, only a third or less of the water column nitrate is consumed at the depth of most intense denitrification [Deutsch *et al.*, 2001]. The remaining nitrate $\delta^{15}\text{N}$ in these most highly denitrified waters is often 15‰ or higher [Brandes *et al.*, 1998; Liu and Kaplan, 1988; Sigman *et al.*, 2003; Voss *et al.*, 2001]. In contrast, almost all of the nitrate is consumed at the oxic/anoxic interface of the Cariaco Basin, yet the highest nitrate $\delta^{15}\text{N}$ we observe, near this interface, is only 9‰ (Figures 3 and 4), much lower than in open ocean regions of denitrification.

[27] In the open ocean regions of denitrification, the kinetic isotope effect (ϵ) of denitrification estimated by application of the Rayleigh model (consumption of a closed pool of nitrate and constant isotopic fractionation) is $20\text{--}30\text{‰}$ [Brandes *et al.*, 1998; Sigman *et al.*, 2003; Voss *et al.*, 2001] ($\epsilon = (^{14}\text{k}/^{15}\text{k} - 1) \times 1000\text{‰}$, where ^{14}k and ^{15}k are the denitrification rates of ^{14}N - and ^{15}N -bearing nitrate). This range of estimates is indistinguishable from the range in estimates of the “intrinsic” (i.e., organism-level) isotope effect from denitrifier cultures [Barford *et al.*, 1999]. If the Rayleigh model were appropriate for the Cariaco Basin, then the data would indicate an isotope effect for denitrification of only $\sim 1.5\text{‰}$ (Figure 6), far smaller than any estimate of the isotope effect intrinsic to denitrifiers.

[28] The fundamental reason for this discrepancy involves the interaction of nitrate consumption and resupply. Deni-

trification occurs only in low $[\text{O}_2]$ waters and thus is restricted to the oxic/anoxic interface and below in the Cariaco Basin. This is evident from most of the $[\text{NO}_3^-]$ depth profiles, which decrease along a “diffusive” (constant slope) trend to the oxic/anoxic interface. At the interface, nitrate is nearly completely consumed by denitrification. To consider the implications of this high degree of nitrate consumption for the N isotopes, imagine that a water parcel with $\sim 10 \mu\text{M}$ nitrate is mixed down to the oxic/suboxic interface, where $9.5 \mu\text{M}$ of that nitrate is subsequently consumed as a closed pool (i.e., according to the Rayleigh model) with an intrinsic isotope effect of 25‰ . This would leave the remaining nitrate $\delta^{15}\text{N} \sim 78\text{‰}$ higher. However, if this water parcel then mixed with an equivalent volume with the initial $10\text{-}\mu\text{M}$ nitrate to form water with a nitrate concentration of $5.25 \mu\text{M}$, the new mixture would have a nitrate $\delta^{15}\text{N}$ only $\sim 3.9\text{‰}$ higher than the initial nitrate. Put more generally, the water parcel that has undergone nitrate consumption, because of its low nitrate concentration, has only a minor influence on the $\delta^{15}\text{N}$ of the final mixing product [Sigman *et al.*, 1999, 2000]. This effect of mixing is small in most open ocean regions of denitrification because

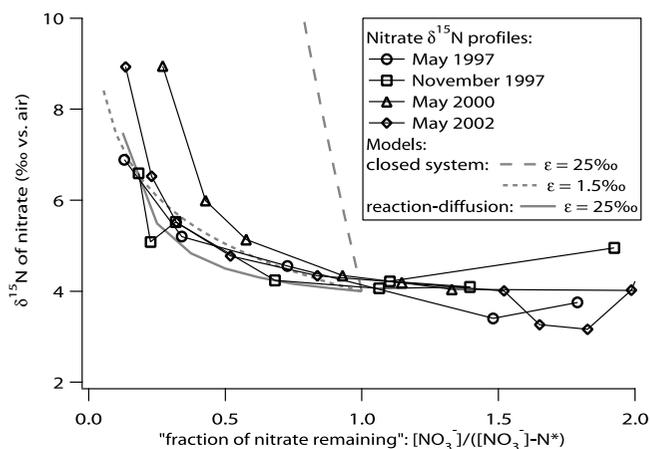


Figure 6. Nitrate $\delta^{15}\text{N}$ versus the fraction of nitrate not consumed by denitrification, estimated as $[\text{NO}_3^-]/([\text{NO}_3^-] - N^*)$, for each of the depth profiles. The trends defined by the Rayleigh (or “closed system”) model of nitrate consumption are shown for isotope effects of 25‰ (dashed line) and 1.5‰ (dotted line). Also shown (solid line) is the trend generated from a reaction-diffusion model of the Cariaco Basin water column, with the profile of nitrate consumption versus depth determined by the mean nitrate concentration profile from the four samplings shown in Figures 3 and 4 and assuming a denitrification isotope effect of 25‰ . This comparison makes that point that the near completeness of nitrate consumption in the Cariaco Basin causes the $\sim 25\text{‰}$ isotope effect of denitrification to be drastically underexpressed. The details of the model fit and comparison with the data should not be overinterpreted. For instance, estimation of the “fraction of nitrate remaining” is very crude; values greater than 1 are physically meaningless and result from application of the formula $[\text{NO}_3^-]/([\text{NO}_3^-] - N^*)$ to the entire water column, which is affected by diverse processes. See color version of this figure at back of this issue.

nitrate is consumed by roughly a third or less of its initial concentration. In those systems, the low- and high- $[\text{NO}_3^-]$ end-members are not so different in $[\text{NO}_3^-]$ that their mixing drastically lowers the Rayleigh-based estimate of the intrinsic isotope effect of denitrification [Brandes *et al.*, 1998; Sigman *et al.*, 2003].

[29] Of course, the denitrification occurring in the Cariaco Basin probably does not proceed by well-defined, discrete consumption and mixing events. A more reasonable model might be a steady state between nitrate consumption at the oxic/anoxic interface and the downward mixing of nitrate from the overlying water (akin to a reaction-diffusion model [Bender, 1990; Brandes *et al.*, 1998]). Regardless of these model details, the basic effect is the same; very little of the intrinsic isotopic fractionation of denitrification is apparent in the water column nitrate. To demonstrate this point, we use a reaction-diffusion model [Sigman *et al.*, 2003] that employs an isotope effect of 25‰ and simulates the downward decrease in $[\text{NO}_3^-]$ in the Cariaco Basin (Figure 6). Because nitrate is nearly completely consumed at the site of denitrification, the nitrate at 200–300 m in the Cariaco Basin is not particularly high in $\delta^{15}\text{N}$ even though the $[\text{NO}_3^-]$ at these depths is extremely low. As a result, no significant isotope signal of denitrification is mixed into the shallow basin waters from below. A similar explanation, that is, nearly complete consumption of nitrate at the site of denitrification, has been applied to sedimentary denitrification to explain the very low isotopic enrichment associated with that process [Brandes and Devol, 1997, 2002; Sigman *et al.*, 2001].

[30] The lack of isotopic expression of denitrification in the Cariaco Basin is central to how the isotopes reflect N cycle processes in the Cariaco, both today and in the past. While denitrification removes nitrate from the upper water column of the Cariaco, it does not render the residual nitrate enriched in ^{15}N . This is a unique situation, in that the N/P effect of water column denitrification (i.e., the production of low $[\text{NO}_3^-]/[\text{PO}_4^{3-}]$ water) and its isotopic effect on nitrate (i.e., the production of high- $\delta^{15}\text{N}$ nitrate) are usually inseparable in the open ocean, which represents a major barrier in efforts to study the response of other processes (i.e., N_2 fixation) to changes in denitrification. In such typical oceanic environments of water column denitrification, an increase in denitrification would increase the $\delta^{15}\text{N}$ of thermocline nitrate, working to raise the $\delta^{15}\text{N}$ of the sinking flux, while any response from N_2 fixation would work to lower the $\delta^{15}\text{N}$ of the sinking flux. Given these opposing isotopic effects of denitrification and N_2 fixation, it is not clear what change in sediment $\delta^{15}\text{N}$ one would expect to observe for a given scenario of coupled changes in denitrification and N_2 fixation. In contrast, in the Cariaco Basin, if an increase in denitrification results in lower thermocline $[\text{NO}_3^-]/[\text{PO}_4^{3-}]$ and N_2 fixation increases in response, the Cariaco sediments should record the sequence of events as a decrease in $\delta^{15}\text{N}$ [Haug *et al.*, 1998]. This unique aspect of the Cariaco Basin is discussed further below.

[31] Denitrification in the Cariaco Basin and similar restricted basins accounts for an insignificant fraction of global ocean nitrate loss. Thus the lack of fractionation during nitrate consumption in the basin is not, in itself, important for the global ocean N isotope budget [Brandes

and Devol, 2002]. However, it does illustrate conceptually (albeit in an extreme way) an effect that should be assimilated into models using the $\delta^{15}\text{N}$ of global ocean nitrate as a tool to reconstruct the water column-to-sediment ratio of global ocean denitrification. Typically, $\sim 25\%$ of the nitrate supplied to open ocean regions of denitrification is consumed (i.e., N^* is $-10 \mu\text{mol kg}^{-1}$ in water with $\sim 30 \mu\text{mol kg}^{-1} \text{NO}_3^-$) [Deutsch *et al.*, 2001]. Under such conditions, the impact of water column denitrification on the $\delta^{15}\text{N}$ of global ocean nitrate is smaller than one would calculate if one assumes that water column denitrification is acting homogeneously upon the global ocean nitrate reservoir. This effect, when included in the global N isotope budget, leads to a modestly higher water column-to-sediment ratio for global ocean denitrification than that calculated without including this effect (C. Deutsch *et al.*, Stable isotope constraints on the glacial/interglacial oceanic nitrogen budget, submitted to *Global Biogeochemical Cycles*, 2004).

4.2. Controls on the $^{15}\text{N}/^{14}\text{N}$ of Nitrate in the Upper Water Column

[32] The nitrate in the shallow Cariaco water column has a $\delta^{15}\text{N}$ of 3–3.5‰, which is lower than the oceanic mean of $\sim 5\%$. ^{15}N depletion of nitrate is also observed in the upper water column in open oligotrophic ocean regions such as the Sargasso Sea [Karl *et al.*, 2002] and the Kuroshio Current [Liu *et al.*, 1996] and may result from the nitrification of newly fixed N, which has a $\delta^{15}\text{N}$ of $\sim -2-0\%$ [Carpenter *et al.*, 1997; Delwiche *et al.*, 1979; Hoering and Ford, 1960]. This interpretation of the shallow nitrate ^{15}N depletion is supported by the observation of a nitrate excess relative to phosphate when compared to the global mean $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$ relationship, both in the Cariaco Basin (Figure 4) and in the Sargasso Sea [Gruber and Sarmiento, 1997; Karl *et al.*, 2002]. However, in the specific case of the Cariaco Basin, we do not have the data to determine whether the nitrate isotopic composition in the shallow Cariaco is dominated by exchange with open Caribbean waters above the basin sill or by processes (e.g., N_2 fixation) occurring within the basin. This represents an uncertainty for paleoceanographic studies using the $\delta^{15}\text{N}$ of basin sediments [Haug *et al.*, 1998]. Moreover, even if this Cariaco-specific question is answered, it still has not been proven that the low $\delta^{15}\text{N}$ of tropical thermocline nitrate is dominantly due to the nitrification of newly fixed N, although it does seem to be the simplest explanation.

[33] From the shallow thermocline toward the surface, nitrate $\delta^{15}\text{N}$ increases, as might be expected from isotopic fractionation during nitrate assimilation by phytoplankton [Wada and Hattori, 1978] (Figures 3 and 4). The nearly complete extraction of nitrate in the surface, when coupled with mixing between the surface and subsurface, should lead to under-expression of the isotope effect, so one would not expect the strong relationship between $[\text{NO}_3^-]$ and nitrate $\delta^{15}\text{N}$ that is observed in nitrate-rich environments [Sigman *et al.*, 1999; Wu *et al.*, 1997]. The logic here is analogous to that described above for the under-expression of the denitrification isotope effect: nearly complete nitrate consumption followed by or coincident with nitrate resupply will weight the nitrate $\delta^{15}\text{N}$ toward the initial $\delta^{15}\text{N}$ of the

supply. If one assumes the Rayleigh model for nitrate assimilation in the surface (i.e., progressive consumption of a closed nitrate pool by assimilation with a constant isotope effect [Mariotti *et al.*, 1981]), comparison of the nitrate $\delta^{15}\text{N}$ increase with the $[\text{NO}_3^-]$ decrease yields a calculated isotope effect (ϵ) of 4.3‰, similar to estimates from other oceanic environments [Altabet, 2001; Altabet *et al.*, 1999; Sigman *et al.*, 1999; Wu *et al.*, 1997]. As the Rayleigh model is certainly inappropriate for this system, this estimate can be taken, at best, as a rough lower limit on the organism-level isotope effect of nitrate assimilation in this system, but not one that we would wish to defend.

4.3. Sinking Flux $\delta^{15}\text{N}$

4.3.1. Controls on the Annual Mean

[34] The annual, flux-weighted mean $\delta^{15}\text{N}$ of the sinking particles intercepted by the 275-m trap is 4.4‰, whereas that for the 1255-m trap is 3.7‰ (Figure 2). While the reason for the $\delta^{15}\text{N}$ difference between the two traps is not understood (see discussion in section 4.3.3), the mean value for the deep trap (3.7‰) is similar to the nitrate being supplied from the thermocline ($\sim 3.5\%$). This isotopic similarity of the nitrate supply and sinking N is expected, in that the nitrate supply is completely consumed in Cariaco surface waters and eventually exported from the surface (largely) as sinking N, so the isotopic composition of the net N export should be equivalent to the N supply. If the shallower trap is used for comparison, the $\delta^{15}\text{N}$ of the sinking flux would be $\leq 0.9\%$ higher than the nitrate supply. These comparisons suggest that N_2 fixation is not a major additional source of fixed N to the Cariaco surface, as it would lower the $\delta^{15}\text{N}$ of the sinking flux below that of the nitrate supply. However, since the nitrate supply and export production of the Cariaco Basin is quite high [Muller-Karger *et al.*, 2001], a very high rate of N_2 fixation would be required to become apparent in the N isotope balance. In general, the isotope balance of the Cariaco Basin appears quite similar to that of the Sargasso Sea near Bermuda [Altabet, 1988], with low- $\delta^{15}\text{N}$ nitrate in the thermocline and a sinking flux $\delta^{15}\text{N}$ that is similar or slightly higher.

4.3.2. Controls on Seasonal Variations

[35] The annual cycle of primary production in Cariaco Basin is controlled, in large part, by seasonal changes in the strength of the trade winds and associated upwelling [Muller-Karger and Aparicio, 1994; Muller-Karger *et al.*, 2001; Richards, 1960]. Zonal winds usually are less than 4 m s^{-1} during summer and fall and increase to 10 m s^{-1} during the winter and spring when the ITCZ has migrated to its most southerly position. Sea surface temperatures (SST) during the summer and fall are typically $28^\circ\text{--}29^\circ\text{C}$, and the surface layer is strongly stratified (Figure 2). Nutrient concentrations in the upper 50 m of the water column are lowest during this period (Figures 2 and 3), as is primary productivity (Figure 2). In association with the increase in wind speed in November–December, there is an upward migration of isotherms and a decrease in SST to $22^\circ\text{--}23^\circ\text{C}$. This upwelling brings nutrient-rich thermocline waters to the surface and is the catalyst for the increase in primary productivity that occurs at the beginning of each year (Figure 2). As already mentioned, our data for 1998 and

1999 suggest that there were two upwelling episodes in each of these years. The initial period of upwelling occurs in January–February and results in a shoaling of the nitracline and the highest productivity recorded each year. This is followed by a brief period during which nutrient concentrations in the upper 100 m decrease and primary production declines. A second shoaling of the nitracline and increase in productivity then occurred in late spring to early summer of both years.

[36] The $\delta^{15}\text{N}$ of the sinking N collected in the 275 m sediment trap (trap A; Figure 2f) varies in response to these seasonal changes in upwelling, as perhaps best illustrated by the sequence of events that occurred during 1997. During the winter (January–March) when upwelling intensified (and presumably nitrate concentrations in the euphotic zone increased), the $\delta^{15}\text{N}$ of particulate nitrogen was low ($\sim 3\text{--}4\%$), perhaps due to preferential uptake of $^{14}\text{NO}_3$ by phytoplankton. As upwelling declined in the late spring and early summer, $\delta^{15}\text{N}$ increased ($>5.0\%$). A second, less intense phase of upwelling occurred in August–September 1997 and resulted in a decrease in the $\delta^{15}\text{N}$ of sinking N. In late 1997, as sea surface temperatures increased to their annual maximum and a strong thermal stratification developed, the $\delta^{15}\text{N}$ of sinking particles increased to 6.0‰.

[37] These changes in the $\delta^{15}\text{N}$ of the sinking flux are somewhat unexpected in that $[\text{NO}_3^-]$ is always less than $1 \mu\text{M}$ in surface waters (Figure 2c). If the surface is always described by complete nitrate consumption, then the sinking flux $\delta^{15}\text{N}$ should not change and should rather be tied to the $\delta^{15}\text{N}$ of the nitrate supply from below. Nevertheless, the sinking flux $\delta^{15}\text{N}$ variations are consistent with some role for nitrate utilization, with lower sinking flux $\delta^{15}\text{N}$ when nitrate supply is higher. This seasonal pattern is difficult to explain by other mechanisms. N_2 fixation could lower the sinking flux, but this would be expected to occur during the more stratified periods [Muller-Karger *et al.*, 2001]. N recycling can cause a seasonal bias in the $\delta^{15}\text{N}$ of the sinking flux by preferentially exporting ^{15}N from the surface layer [Altabet and Small, 1990; Checkley and Entzeroth, 1985; Checkley and Miller, 1989], but this should cause productive episodes to be associated with an initial increase in the $\delta^{15}\text{N}$ of the sinking flux, followed by a decrease. Upwelling in the Cariaco is strongest along the margin to the south of our study site, and this may transport small quantities of nitrate into the surface ocean at our site. Future work might attempt to assess the role of coastal upwelling and lateral nutrient transport in the N isotope variations observed in the sediment traps.

4.3.3. Changes With Depth

[38] In various settings and for different types of materials, there is evidence for ^{15}N enrichment of organic nitrogen during degradation, suggestive of isotope fractionation associated with this process. In the ocean, perhaps the best examples of this general trend are the $\delta^{15}\text{N}$ increase of suspended particles from the surface into the ocean interior [Saino and Hattori, 1980] and the $\delta^{15}\text{N}$ increase from sinking N to the underlying sedimentary organic N [Altabet and Francois, 1994].

[39] The data reported here for the Cariaco Basin show that there is an average decrease in $\delta^{15}\text{N}$ of $\sim 0.7\%$ between

sinking particles collected in the water column at 275 m depth (mean of 4.4‰) and those collected at 1255 m (mean of 3.7‰; Figure 2f), with surface sediment $\delta^{15}\text{N}$ being more similar to that of the deep sediment trap (Table 1). The surface sediments also show a modest depth-dependent $\delta^{15}\text{N}$ decrease, from 3.6‰ at 192 m to 3.3‰ at 1380 m water depth (Table 1). Our observed decrease in $\delta^{15}\text{N}$ from the shallow trap to the deep trap seems counterintuitive if the same fractionation process that alters suspended particles also occurs during the regeneration of settling particles. Despite this, we are not the first to observe a decrease in the $\delta^{15}\text{N}$ of sinking particles. Studies from various open ocean regions have observed a lower mean $\delta^{15}\text{N}$ for sinking particles caught in deeper sediment traps than in shallower ones. For instance, a 3‰ decrease in sinking particle $\delta^{15}\text{N}$ from 1000 and 3700 m has been reported at the North Atlantic Bloom Experiment site [Altabet *et al.*, 1991], with similar trends occurring in the northwest Pacific [Saino and Hattori, 1987] and the Antarctic [Wada *et al.*, 1987]. It is unclear why the $\delta^{15}\text{N}$ of these two types of particles, suspended and sinking, changes differently with depth in the water column. Altabet *et al.* [1991] suggested that the decrease in $\delta^{15}\text{N}$ with depth may be due to either selective removal of compounds that are enriched in ^{15}N , such as amino acids, or the addition of material from a deep source that is enriched in ^{14}N . While we do not have the data to determine whether this first process is occurring in Cariaco Basin, we do not observe an increase in particle flux with depth and thus cannot attribute the decrease in $\delta^{15}\text{N}$ with depth to subsurface advective transport of particles with a lower isotopic composition.

[40] A decrease in the sinking particle $\delta^{15}\text{N}$ with depth has also been observed in the low oxygen zones of the Peru margin [Libes and Deuser, 1988], the Black Sea [Fry *et al.*, 1991] and the Baltic Sea [Voss *et al.*, 1997]. This decrease under suboxic conditions has been attributed to isotopic fractionation that occurs when chemotrophic bacteria assimilate inorganic nitrogen (i.e., ammonium). However, given the similar nature of the downward decrease in sinking particles observed in both oxic and suboxic regions of the ocean water column, we would favor a single explanation that applies under both oxic and suboxic conditions. Thunell *et al.* [2000] have demonstrated that water column degradation of fresh organic matter and the systematic decrease in carbon flux with depth in this anoxic setting is comparable to what has previously been reported for the open ocean due to aerobic decomposition. Sediment fluxes measured for the deepest trap (1255 m) indicate that less than 5% of the organic matter produced in Cariaco surface waters escapes decomposition and reaches this depth in the water column [Thunell *et al.*, 2000]. Furthermore, the particulate organic nitrogen fluxes at 1255 m are, on average, only 30% of those measured at 275 m, clearly indicating active bacterial decomposition of the sinking flux under anaerobic conditions. Thus this study adds still more motivation to find a mechanism for lowering sinking flux $^{15}\text{N}/^{14}\text{N}$ during degradation, and we do not see any reason to focus on the anoxic conditions of the basin waters as the cause for this decrease.

[41] As just mentioned, the apparent $\delta^{15}\text{N}$ change between the 275-m and 1255-m traps is associated with the removal of

roughly 70% of the sinking particulate nitrogen flux. Thus it is roughly true that the remineralized N should have a $\delta^{15}\text{N}$ similar to the sinking flux, $\sim 4.5\%$. Indeed, the $\delta^{15}\text{N}$ of the ammonium in the anoxic basin water is indistinguishable from this value (Figure 5). The $\delta^{15}\text{N}$ of ammonium increases toward the oxic/anoxic interface, as $[\text{NH}_4^+]$ decreases, but the measured increase is small, only $\sim 1\%$. The increase is presumably due to ammonium oxidation. For marine strains of ammonia oxidizers, the intrinsic isotope effect appears to be $\sim 15\text{--}20\%$ [Casciotti *et al.*, 2003]. As described above for nitrate undergoing denitrification, the small magnitude of the $\delta^{15}\text{N}$ increase in the ammonium undergoing nitrification is consistent with the coupled effects of nearly complete oxidation of ammonium near the oxic/anoxic interface and upward mixing of ammonium that has not been enriched in ^{15}N by oxidation. The very small degree of ^{15}N enrichment of the ammonium in the upper Cariaco Basin waters is unique when compared to other studies [Velinsky *et al.*, 1991; Voss *et al.*, 1997]. We expect that it results from the stability of the chemical stratification in the Cariaco, which encourages almost complete oxidation of ammonium close to the oxic/anoxic transition at ~ 275 m.

[42] It is possible that some reaction other than O_2 -driven ammonium oxidation is occurring in the Cariaco Basin. While we cannot rule out the possibility of such a process, there is not yet any evidence for it. Our measurements of deep ammonium $\delta^{15}\text{N}$ are similar to the sinking flux $\delta^{15}\text{N}$, indeed, indistinguishable from the 275-m trap data and $\sim 0.8\%$ higher than the deeper trap. Given that some increase in the deep ammonium $\delta^{15}\text{N}$ might be expected due to the gradual downward mixing of higher $\delta^{15}\text{N}$ ammonium from near the oxic/anoxic interface, this comparison does not suggest the need for in situ consumption of ammonium in the deep water. Several other findings are consistent with this conclusion. First, Richards and Benson [1961] concluded on the basis of N_2 concentration measurements that heterotrophic denitrification alone is producing N_2 in the anoxic basin water. Second, the accumulation ratios of dissolved inorganic carbon, ammonium, and phosphorus, are consistent with Redfield-like ratios for the material being remineralized in the deep basin [Zhang and Millero, 1993]. Third, the time-dependent accumulation of H_2S and ammonium in the deep waters suggest that the basin was last oxic in ~ 1915 [Zhang and Millero, 1993], and the sinking fluxes from our sediment traps would yield an appropriate deep concentration of ammonium over the subsequent anoxic period (data not shown). At the oxic/anoxic interface, where nitrate is available and anaerobic ammonium oxidation (anammox) could potentially occur, we do not have the detailed measurements that would be needed to offer constraints on the role of anammox. We know of no reason to posit that anammox lacks a significant organism-level isotope effect, so the minimal $\delta^{15}\text{N}$ increase in ammonium near the oxic/anoxic interface is not particularly well explained in terms of anammox.

4.4. Connection Between the Surface Ocean and the Seafloor

[43] Surface sediments from our Cariaco Basin box core samples have an average $\delta^{15}\text{N}$ of 3.4‰ (Table 1), very

similar to that of the sinking flux intercepted by the deep sediment trap. In the open ocean, where sedimentation rates are low and organic matter preservation is poor, the $\delta^{15}\text{N}$ of surface sediments is typically 3–5‰ higher than that of the deep sinking particles [Altabet and Francois, 1994]. However, the high sedimentation rates ($>30\text{ cm kyr}^{-1}$) and low oxygen conditions that characterize Cariaco Basin and enhance organic matter preservation on the seafloor also appear to minimize diagenetic alteration of the isotope signal. As described above, the mean $\delta^{15}\text{N}$ of the sinking flux is very similar to that of the water column nitrate being mixed and upwelled into the surface. Thus the surface sediment $\delta^{15}\text{N}$ of the Cariaco Basin is similar to the $\delta^{15}\text{N}$ of thermocline nitrate in the basin. A compilation of data from other sites suggests that this similarity in $\delta^{15}\text{N}$ between nitrate at the base of the euphotic zone and sediments on the seafloor applies generally to depositional environments characterized by high export production, low O_2 , and high organic matter preservation (Figure 7; Table 2). As these environmental characteristics are mechanistically linked, we cannot say precisely which is most critical in reducing isotopic alteration of the organic N in the seafloor sediments.

5. Conclusions

[44] We find that denitrification in the basin causes very little increase in the $^{15}\text{N}/^{14}\text{N}$ of nitrate in the Cariaco Basin.

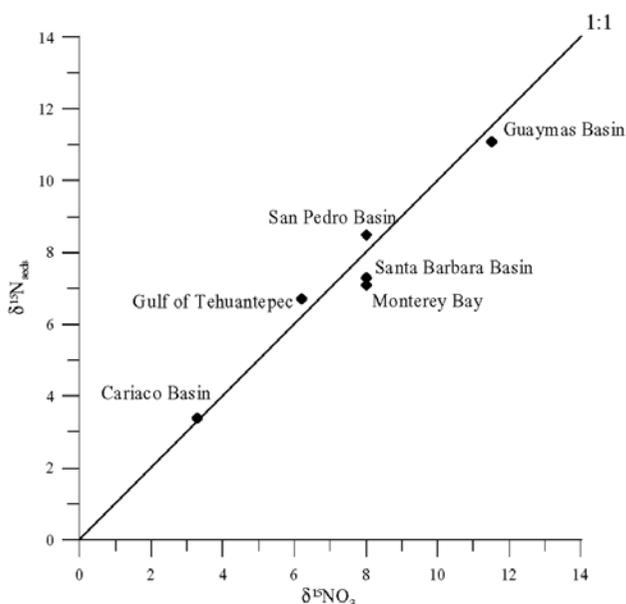


Figure 7. Plot of the $\delta^{15}\text{NO}_3$ water samples from the base of the euphotic zone versus the $\delta^{15}\text{N}$ of surface sediment samples from the Cariaco Basin (this study), Gulf of Tehuantepec [Thunell and Kepple, 2004], Monterey Bay [Altabet et al., 1999], Santa Barbara Basin [Liu, 1979; Emmer and Thunell, 2000], San Pedro Basin [Altabet et al., 1999] and Guaymas Basin [Pride et al., 1999]. In each of these continental margin settings, the $\delta^{15}\text{N}$ of the sediments is very similar to the isotopic composition of thermocline nitrate.

Table 2. Nitrogen Isotope Values for Surface Sediments and Dissolved Nitrate at the Base of the Euphotic Zone From Various Continental Margin Locations

Location	$\delta^{15}\text{N}_{\text{sed}}$	$\delta^{15}\text{N}_{\text{nitrate}}$	Data Source
Cariaco Basin	3.4	3.3	this study
Guaymas Basin	11.1	11.5	Pride et al. [1999], Altabet et al. [1999]
Gulf of Tehuantepec	6.7	6.2	Thunell and Kepple [2004]
Monterey Bay	7.1	8.0	Altabet et al. [1999]
Santa Barbara Basin	7.3	8.0	Emmer and Thunell [2000], Liu [1979]
San Pedro Basin	8.5	8.0	Altabet et al. [1999]

This appears to be due to the fact that nitrate is completely consumed at the oxic/anoxic interface, so that the organism-level isotope effect cannot be expressed. This explanation is analogous to that for sedimentary denitrification [Brandes and Devol, 1997] and has implications for the interpretation of mean ocean nitrate $\delta^{15}\text{N}$ as a measure of the relative roles of sedimentary versus water column denitrification in global ocean nitrate loss [Brandes and Devol, 2002]. Specifically, the water column denitrification occurring in the Cariaco Basin does not, in net, represent a fractionating loss of nitrate from the ocean, so that it violates the distinction between water column and sedimentary denitrification upon which the homogenous-ocean isotope budgets are based [Brandes and Devol, 2002]. While the Cariaco itself does not represent a globally significant sink of fixed N, these results do beg the question of whether underexpression of the organism-level isotope effect is common among environments of water column denitrification.

[45] The $\delta^{15}\text{N}$ of nitrate in the Cariaco Basin decreases toward the surface to a minimum in the shallow thermocline, reaching as low as 3‰, which is significantly lower than the global mean $\delta^{15}\text{N}$ of 5‰. This upward decrease has also been noted in the Sargasso Sea [Karl et al., 2002], and we do not know whether the Cariaco Basin profile is produced within the basin or imported from the open Caribbean. In either case, one reasonable explanation for the low $\delta^{15}\text{N}$ of nitrate in the Cariaco thermocline is that N_2 fixation in the surface produces low- $\delta^{15}\text{N}$ organic N, which is subsequently remineralized and nitrified to nitrate in the thermocline.

[46] The sinking flux $\delta^{15}\text{N}$ is similar to the subsurface nitrate $\delta^{15}\text{N}$. While seasonal variations in upwelling and sinking flux $\delta^{15}\text{N}$ do occur, the annual mean sinking flux $\delta^{15}\text{N}$ is not a function of nutrient utilization because of the nearly complete consumption of nitrate at the surface. The lack of ^{15}N depletion in the sinking flux relative to the nitrate supply suggests that N_2 fixation is a minor contributor of N to the surface export production, relative to the supply of nitrate from below. However, this does not preclude a significant rate for N_2 fixation, as the supply of nitrate to the Cariaco surface is high relative to the open Caribbean [Muller-Karger et al., 2001].

[47] The $\delta^{15}\text{N}$ of the Cariaco Basin sediment is similar to the sinking flux $\delta^{15}\text{N}$, lacking the large isotopic offset between sinking flux and sediment that has been observed in open ocean environments with lower sedimentary N preservation. In general, the $\delta^{15}\text{N}$ from the deep sediment

trap fits both the subsurface nitrate $\delta^{15}\text{N}$ and the sediment $\delta^{15}\text{N}$ well, while the shallower trap is enriched in ^{15}N relative to those N pools. This observation of decreasing $\delta^{15}\text{N}$ with depth is common in sediment trap studies from diverse environments [Altabet *et al.*, 1991; Lourey *et al.*, 2003; Voss *et al.*, 1996] and thus requires a general explanation.

[48] In sum, the sediment $\delta^{15}\text{N}$ in the Cariaco Basin records the thermocline nitrate $\delta^{15}\text{N}$. Subsurface nitrate is not significantly impacted by the denitrification occurring at the oxic/anoxic interface. As a result, the Cariaco Basin may be an ideal site to monitor other changes, such as in N_2 fixation. One major remaining uncertainty is whether the shallow thermocline chemistry and nitrate isotopic composition of the Cariaco Basin is set by processes within the basin or is communicated into the basin from the Caribbean thermocline. In addition, in the open Atlantic and elsewhere, the role of N_2 fixation in the low $\delta^{15}\text{N}$ of thermocline nitrate has not been definitively determined.

[49] Water column and seafloor conditions in the Cariaco have changed in the past, as indicated by shifts between sediment lamination (the condition in modern Cariaco Basin) and bioturbation (as characterizes sediments from the last ice age and the Younger Dryas). It may be that there has been significant isotopic alteration of sinking and sedimentary N in the past, in particular, when sediment bioturbation indicates that bottom waters were oxygenated. Similarly, there may have been times in the past when N_2 fixation was so active in the basin that the $\delta^{15}\text{N}$ of the sinking flux was significantly lower than that of the subsurface nitrate supply. Finally, as sea level changes, the degree of exchange with the open Atlantic will change, affecting the origin of the nitrate in thermocline waters of the Cariaco. Addressing the major uncertainties in the modern Cariaco and evaluating the meaning of the sediment N isotope record from the basin must be approached as a single goal.

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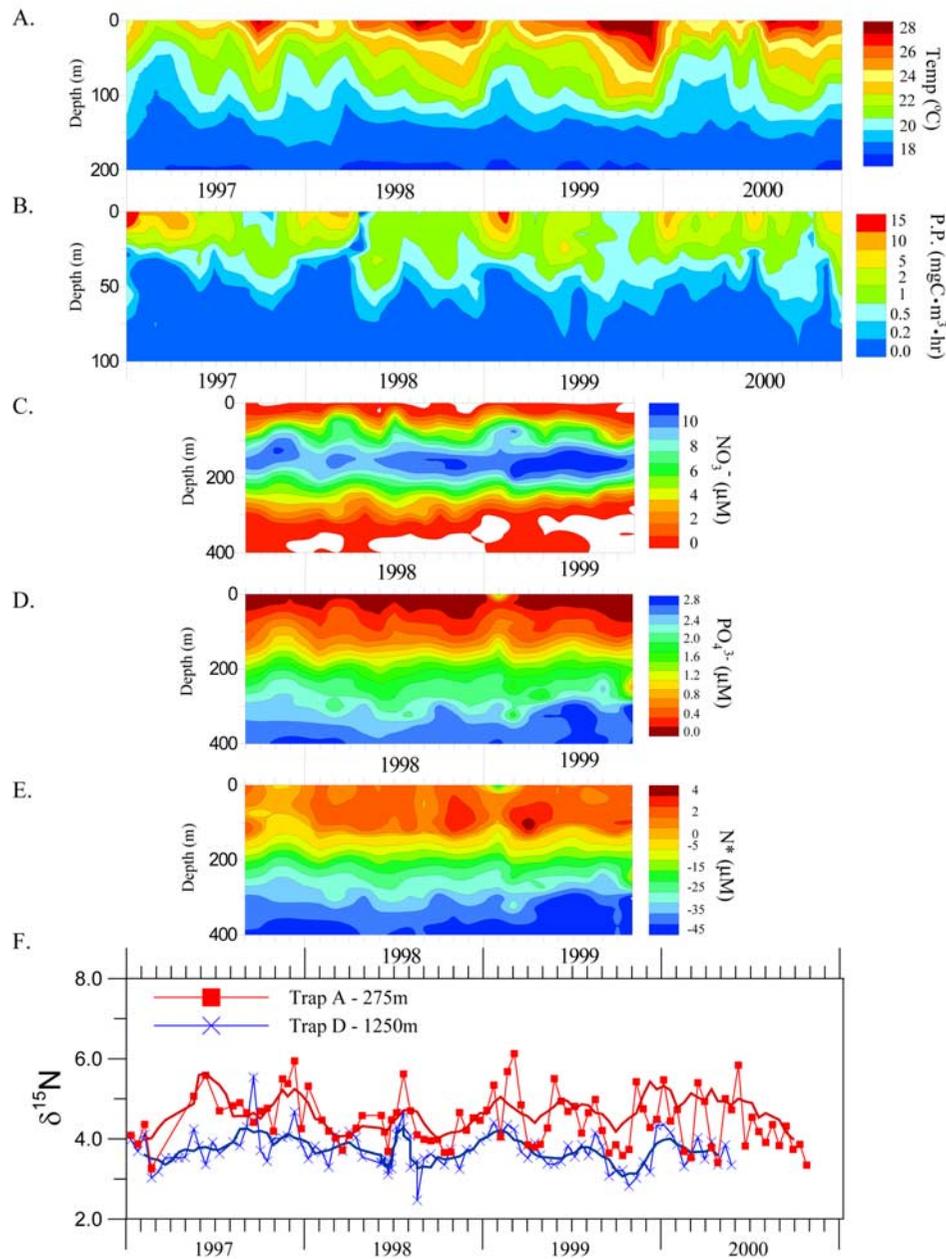


Figure 2. Seasonal variations in (a) temperature, (b) primary productivity, (c) nitrate concentration, (d) phosphate concentration, and (e) N^* (see text) in the upper water column at the Cariaco Basin study location. (f) Seasonal variations in the $\delta^{15}\text{N}$ of sediment trap samples collected at 275 m (trap A) and 1250 m (trap D) at the Cariaco Basin study site.

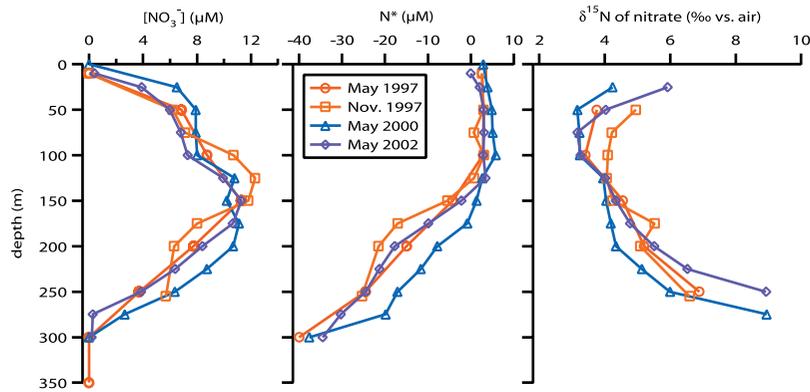


Figure 4. Compilation of the profiles of $[\text{NO}_3^-]$, N^* , and nitrate $^{15}\text{N}/^{14}\text{N}$.

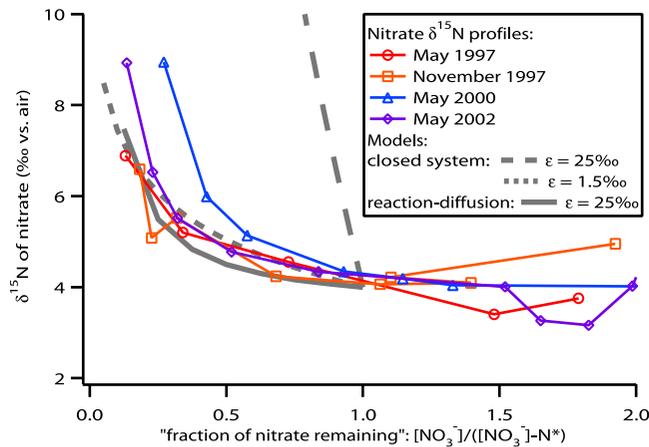


Figure 6. Nitrate $\delta^{15}\text{N}$ versus the fraction of nitrate not consumed by denitrification, estimated as $[\text{NO}_3^-]/([\text{NO}_3^-] - \text{N}^*)$, for each of the depth profiles. The trends defined by the Rayleigh (or “closed system”) model of nitrate consumption are shown for isotope effects of 25‰ (dashed line) and 1.5‰ (dotted line). Also shown (solid line) is the trend generated from a reaction-diffusion model of the Cariaco Basin water column, with the profile of nitrate consumption versus depth determined by the mean nitrate concentration profile from the four samplings shown in Figures 3 and 4 and assuming a denitrification isotope effect of 25‰. This comparison makes that point that the near completeness of nitrate consumption in the Cariaco Basin causes the $\sim 25\%$ ‰ isotope effect of denitrification to be drastically underexpressed. The details of the model fit and comparison with the data should not be overinterpreted. For instance, estimation of the “fraction of nitrate remaining” is very crude; values greater than 1 are physically meaningless and result from application of the formula $[\text{NO}_3^-]/([\text{NO}_3^-] - \text{N}^*)$ to the entire water column, which is affected by diverse processes.