Distinguishing between water column and sedimentary denitrification in the Santa Barbara Basin using the stable isotopes of nitrate

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[1] Below its sill depth, the Santa Barbara Basin (SBB) is commonly suboxic ($[O_2] \sim 3$ μM), with only brief periods of ventilation. Associated with development of suboxia, the concentration of nitrate decreases with depth into the basin without an associated decrease in phosphate, indicating that a substantial fraction of the nitrate supplied to the basin is removed by denitrification. Coincident with the decrease in nitrate concentration across the "redoxcline" (the interface between oxic and suboxic waters) within the SBB, there is an increase in the $^{15}N/^{14}N$ of that nitrate, as would be anticipated from the isotopic fractionation associated with denitrification. However, the increase in $^{15}N/^{14}N$ of nitrate is much smaller than occurs in the open eastern tropical North Pacific (ETNP) for a comparable amount of nitrate loss. Both the concentrations of N species within the basin and measurements of nitrate $^{18}O/^{16}O$ suggest that the lower-than-expected ^{15}N enrichment in the suboxic SBB involves denitrification, rather than being due to some unknown source of low-$^{15}N/^{14}N$ N to the deep SBB. Calculations with a range of models of nitrate supply and consumption indicate that the degree of nitrate consumption in the basin is too small for differences in water circulation to explain the isotopic differences between the Santa Barbara Basin and the open ETNP. Previous studies indicate that the isotope effect of sedimentary denitrification is negligible due to nitrate diffusion in sediment pore waters. Thus we infer that the small magnitude of the isotopic enrichment of SBB water column nitrate is due to the importance of sedimentary denitrification within the basin. Assuming that water column and sedimentary denitrification have isotope effects of 25 and 1.5 per mil, respectively, our results suggest that sedimentary denitrification accounts for more than 75% of the nitrate loss within the suboxic SBB.

1. Introduction

[2] Denitrification, the dissimilatory reduction of NO_3^- to N_2 by heterotrophic bacteria, is by far the dominant sink of fixed N in the ocean [*Cline and Kaplan*, 1975; *Codispoti and Christensen*, 1985; *Deutsch et al.*, 2001; *Naqvi et al.*, 1982; *Seitzinger*, 1988]. It occurs in the water column and in marine sediments where there is nitrate but little available O_2 (less than roughly 4–5 μM) [*Cline and Richards*, 1972; *Codispoti et al.*, 2001]. The same conditions are required for denitrification regardless of locale: low levels of O_2, available nitrate, and a carbon source. However, the sensitivity of marine denitrification to environmental changes (e.g., in ocean circulation, productivity, or sea level) may differ greatly depending on whether denitrification is concentrated in the water column or in the sediments. Thus discerning the respective roles of water column and sedimentary denitrification is central to the development of a predictive understanding of the oceanic N budget.

[3] The eastern tropical North Pacific (ETNP) has been recognized as an important region for denitrification, associated with extremely low O_2 concentrations in the mid-depth water column. Within the ETNP, a lateral gradient in O_2 concentration exists along the coast of California and Mexico, with a more intense O_2 minimum zone to the south. Exceptions to this regional trend occur in a series of borderland basins, which are blocked from exchange with the oceanic water column by basin sills, leading basin water to become O_2-deficient due to oxidation of the organic carbon rain from the surface into the basin. The Santa Barbara Basin

(SBB) is among the most studied of the borderland basins.

[4] Flushing of the SBB typically occurs in the spring, after which circulation is restricted, "suboxia" develops ($[O_2] \sim 3$ μM [*Zheng et al.*, 2000]), and denitrification begins, as indicated by the loss of nitrate from basin waters below the redoxcline [*Kuwabara et al.*, 1999; *Reimers et al.*, 1990; *Sholkovitz and Gieskes*, 1971]. The quantity of nitrate consumed by denitrification can be estimated as the difference between the measured nitrate concentration and the nitrate concentration that would be expected on the basis of the phosphate concentration, assuming a globally defined "Redfield" N:P relationship [*Deutsch et al.*, 2001]. This measure of nitrate loss, while a critical constraint, does not, by itself, illuminate how the loss of nitrate by denitrification is partitioned between the water column and the sediments in the SBB.

[5] Denitrification, like most biogeochemical reactions, discriminates between the stable isotopes of N. ^{14}N-bearing nitrate is preferentially consumed, leaving the residual nitrate pool enriched in ^{15}N, or higher in δ^{15}N, where $\delta^{15}N = (^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{reference}) - 1)*1000‰$, the isotopic reference being atmospheric N_2. The degree of discrimination during denitrification is expressed by its isotope effect (ε), which is approximately the δ^{15}N difference between the pool from which nitrate is being drawn and the nitrate that is being consumed at any moment. The δ^{15}N of nitrate in oceanic waters clearly reflects the occurrence of water column denitrification, with denitrification in the O_2-deficient water column of open ocean regions (e.g., the eastern tropical Pacific and the Arabian

Sea) leaving the residual nitrate enriched in ^{15}N [*Cline and Kaplan*, 1975; *Liu and Kaplan*, 1989]. The degree of isotopic enrichment suggests an isotope effect for open ocean denitrification of 20–30‰ [*Altabet et al.*, 1999; *Brandes et al.*, 1998], which is consistent with some culture-based estimates [*Barford et al.*, 1999; *Mariotti et al.*, 1981]. However, the "effective" isotope effect of denitrification can be less than the "intrinsic" (or biological) isotope effect if denitrification is limited by the rate of nitrate supply to denitrifying bacteria. This appears to occur in ocean margin sediments over a broad range of conditions [*Brandes and Devol*, 1997; *Sigman et al.*, 2001] and in analogous groundwater environments [*Mariotti et al.*, 1988], where nitrate is almost completely consumed within the zones of denitrification, resulting in an "effective" isotope effect near zero ($\sim$1.5‰ as estimated by *Brandes and Devol* [2002]).

[6] This difference in isotopic behavior between water column and sedimentary denitrification provides a potential tool for constraining the relative importance of denitrification in the water column versus the sediments in the overall denitrification rate. Here, we report isotopic measurements of nitrate in the SBB that show an increase in δ^{15}N with progressive nitrate loss that is much less than we (and others) observe in the O$_2$-deficient zone of the open ETNP [*Altabet et al.*, 1999; *Brandes et al.*, 1998; *Liu and Kaplan*, 1989]. We apply a range of models for nitrate consumption within the SBB to demonstrate that the data require an "effective" isotope effect that is much lower than the intrinsic isotope effect of denitrification as measured in the open ETNP water column. This leads to the conclusion that most of the denitrification occurring within the suboxic zone of the SBB is occurring within the sediments.

[7] Nitrate isotope data for the SBB have previously been reported [*Liu and Kaplan*, 1982, 1989; *Liu*, 1979]. In his dissertation, *Liu* [1979] noted the anomalously low degree of nitrate isotopic enrichment relative to the degree of nitrate consumption in the SBB, and, as we do below, he explored a set of nitrate supply models to explain the data.

Finally, despite the absence of any data at the time on the isotopic effects of sedimentary denitrification, he suggested that high denitrification rates in the sediments played a role in the low isotope effect that his data suggested: "The low α value is attributed to the high growth rate of denitrifying organisms and loss of nitrate to sediments with little or no isotopic fractionation" (chap. 3, p. 167). Besides indicating Liu's scientific intuition, this statement attests to the compelling nature of the interpretation presented here. Below, we are able to make a strong case for a dominant role for sedimentary denitrification in SBB through comparison of the SBB data with a large data set from the open ETNP, simple model calculations, and coupled measurement of nitrogen and oxygen isotopes in nitrate from the SBB.

2. Materials and Methods

2.1. Sample Collection

[8] Water samples were collected by hydrocast from several cruises off the California coast: (1) a sediment geochemistry cruise aboard the RV *Pt. Sur* in late November of 1995 [*Kuwabara et al.*, 1999; *Zheng et al.*, 2000], (2) a sediment trap deployment cruise aboard the RV *Yellowfin* in late April of 1999, and (3) coring cruise OXMZ01MV aboard the RV *Melville* in November of 1999. During cruises (1) and (2), samples were collected only from the SBB, while during cruise (3), samples were collected from the SBB and from open ETNP stations extending from near the SBB to the southern tip of Baja California (Figure 1). Samples were collected in distilled water-rinsed polyethylene bottles after two rinses with sample water and were preserved by acidification to a pH of 2–3 with 50% reagent-grade hydrochloric acid. The samples from cruise (3) were frozen upon arrival at the lab.

[9] In addition, we have included in our plots two SBB depth profiles reported by *Liu* [1979], one from a cruise that was apparently shortly after flushing of the SBB ("SNOW", August 1977) and one from a cruise a year later ("GIN", August 1978) [*Liu*, 1979]. The methods of sample collection and analysis are described by *Liu* [1979].
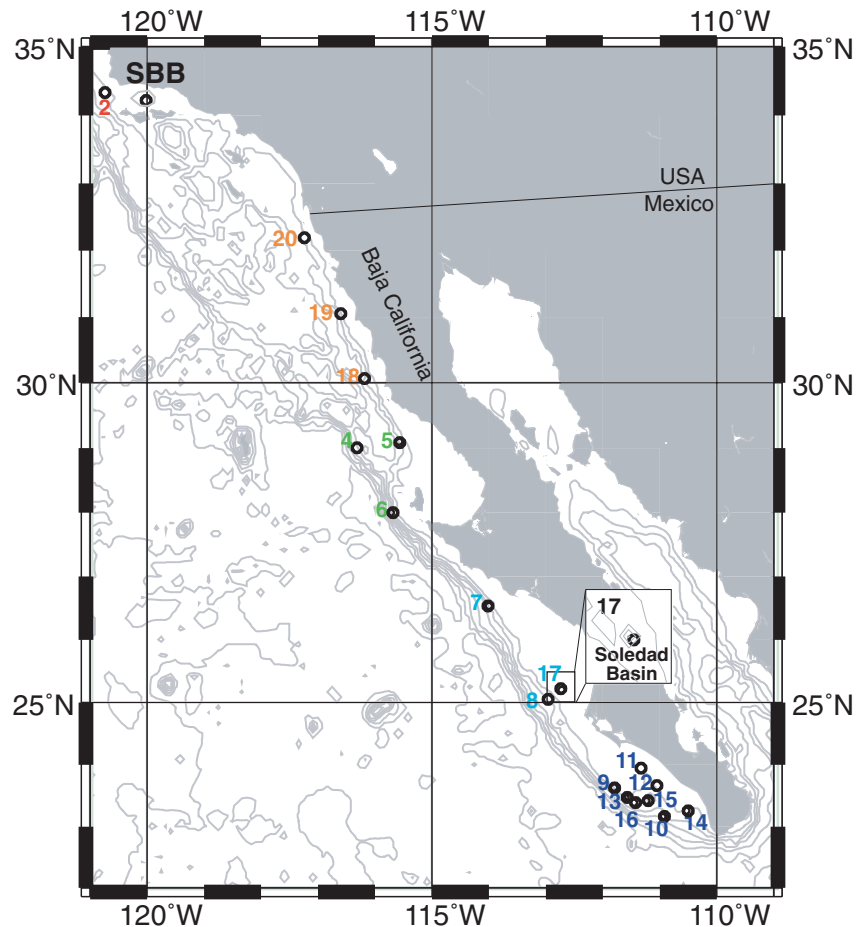
Figure 1. Hydrocast sampling locations along the eastern margin of the North Pacific off the California/Baja California coast. Hydrocast data from within the Santa Barbara Basin are reported for three cruises at different times: fall of 1995, spring of 1999, and fall of 1999. Spring and fall casts provide nutrient and δ^{15}N of nitrate profiles from periods of flushing (spring) and basin suboxia (fall). The numbered stations outside of the SBB are all from the fall of 1999 (cruise OXMZ01MV of the RV *Melville*, see text). The color scheme used here is maintained in subsequent figures. Topographic contours are shown at 750 m intervals; this contouring captures neither the Santa Barbara Basin (SBB) nor the Soledad Basin (OXMZ01MV station 17). To show the extent of these basins we have added the 500 m contour of the SBB and inlaid an expanded view of the Soledad Basin showing the 400, 500 and 600 m contours.

2.2. Dissolved Oxygen and Nutrient Concentration Measurements

[10] For hydrocast samples collected during cruises (1) and (3), the concentrations of phosphate and nitrate were measured at sea by automated colorimetric methods, and the concentration of dissolved O_2 was measured by Winkler titration or electrode calibrated with Winkler titrations [*Kuwabara et al.*, 1999]. The samples collected during cruise (2) were analyzed for phosphate nitrate+nitrite in the lab; no [O_2] measurements were made. The concentration of nitrate+nitrite in these samples was

determined by reduction to NO followed by chemiluminescence detection of NO [*Braman and Hendrix*, 1989]. For these samples, phosphate concentration was measured by manual colorimetric methods, after *Hansen and Koroleff* [1999]. Measurements of [NO_2^-] during cruise (2) in the SBB water column suggest that it is almost always less than 1 μM [*Liu*, 1979].

2.3. Nitrate Isotopic Analysis

[11] Natural abundance-level measurements of the δ^{15}N of nitrate (plus nitrite) were made by two

methods. For the sample set collected during the 1995 cruise, we used the "passive ammonia diffusion" method for nitrate extraction. In this method, nitrate and nitrite are quantitatively converted to ammonia by Devarda's alloy under basic conditions, with the ammonia diffusing out of the seawater sample and becoming immobilized as ammonium on an acidified glass fiber disk that is protected by a porous Teflon (^{TM}) packet [*Sigman et al.*, 1997]. The ammonium was combusted by a Carlo Erba elemental analyzer, with sequential oxidation and reduction converting the sample quantitatively to N_2 gas, and the resulting N_2 was analyzed by an on-line Finnigan DeltaPlus stable isotope ratio mass spectrometer. The passive ammonia diffusion method requires $\sim$2 μmol N and gives a standard deviation for isotopic analysis of $\sim$0.2‰ down to 5 μM nitrate. The blanks inherent in this procedure are from Devarda's alloy and seawater dissolved organic nitrogen. An isotopic correction was made for the Devarda's alloy blank but was not made for the dissolved organic nitrogen blank, which depends on the individual water sample.

[12] The second method of nitrate isotopic analysis, which was used for the samples collected during 1999, is the quantitative conversion of nitrate and nitrite to N_2O by a strain of bacterial denitrifier that lacks nitrous oxide reductase activity, followed by isotopic analysis of the product N_2O by continuous flow isotope ratio mass spectrometry (the "denitrified method") [*Sigman et al.*, 2001]. This method is much more sensitive than previous methods, requiring 10–20 nmol N per analysis, and giving a precision of $\sim$0.2‰ (1 s.d.) down to 1 μM nitrate. Individual analyses are referenced to injections of N_2O from a pure gas cylinder and then standardized using an internationally accepted nitrate isotopic reference material (IAEA-N3). The oxygen isotope data for nitrate reported in Figure 6 were also collected using the "denitrifier method" [*Casciotti et al.*, 2002]. In addition to the methodological concerns that have been addressed for measurement of the nitrogen isotopes by this method, the oxygen isotope measurements has required the evaluation of (and correction for) (1) fractionation during oxygen atom removal, and (2) exchange with oxygen atoms from water, during reduction of nitrate to N_2O [*Casciotti et al.*, 2002]. Replicate nitrate $\delta^{18}O$ analyses indicate a standard deviation of $\sim$0.5‰ or better.

3. Results

[13] The SBB and open ETNP profiles show different trends in nutrient concentration. Nitrate concentration ([NO_3^-]) increases with depth at all stations except inside the SBB, where it decreases from a $\sim$36 μM maximum above sill depth to $\sim$20 μM within the basin in the fall profiles (Figure 2b) [*Kuwabara et al.*, 1999]. Both in the open ETNP and in the SBB, phosphate concentration ([PO_4^{3-}]) increases with depth to $\sim$3.7 μM (Figure 2c). In the SBB profile from April 1999, [NO_3^-] and [PO_4^{3-}] are relatively invariant across the sill depth. Previous work in the basin supports the interpretation that this profile was taken shortly after flushing of the basin, which tends to occur in the spring [*Reimers et al.*, 1990]. This variation is also seen in the [NO_3^-] data of *Liu* [1979] (Figure 2b, gray symbols).

[14] More directly relevant to our study of denitrification are the depth profiles of N* (Figure 2d), a parameter that quantifies the deviation of the [NO_3^-]:[PO_4^{3-}] ratio from the "Redfield" N:P stoichiometry of 16:1. N* is defined here as [NO_3^-] − (16*[PO_4^{3-}]) + 2.9 [*Deutsch et al.*, 2001; *Gruber and Sarmiento*, 1997]. Generally, negative N* values indicate a net loss of nitrate, typically due to denitrification, whereas positive N* values suggest a net addition of new nitrate, typically due to the nitrification of newly fixed N. As in *Deutsch et al.* [2001], we have removed the multiplier term (0.875) that was included in the expression by *Gruber and Sarmiento* [1997] to quantify the role of N_2 fixation.

[15] While N* is generally negative throughout the ETNP, there are depth zones of N* minima that indicate in situ denitrification or exchange with a region of denitrification (Figure 2d). In the open ETNP, the N* minimum is associated with the mid-depth [O_2] minimum zone (Figure 2a), with both
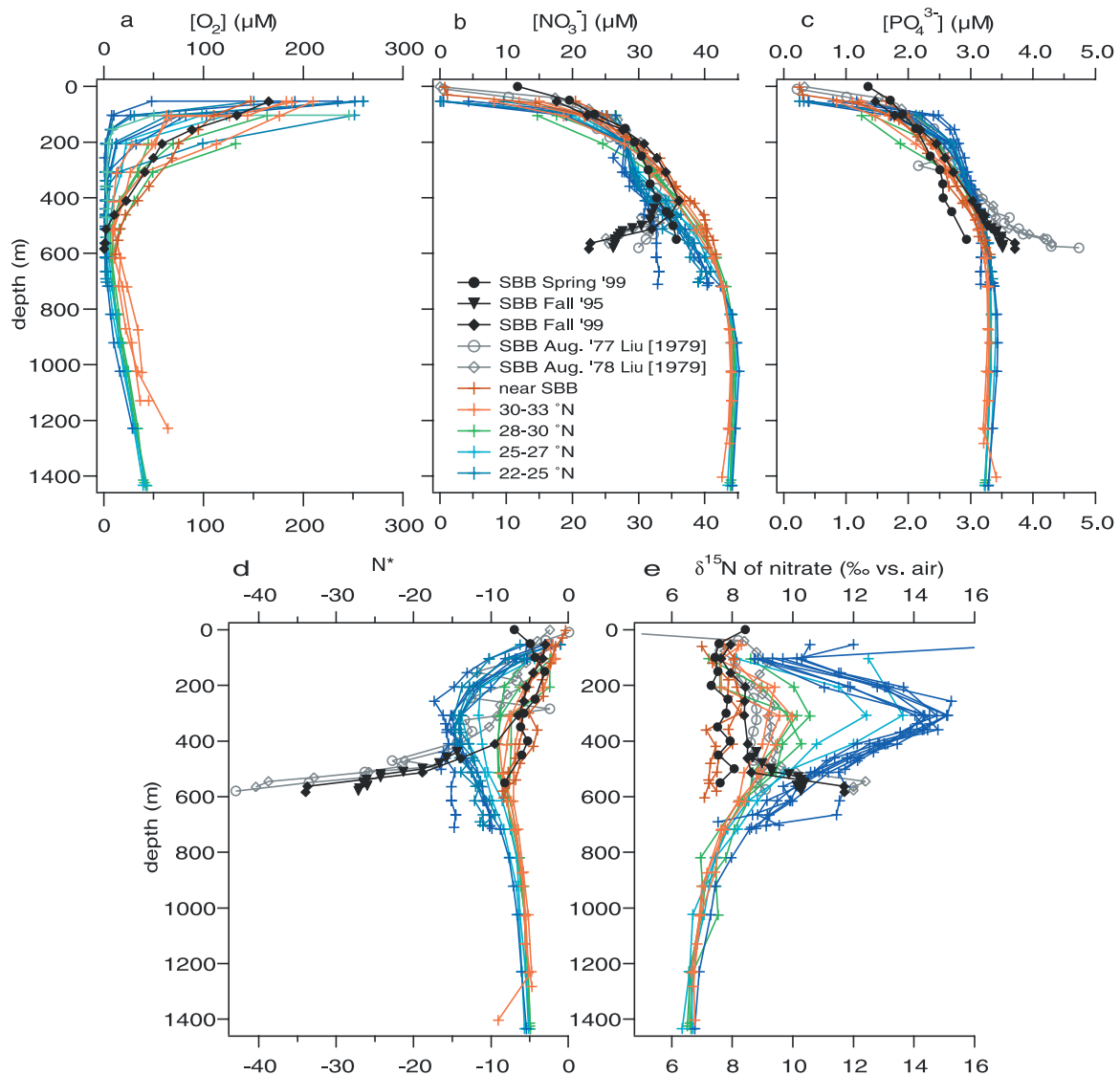
Figure 2. Profiles of (a) $[O_2]$, (b) $[NO_3^-]$, (c) $[PO_4^{3-}]$, (d) N*, and (e) nitrate $\delta^{15}N$, for all stations except OXMZ01MV station 17 (see text and Figure 7). Dissolved $[O_2]$ data were not available for some stations. SBB profiles are in black (closed symbols). Data from *Liu* [1979] for two cruises in the SBB are also shown (gray open symbols, see text). Note the sharp decrease in $[NO_3^-]$ and N* below the sill depth ($\sim$475 m) in the SBB. Relative to the nitrate deficit indicated by N*, the $\delta^{15}N$ of nitrate increases far less in the SBB than in the open ETNP sites (stations 9–16 in particular).

O_2 depletion and the N* minimum becoming more pronounced toward the south. This is consistent with the requirement of very low $[O_2]$ (<4–5 μM O_2) for denitrification to proceed rapidly in the water column. The expectation based on the $[O_2]$ data is that water column denitrification is only active in the stations south of 25°N (deep blue symbols in Figure 2). The N* minimum of the more northern stations results from the coastal

undercurrent carrying northward the low-N* signal caused by denitrification [*Altabet et al.*, 1999; *Liu and Kaplan*, 1989; *Wooster and Jones*, 1970]. In the SBB, the lowest $[O_2]$ occurs below sill depth in the basin; $[O_2]$ measurements of the basin water during the fall cruises were all less than 2.5 μM (Figure 2a) [*Zheng et al.*, 2000]. The lowest N* of the SBB profiles are associated with these $[O_2]$-deficient basin waters. The N* data indicate a

greater nitrate deficit in the SBB than in the ETNP relative to the ventilating waters.

[16] Both in the open ETNP and within the SBB, comparison of profile data demonstrates qualitatively that nitrate $\delta^{15}N$ (Figure 2e) is strongly anti-correlated with N* (Figure 2d), as would be expected from isotope discrimination during denitrification [*Altabet et al.*, 1999; *Brandes et al.*, 1998]. For instance, at OXMZ01MV station 16 off the southern tip of Baja California, nitrate $\delta^{15}N$ increases to ∼14‰ at 310 m, the depth of the N* minimum in that profile. This anti-correlation is maintained in the more northern profiles, although both the N* minima and nitrate $\delta^{15}N$ maxima are less pronounced and are probably the result of exchange with denitrifying waters in the south, as opposed to in situ denitrification. The nitrate $\delta^{15}N$ of waters above sill depth in the SBB (∼8‰) is similar to that of neighboring profiles from outside the basin, indicating that the shallow waters above the basin are dominated by regional processes, as should be expected given the lack of barriers to exchange. Nitrate $\delta^{15}N$ within the SBB, unlike in the nearby profiles from outside the basin, increases sharply near the sill depth of the basin (∼475 m), coincident with the decrease in N*. Nitrate $\delta^{15}N$ reaches 11–12‰ in the suboxic basin waters.

[17] However, it is clear from visual inspection of the depth profiles that the degree of isotopic enrichment in the SBB is less than one would have expected given the very large nitrate deficit found in the SBB and the $\delta^{15}N$/N* relationship of the open ETNP data (Figures 2d and 2e). That is, for every unit of nitrate removed, we observe a smaller ^{15}N enrichment in the residual nitrate pool in the SBB than in the open ETNP. A more quantitative comparison of the data is provided by plotting the nitrate $\delta^{15}N$ data as a function of the estimated amount of nitrate that remains after denitrification (Figure 3). One measure of nitrate removal by denitrification is the change in N* from the initial ventilating waters, in which it is assumed that $[NO_3^-]_{initial} = [NO_3^-]_{observed} - N^*$, where $[NO_3^-]_{observed}$ is the measured nitrate concentration of a water sample and $[NO_3^-]_{initial}$ is the calculated nitrate concentration of the initial ventilating water. In this case, the fraction of nitrate that remains ("f")

is $[NO_3^-]_{observed}/([NO_3^-]_{observed}-N^*)$. In Figure 3, the nitrate isotope data are plotted versus the natural logarithm of f (see below for justification of the natural logarithm).

[18] Remineralization of organic matter in the suboxic waters can complicate N* as a measure of denitrification. Regeneration under suboxic conditions, while releasing phosphate, typically produces ammonium but not nitrate, potentially generating an apparent nitrate deficit that is not due to denitrification. Two other possibilities also deserve attention. First, there is evidence that organic phosphorus is more efficiently regenerated in suboxic sediments [*Ingall and Jahnke*, 1994], potentially causing a small increase in the ratio of phosphorus to nitrogen released to the water. Second, iron oxide-bound phosphorus could be released to the suboxic SBB waters as iron is reduced and the iron oxide phase dissolves [*Reimers et al.*, 1996; *Shiller et al.*, 1985].

[19] To account for all of these potential effects, we plot the SBB data both with and without the component of the apparent nitrate deficit that is due to the difference in $[PO_4^{3-}]$ between the deep SBB and the waters above (Figures 3a and 3b, respectively). It should be noted that the temperature and salinity of the SBB deep water (as sampled during the cruise in November 1999) are intermediate between water at sill depth (475 m) from outside the basin (station 2) and water from just above sill depth within the SBB profile. These data suggest that "initial water" for the deep SBB should be intermediate between the water near sill depth from the SBB profile and the water near sill depth from station 2. However, the $[PO_4^{3-}]$ and $[NO_3^-]$ of these two waters are very similar. Thus we feel justified in our use of the SBB sill depth water as the sole measure of the initial $[PO_4^{3-}]$ in our calculations.

[20] Removing the contribution of $[PO_4^{3-}]$ variations to the calculated nitrate deficit represents an upper-limit correction for the effect that suboxic remineralization could have. On the one hand, several lines of evidence suggest that a significant part of the $[PO_4^{3-}]$ increase is from the release of iron−bound P. First, the pore water profiles of *Reimers et al.* [1996] indicate that $[PO_4^{3-}]$
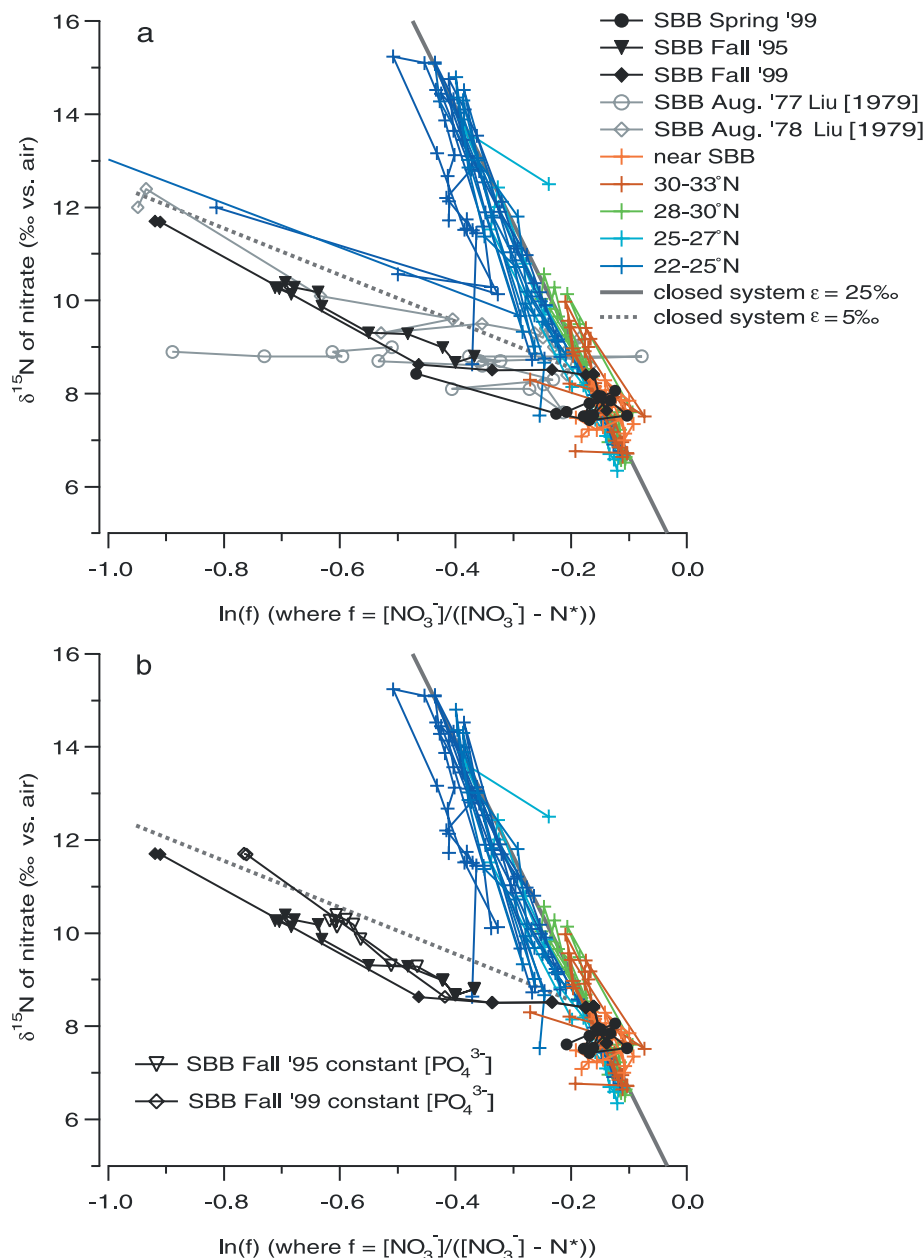
increases more sharply than $[NH_4^+]$ with depth in SBB sediments, suggesting a significant role for the release of iron oxide-bound phosphorus sediment in the benthic flux of phosphate. Second, we have used sediment trap measurements of the organic carbon flux into the SBB [*Thunell*, 1998] to estimate the $[PO_4^{3-}]$ increase that should occur from its remineralization. This admittedly uncertain approach suggests that less than half of observed seasonal increase in $[PO_4^{3-}]$ can be

attributed to the organic matter remineralization. On the other hand, several other observations suggest that remineralization can explain all of the $[PO_4^{3-}]$ increase. First, the concentrations of silicate and phosphate increase in a 64:1 ratio, which is indistinguishable from the ratio of increase that would be expected from the remineralization of diatoms that grew under iron limitation and is higher than would be expected for diatoms grown under iron sufficiency [*Hutchins and Bru-*

land, 1998]. Second, the relationship of $[PO_4^{3-}]$ with $[O_2]$ and DIC $\delta^{13}C$ in the SBB suggest that the $[PO_4^{3-}]$ increase into the basin can be explained completely by organic matter remineralization [*van Geen et al.*, 1995]. Third, with regard to ammonium production and its effect on the apparent nitrate deficit, the SBB water column lacks significant ammonium and nitrite, and N_2/Ar measurements point to coupled nitrification and denitrification in the sediments (discussed more below) [*Barnes et al.*, 1975]. These observations suggest that most of the ammonium produced by suboxic diagenesis is eventually removed by denitrification, as opposed to accumulating in the bottom water. Thus we suspect that the actual nitrate deficit from denitrification is intermediate between that calculated including the contribution from $[PO_4^{3-}]$ variations (filled black symbols in Figure 3) and that calculated from the $[NO_3^-]$ decrease alone (open black symbols in Figure 3).

[21] Regardless of the above details, the degree of isotopic enrichment for a given amount of denitrification is dramatically lower in the SBB than in the open ETNP (Figure 3). To put this difference in perspective, it is instructive to consider the data in the context of the Rayleigh model for nitrate supply and consumption, in which we assume that (1) each water parcel has the same initial composition and behaves subsequently as a closed system in which

nitrate is consumed by denitrification, and (2) the isotope effect associated with denitrification is constant throughout the consumption process. If this model applies, as nitrate consumption occurs, a water parcel should travel along a straight trajectory toward the upper left in a diagram of nitrate $\delta^{15}N$ vs. ln(f), and the slope of the trend is determined by the isotope effect of the consumption process (or rather its negative value by our definition). The pitfalls of the Rayleigh model for our system will be considered below. Taking this model as a starting point, we find that the open ETNP data fit well with a single Rayleigh consumption trend for which the isotope effect is 25‰, as reported previously [*Altabet et al.*, 1999; *Brandes et al.*, 1998]. The fit is remarkably good given that other processes, in particular, nutrient uptake by phytoplankton in the surface ocean, will pull the data off the common trend, as does occur for the shallowest samples of several stations (Figure 3a). The SBB data, in contrast, fit a completely different Rayleigh consumption trend, for which the isotope effect is only ~5‰. Thus the isotopic impact of denitrification in the SBB is roughly one-fifth that of denitrification in the open ETNP.

4. Interpretation

[22] Three broad categories of explanation can be posed for the anomalously low degree of isotopic

Figure 3. (opposite) (a) $\delta^{15}N$ of nitrate vs. ln(f) for all sites, where f is intended to indicate the fraction of initial nitrate not consumed by denitrification and is defined as $[NO_3^-]/[NO_3^-]_{initial}$ where $[NO_3^-]_{initial} = [NO_3^-] - N^*$. The slope of the trends defined by the data provide an estimate of the isotope effect (ε) of nitrate consumption by denitrification, if the Rayleigh model, which describes a closed nitrate pool being consumed with a constant isotope effect, is assumed. There is a clear difference in trend between the open ocean profiles and the SBB. The open ETNP data describe a slope appropriate for an isotope effect of 25‰, and the SBB data approximate a slope appropriate for an isotope effect of 5‰. The position of the trendline describing the SBB data (gray dashed line) is set to intercept the SBB station from fall of 1999 (solid diamonds) at a sampling depth just above the sill depth of ~475 m. In (b), the value of N^* is recalculated for SBB samples below the sill depth, holding $[PO_4^{3-}]$ constant at the value observed near sill depth (open symbols); the goal of this recalculation is to quantify the potential effect of anaerobic organic matter decomposition and iron-bound phosphorus release in the suboxic SBB, which produces phosphate but not nitrate, on the apparent nitrate deficit (see text). Assuming that any change in $[PO_4^{3-}]$ below the sill depth is due to remineralization places an upper limit on ln(f) and thus on our estimate of ε, since not all of the basin $[PO_4^{3-}]$ variation will be associated with these processes. Even with the adjustment for constant $[PO_4^{3-}]$ below the sill depth, SBB samples fall along a trend that describes a much lower ε than the open ETNP sites. Some data shown in (a) are removed in (b) (and in Figure 5), to simplify interpretation and reduce the number of overlapping symbols. First, the near-surface (0–50 m) data points strongly affected by phytoplankton uptake of nitrate (from the SBB station from spring of 1999 and from open ETNP stations 11, 12, and 14 from fall of 1999) have been removed in (b), in order to focus on the effect of denitrification on the $\delta^{15}N/ln(f)$ relation. Second, the data from *Liu* [1979] have been removed.
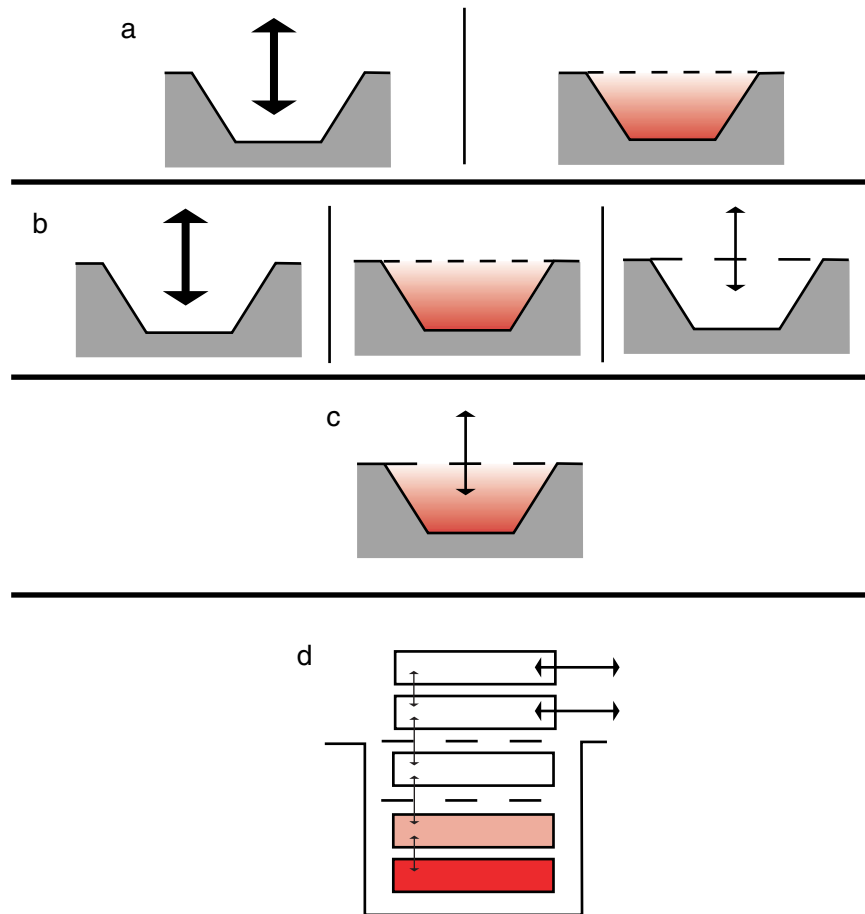
Figure 4. Cartoons of the four models of nitrate supply considered for the SBB. (a) The Rayleigh model, in which the nitrate pool of the deep basin is closed after a complete flushing and the isotope effect of denitrification is constant. (b) Rayleigh consumption followed by incomplete mixing of the basin water with overlying water of initial composition. (c) One-box steady state model, in which a single homogenous volume of basin water maintains a steady state between nitrate consumption and re-supply from an infinite reservoir of nitrate at initial composition. (d) Layered steady state model, as in (c) except that neither suboxic basin water nor the overlying water is assumed to be of uniform composition. In the actual model depicted in (d), there are seven layers above sill depth and thirteen below sill depth.

enrichment associated with nitrate loss in the Santa Barbara Basin. First, the Rayleigh model applied above assumes a closed system, and open system aspects of the SBB may reduce the nitrate isotopic enrichment associated with the nitrate deficit, independent of any variations in the isotope effect of denitrification. Second, there may be a source of extremely low-δ^{15}N nitrate to the deep Santa Barbara Basin. Third, it may be inappropriate to apply the intrinsic isotope effect of 20–30‰ to denitrification in the SBB. Below, we evaluate the first possibility by calculating the nitrate δ^{15}N/[NO$_3^-$] relationship generated by several different models of water column nitrate supply and consumption in the SBB, which we then compare with the relation-

ship from the Rayleigh model and with the data from the SBB. This comparison is analogous to the analysis of oceanic O$_2$ isotope data by *Bender* [1990]. The models that we employ are summarized below (Figure 4).

4.1. Models

4.1.1. Rayleigh Model

[23] A closed nitrate pool is consumed with a constant isotope effect, in which case the δ^{15}N of the residual nitrate pool is described by the equation [*Mariotti et al.*, 1981]:

$$\delta^{15}NO_3^- = \delta^{15}NO_{3initial}^- - \varepsilon\{\ln\left([NO_3^-]/[NO_3^-]_{initial}\right)\} \quad (1)$$

[24] The $[NO_3^-]_{initial}$ and $\delta^{15}NO_{3\ initial}^-$ are assigned according to analyses of samples from just above the sill depth of ~475 that were collected during the November 1999 cruise; this water chemistry was confirmed by samples taken on other cruises in the SBB and at other stations from just outside the SBB (Figure 2). The Rayleigh model would be an adequate description of the deep Santa Barbara Basin if the basin occasionally undergoes complete flushing (resetting the composition of the water to $\delta^{15}NO_{3\ initial}^-$ and $[NO_3^-]_{initial}$), after which nitrate consumption in the basin occurs without significant exchange with waters above the redoxcline (Figure 4a). If the SBB was adequately described by sporadic, essentially complete flushing events followed by the development of suboxia and denitrification [*Reimers et al.*, 1990; *Sholkovitz and Gieskes*, 1971], the Rayleigh model would be plausible for this setting. However, its full suitability depends on the rate of diffusive mixing within the suboxic basin and across the redoxcline and on the importance of other mechanisms of basin ventilation (see below).

4.1.2. Mixing "Events" Among Closed Pools of Nitrate

[25] Partial consumption of nitrate occurs in a closed parcel of water, as in the Rayleigh model, but then this water parcel is mixed (over a continuous range of proportions) with water of its initial composition. The result of this mixing is plotted for a degree of nitrate consumption that corresponds to the greatest degree of nitrate consumption observed in our samples. This model would apply in the case that the deep SBB is occasionally reset by complete flushing, followed by Rayleigh consumption, then by a single partial mixing event (Figure 4b). Note that this specific model is improbable - Rayleigh consumption interspersed with multiple partial mixing events would be more reasonable. Nevertheless, this calculation demonstrates the fundamental effect of a discrete partial mixing event, which is to pull the $\delta^{15}N/[NO_3^-]$ relationship of the basin water below the Rayleigh trend for a given isotope effect. Qualitatively, this occurs because the $[NO_3^-]$ of a mixing product is in proportion to the volumes of the two waters that are mixed, while its nitrate $\delta^{15}N$ is in proportion to the product of volume and $[NO_3^-]$ of each mixing end-member (i.e., the high-$[NO_3^-]$ end-member has a greater effect on the nitrate $\delta^{15}N$ of the mixing product).

4.1.3. One-Box Steady State Model

[26] For a single, homogenous water parcel, a steady state is maintained between nitrate consumption and net nitrate resupply by mixing with an infinite reservoir of nitrate set at initial conditions. In this case, the following equation applies to the residual nitrate pool:

$$\delta^{15}NO_3^- = \delta^{15}NO_{3initial}^- + \varepsilon\left([NO_3^-]/[NO_3^-]_{initial}\right) \quad (2)$$

[27] This model would apply if "new" water (with $\delta^{15}NO_{3\ initial}^-$ and $[NO_3^-]_{initial}$) is constantly being mixed into the suboxic SBB water, balancing the loss of nitrate by denitrification so as to yield a steady state (Figure 4c). This can be thought of as an end−member alternative to the Rayleigh model. This model would apply if the rate of mixing across the redoxcline is so great that the residence time of the suboxic water is much less than the time that passes between flushing events.

4.1.4. Layered Steady State Model

[28] The layered steady state model is the same as the one-box steady state model, except that the suboxic SBB is not assumed to be a uniform volume, and the water above the sill depth of the SBB is not assumed to be an infinite reservoir (although the waters above sill depth are still assumed to exchange with an infinite reservoir). The SBB is modeled as a vertically layered system, with exchange among the layers, exchange of the layers above the sill depth with an infinite reservoir (the regional water column), and nitrate consumption (with a constant ε) occurring in the layers of the suboxic SBB (Figure 4d). The depth profile of nitrate consumption that we use here approximates closely the decrease in N* into the suboxic basin observed during the OXMZ01MV (November 1999) cruise. Several different depth profiles of nitrate consumption were considered for the sub-
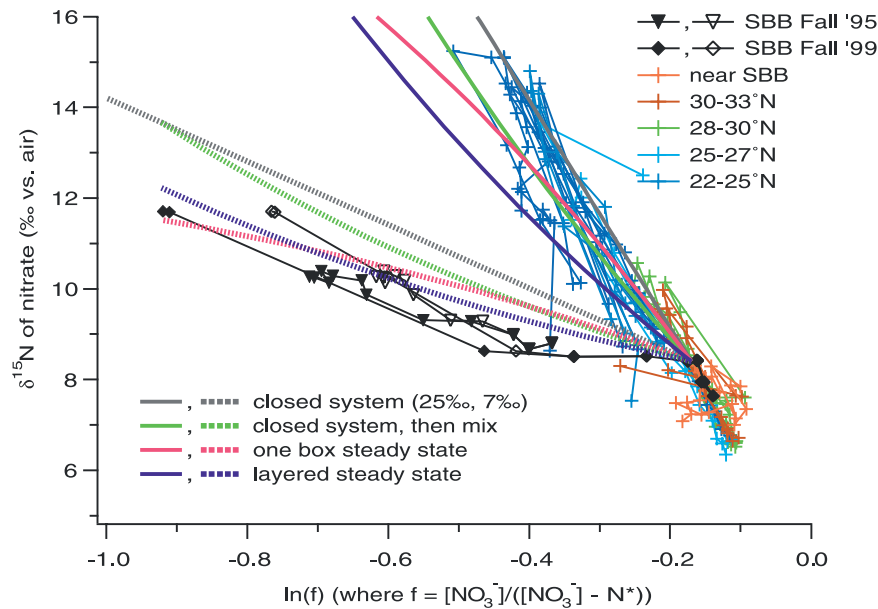
Figure 5. Model trends are overlain on the data in δ^{15}N of nitrate vs. ln(f) space. Results from each model are shown for two different values of the isotope effect: ε = 25‰ (solid lines) and ε = 7‰ (dashed lines). The initial conditions of the models are taken from just above the sill depth of ~475 in the SBB using the profile from fall of 1999 (filled black diamonds). The mixing and steady state models all show shallower slopes than the Rayleigh model, but none of the models can describe the relationship between the low nitrate δ^{15}N and the extremely high nitrate deficit observed in the SBB without resorting to an isotope effect of 7‰ or less. The data shown are as in Figure 3b, with the exception that the SBB profile from the spring of 1999 (a period of basin flushing) has been removed to clarify the relationship between the model trends and the most relevant (fall) data.

oxic SBB, but sensitivity tests demonstrated that this had minimal effect (results not shown), the critical parameter simply being the minimum $[NO_3^-]$ that occurs in the steady state depth profile.

4.2. Data/Model Comparison

[29] Here, we compare the data with multiple models of water column nitrate supply and consumption, recognizing that each is a simplification of reality. The relevance of the time-dependent models (4.1.1 and 4.1.2) or the steady state models (4.1.3 and 4.1.4) for the SBB can be gauged by the residence time of the SBB waters. If the residence time is short relative to the annual cycle of basin flushing, then the steady state models will be more appropriate. *Chung* [1973] reports a ^{222}Rn-based estimate of 3.9 cm^{2}sec^{-1} for vertical eddy diffusivity in the SBB, which yields a rough mixing time of 0.6–0.8 year for the basin water, implying that significant exchange across the redoxcline may occur between major flushing events, but not so much that the basin water is replaced repeatedly between major flushing

events. This indicates that neither closed system nor steady state conditions apply generally for the SBB. Nevertheless, our model calculations constrain the range of effects that these end-member models have on the δ^{15}N/ln(f) trend.

[30] The mixing and steady state models yield lower trends in nitrate δ^{15}N/ln(f) space than does the Rayleigh model (Figure 5). This is to be expected: any mixing between water parcels of different $[NO_3^-]$ yields a water parcel the nitrate δ^{15}N of which is biased toward the nitrate δ^{15}N of the higher-$[NO_3^-]$ water. In the case of denitrification, the "initial" water parcel is the mixing end-member with the higher $[NO_3^-]$, and it has a lower δ^{15}N, leading the resupply of nitrate by mixing to lower the nitrate δ^{15}N below the Rayleigh trend. The logical extreme of this effect occurs when nitrate is completely removed from a water parcel; when this parcel mixes with water of its initial composition, the mixing product will have a $[NO_3^-]$ which is half that of the initial $[NO_3^-]$ (the volume-weighted averages of the two mixing end-mem-

bers) but which will have a nitrate $\delta^{15}N$ that is identical to "undenitrified" water. Nevertheless, if we assume an isotope effect of 25‰ for denitrification, the decrease in the nitrate $\delta^{15}N/[NO_3^-]$ trend associated with discrete mixing events (section 4.1.2; solid green line in Figure 5) or continuous resupply of nitrate (sections 4.1.3 and 4.1.4; solid magenta and purple lines in Figure 5) is far from adequate to explain the extremely low nitrate $\delta^{15}N/[NO_3^-]$ relationship of the SBB samples (Figure 5).

[31] More processes than are included in our models have been recognized in the SBB. In particular, *Chung* [1973] and *Sholkovitz and Soutar* [1975] report clear evidence for small, discrete ventilation events by turbidity currents that originate from above the redoxcline, transporting oxic water to the basin floor. The entrained water then mixes up from the bottom. This mechanism of ventilation may be coupled with upward advection of water throughout the basin [*Liu*, 1979], as is the case in other borderland basins [*Hammond et al.*, 1990]. We have incorporated various combinations of new water supply to the bottom and upward advection in our layered steady state model. For a given degree of net nitrate consumption in the SBB, this overturning acts to increase the slope of the trend in $\delta^{15}N/\ln(f)$ space (i.e. decrease its difference from the Rayleigh model trend; results not shown). In contrast, *Liu* [1979] found that virtually any slope in $\delta^{15}N/\ln(f)$ space could be eliminated by including an adequately rapid overturning; from his perspective, this greatly limited his ability to draw conclusions from the nitrate isotope data. As we understand it, the difference in our results (and our interpretation) is due to the fact that, in all of our models, we use the deep SBB $[NO_3^-]$ as a constraint on the balance between nitrate supply and uptake, whereas *Liu* [1979] did not. This underscores the point made above that the degree of nitrate consumption ($[NO_3^-]/[NO_3^-]_{initial}$) largely controls the range in the $\delta^{15}N/\ln(f)$ trends that different models predict. Given the low degree of nitrate consumption observed in the SBB, it matters little whether we use the Rayleigh model or the steady state model to estimate the net isotope effect of denitrification from our data, because the slopes in $\delta^{15}N/\ln(f)$ space predicted by these models are very

similar for a given ε. If the degree of nitrate consumption in the suboxic SBB were much greater than presently observed, then the slope in $\delta^{15}N/\ln(f)$ space predicted for a given ε would depend greatly on the model used.

[32] This leaves two alternatives for explaining the SBB data: (1) there is a source of extremely low-$\delta^{15}N$ nitrate in the deep Santa Barbara Basin; or (2) an anomalously low isotope effect applies to the denitrification that occurs in the SBB.

[33] A source of extremely low-$\delta^{15}N$ nitrate is unlikely. The $\delta^{15}N$ of sinking N and sedimentary N in the SBB is indistinguishable from the $\delta^{15}N$ of the upwelled nitrate (~7‰ [*Altabet et al.*, 1999]), as one would expect when upwelled nitrate is almost completely consumed in surface waters. As a result, the only way to produce extremely low-$\delta^{15}N$ nitrate in the SBB is for extreme fractionation to occur upon remineralization to ammonium and/or the subsequent oxidation to nitrate, and for the remineralization step or nitrification step to be highly incomplete. While we have not measured the $\delta^{15}N$ of ammonium in the SBB, the $\delta^{15}N$ that we and others have measured for ammonium in other suboxic environments has been similar to the $\delta^{15}N$ of the organic N source to those environments (R. Thunell et al., manuscript in preparation, 2003), and the net isotopic effect of nitrification on the nitrate pool appears to minimized by the completeness with which ammonium is consumed [*Velinsky et al.*, 1991].

[34] Measurements of N_2/Ar in the water column and pore waters of the SBB indicate a source of N_2 in SBB sediments that is roughly four times that expected from the downward flux of nitrate [*Barnes et al.*, 1975]. This suggests that there is strong coupling between nitrification and denitrification in SBB sediments. This may explain why ammonium is typically below 1 μM in SBB water: any potential outgoing flux of ammonium is converted to N_2. We can imagine three mechanisms for this conversion: (1) normal ammonium oxidation, using the scarce but time-variant supply of O_2 that diffuses in from bottom waters, coupled to denitrification [*Barnes et al.*, 1975], (2) anaerobic nitrification using manganese or iron oxides

coupled to denitrification [*Hulth et al.*, 1999], or (3) some form of "anammox" reaction [*Jetten et al.*, 1999] whereby ammonium and nitrite/nitrate are combined to produce N_2 [*Bender et al.*, 1989]. The lack of nitrite in SBB waters [*Barnes et al.*, 1975; *Liu*, 1979] indicates that ammonium oxidation, if it does occur in the SBB, is closely coupled to either denitrification or nitrate oxidation. If ammonium oxidation leads to the production of nitrate that mixes back into the water column, this would represent a significant source of low-$\delta^{15}N$ nitrate only if there were other mechanisms of ammonium loss that had a lower isotope effect than the reaction converting ammonium to nitrate, and only if none of the product nitrate was denitrified before being mixed back into the water column. Thus we think it unlikely that nitrification represents a significant source of low-$\delta^{15}N$ nitrate to the SBB water column.

[35] This conclusion is supported by the $\delta^{18}O$ of SSB nitrate collected during the OXMZ01MV cruise in November 1999 (Figure 6). The ratio of increase in nitrate $\delta^{15}N$ and $\delta^{18}O$ across the SBB redoxcline ($\sim$1:1) is indistinguishable from the ratio of O and N isotopic enrichment that we have measured for open ETNP profiles from this cruise [*Sigman*, 2000]. This suggests that the SBB isotope variations are driven solely by denitrification, rather than by an input of nitrate that has an unusually low $\delta^{15}N$ (see caption of Figure 6 for explanation). One

caveat to this use of the oxygen isotope data is that the 1:1 N:O ratio for the isotope effects of denitrification that we adopt here for the ocean [*Sigman*, 2000] is greater than that observed in freshwater studies (1:0.6 [*Lehmann et al.*, 2003]). Ongoing work seeks to verify and constrain the cause of this difference [*Casciotti et al.*, 2002].

[36] If the arguments above are correct, then we are left with one explanation for the low ^{15}N enrichment of nitrate in suboxic SBB waters: the isotope effect assumed for denitrification must be much smaller than in the open ETNP. While the isotope effect that best fits the data depends on the model and the assumptions regarding the source of the phosphate increase into the deep basin (see above), an isotope effect of 7‰ (Figure 5, dashed lines) approximates a rough upper limit; this value is dramatically lower than is inferred here for the open ETNP ($\sim$25‰; Figures 4 and 5) and for open ocean denitrification zones in general (20–30‰ [*Altabet et al.*, 1999; *Brandes et al.*, 1998]).

[37] Why would the isotope effect of denitrification in the SBB be lower than in the suboxic waters of the ETNP? One potential explanation is that a lower intrinsic isotope effect characterizes the denitrifiers in the SBB. Such variability might have genetic or environmental causes. As an example of the latter, *Bryan et al.* [1983] observed that the isotope effect of nitrite reduction by *P. stutzeri* decreases sharply with increasing supply of reduc-

Figure 6. (opposite) (a) Depth profiles of nitrate $\delta^{15}N$ (filled symbols) and $\delta^{18}O$ (open symbols) from within the SBB (red) and station 2 (black) from outside the SBB. Horizontal lines indicate the sill depth of the SBB (475 m) and the approximate depth below which $[O_2] < 3$ μM. (b) The $\delta^{18}O$ of the nitrate versus its $\delta^{15}N$, for the SBB profile (filled circles), which shows that the increases in nitrate $\delta^{18}O$ and $\delta^{15}N$ into the suboxic basin are equal (^{18}O:^{15}N ratio of variations $\sim$1). This same ratio of nitrate $\delta^{18}O$ and $\delta^{15}N$ increase due to denitrification is observed in the open ETNP as well [*Sigman*, 2000]. The crosses indicate the changes in nitrate $\delta^{18}O$ and $\delta^{15}N$ that would be expected if both O and N isotopes followed the Rayleigh model for uptake with an isotope effect of 25‰. The blue crosses are calculated assuming that denitrification accounts solely for the decrease of nitrate into the basin (the constant-$[PO_4^{3-}]$ case, open SBB symbols in Figures 3b and 5), while the black crosses assume that denitrification explains the entire amplitude of N* decrease (the solid SBB symbols in Figures 3b and 5). From both of these calculations, nitrate with a $\delta^{18}O$ of 0‰ (vs. SMOW) and a $\delta^{15}N$ of -13‰ (vs. air) is then added to the deep basin until the nitrate $\delta^{15}N$ equals that observed in the deepest basin sample (blue and black dotted lines and open squares). This added nitrate would be $\sim$20‰ lower than the $\delta^{15}N$ of the sinking flux into the SBB ($\sim$7‰ [*Altabet et al.*, 1999]). Thus this addition is intended to test the isotopic effect of a source of low-$\delta^{15}N$ N to the deep SBB nitrate pool. It indicates that, if this process were important, the measured nitrate $\delta^{18}O$ would have been significantly higher. Even with such a low $\delta^{15}N$ for the added nitrate, 9–14 μM must be added to reach the observed deep SBB nitrate $\delta^{15}N$, which effectively violates observations of $[NO_3^-]$ in the deep SBB; an even lower $\delta^{15}N$ for the added nitrate would be required to reduce this violation of the $[NO_3^-]$ data. Consequently, the coupled isotope measurements suggest that a source of low-$\delta^{15}N$ nitrate to the SBB cannot explain the low degree of isotopic enrichment in the deep SBB. This supports the view that the small degree of ^{15}N enrichment in the SBB involves denitrification.
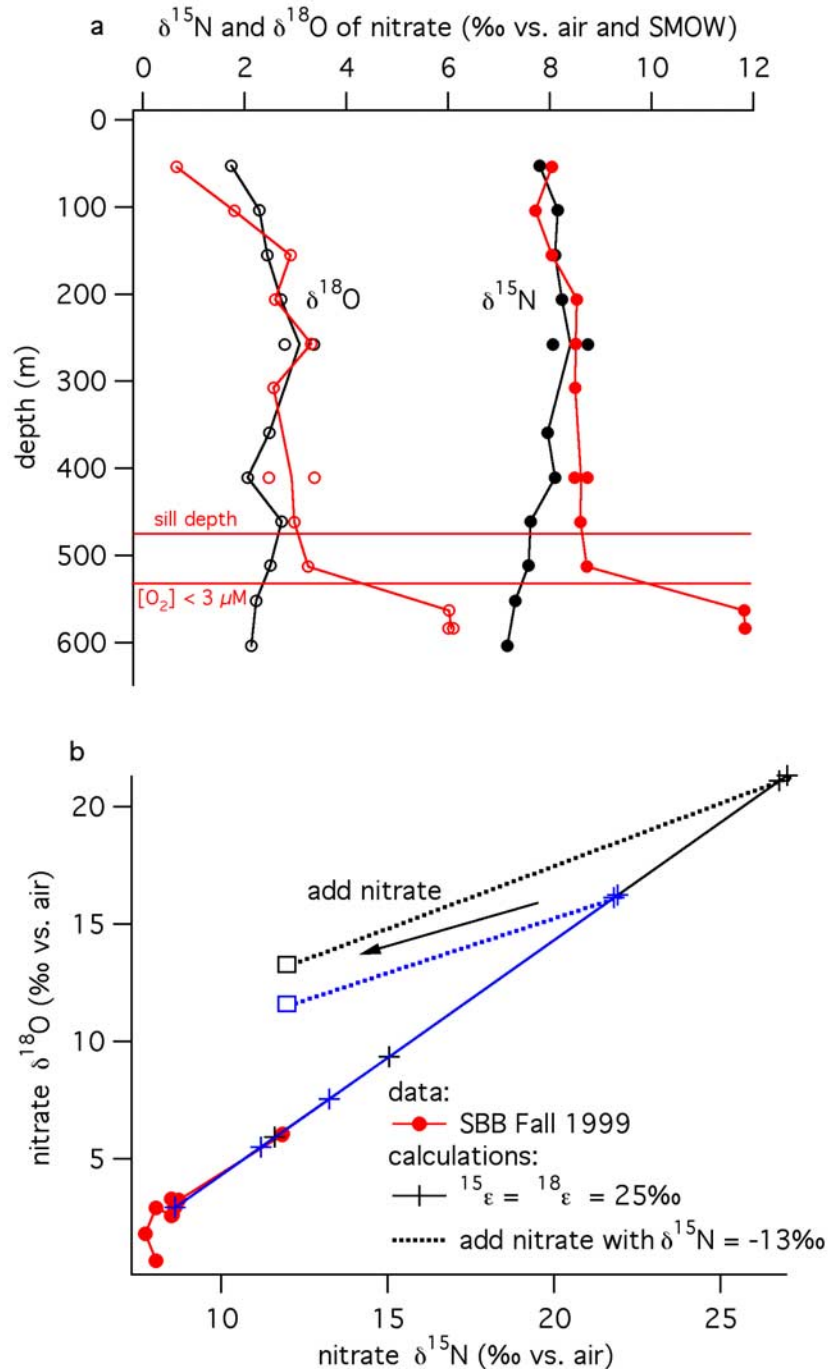
tant. Yet *Barford et al.* [1999], in a study of nitrate consumption by the same denitrifier with a very high concentration of reductant (20 mM acetate), measured an isotope effect of $\sim$28‰, in line with our open ETNP measurements. *Barford et al.* [1999] also found that the isotope effect of denitrification does not change as a function of O_2 concentration, despite the effect that O_2 concentration has on the rates of the various components of the denitrification pathway. Moreover, field data from the ETNP and Arabian Sea do not suggest distinguishable isotope effects for denitrification in these appreciably different oceanographic settings [*Brandes et al.*, 1998]. Even if the rate of denitrification does control the isotope effect of nitrate consumption, we argue against this option as a way to explain the SBB/open ETNP difference on the grounds that it is unlikely that the water column

conditions for denitrification are vastly different between the suboxic SBB and the suboxic ETNP.

[38] This leads us to conclude that some process in the deep SBB must reduce the "effective" isotope effect of denitrification to a value much lower than the "intrinsic" (i.e. biological) isotope effect. As described above, molecular diffusion of nitrate within sediment pore waters has been observed to have exactly this impact on the isotope effect of sedimentary denitrification, in different sedimentary environments: Puget Sound sediments [*Brandes and Devol*, 1997], the Washington and Mexican continental margins in the Pacific [*Brandes and Devol*, 2002] and at 3000 m depth on the Carolina slope in the Atlantic [*Sigman et al.*, 2001]. *Brandes and Devol* [2002] suggest an operational mean value of 1.5‰ for the effective isotope effect for sedimentary denitrification. Thus the low effective isotope effect observed for denitrification in the deep SBB suggests that the integrated rate of sedimentary denitrification is much greater than that of water column denitrification within the basin.

[39] For each of the models of nitrate consumption and supply described above, it can be shown that the observed isotope effect of nitrate consumption (ε_{obs}) is well approximated by the rate-weighted average of the intrinsic isotope effects of the component terms of nitrate consumption, in our case, water column and sedimentary denitrification:

$$\varepsilon_{obs} = (\varepsilon_{wc} \times D_{wc} + \varepsilon_{sed} \times D_{sed})/(D_{wc} + D_{sed}) \qquad (3)$$

where D_{wc} and D_{sed} are the respective denitrification rates of water column and sedimentary denitrification and ε_{wc} and ε_{sed} are their respective isotope effects. Assuming values of 25‰ and 1.5‰ for ε_{wc} and ε_{sed}, respectively, and given an ε_{obs} of 7‰ for denitrification within the SBB (Figure 5), the calculated fraction of nitrate loss due to sedimentary denitrification is 76%. The uncertainty in this calculation is difficult to quantify, in that it involves the data, the models of the nitrate supply, and the isotope effects assumed for water column and sedimentary denitrification. Perhaps most critically, the isotope effect for sedimentary denitrification has not yet been fully characterized over a suitable range of conditions. Our strong feeling is that the calculated fraction of denitrification in the sediments is probably an underestimate, in that 7‰ seems to provide an upper limit on the value of ε_{obs}. Moreover, the evidence described above suggests that there is a coupling of nitrification and denitrification in SBB sediments, which would indicate that a significant portion of the phosphate increase into the basin is due to anaerobic degradation, the ammonium from which has been denitrified in the sediments. In this case, the filled symbols for the SBB in Figures 3b and 5 are more representative of the nitrate deficit than are the open symbols. Regardless of such details, the isotope data strongly suggest that sedimentary denitrification is the dominant mechanism of nitrate loss in the SBB.

[40] To this point, our comparison of the SBB data with the other ETNP data has not considered the potential role of sedimentary denitrification outside the SBB. However, this process is probably proceeding at relatively high rates throughout the sediments of the eastern Pacific. Therefore, we must ask whether there is any suggestion of an isotopic impact of sedimentary denitrification in our open ETNP profiles. We see no clear evidence for this, but there are relatively subtle observations about which we wish to speculate. Station 17 from 25°S along the Baja California margin is within a bathymetric depression known as the Soledad Basin. This station is within the regional O$_2$-deficient zone of the ETNP, with [O$_2$] less than 5 μM below 200 m, while the basin sill is at ~400 m. As a result, one would expect the rate of water column denitrification to be comparable to other stations in that latitude range. However, the δ^{15}N/ln(f) trend of the Soledad Basin falls slightly below the mean trend of the other stations (Figure 7, filled magenta triangles). To explain this admittedly subtle observation, it may be that the basin margins and the broad surrounding shelf result in a higher ratio of sedimentary to water column denitrification within the Soledad Basin than is observed across the rest of the Baja margin. Moreover, we find it interesting that station 8, which is just to the west of station 17 (Figure 1), does not separate from the most southern group of stations (dark blue crosses
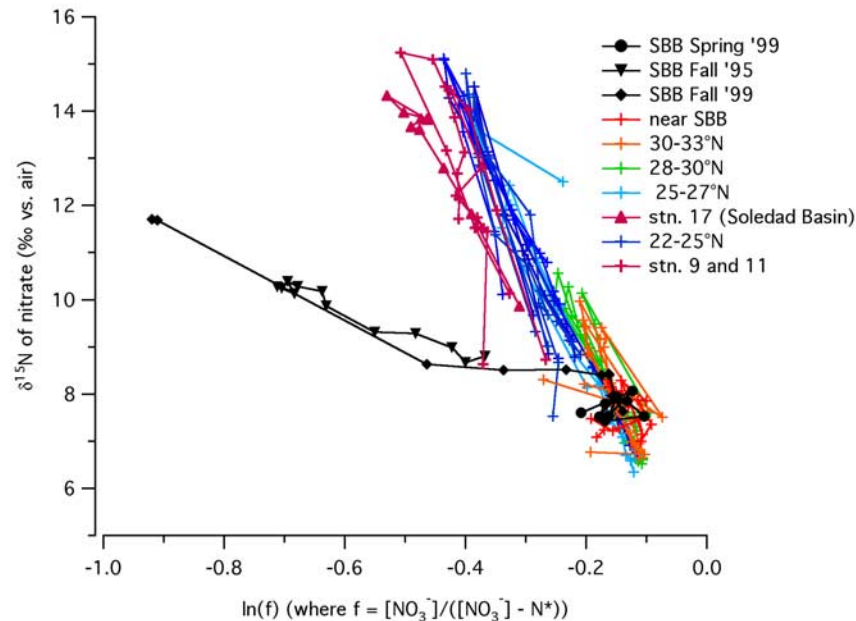
Figure 7. δ^{15}N of nitrate vs. ln(f) for all sites, as in Figure 3, with station 17 from within Soledad Basin included (filled magenta triangles). Soledad Basin stands out as an intermediate case between the open ETNP and the Santa Barbara Basin. The Soledad Basin has an [O$_2$] of less than 5 μM below 200 m, while the basin sill is ~400 m. We infer that water column denitrification is the dominant mechanism of the nitrate deficit in the basin but that there is extensive sedimentary denitrification across the broad shelf area surrounding the basin, contributing to the uniformly low δ^{15}N of nitrate (relative to the nitrate deficit) at station 17. In addition, the symbols of stations 9 and 11 have been altered from their thin blue crosses in Figures 3 and 5 to bold magenta crosses, to show that they have a slightly lower slope in nitrate δ^{15}N/ln(f) space than do the more southern stations at the southern tip of Baja (see text).

in Figure 7). This station sits over deep water, off the continental margin (Figure 1), so that it might be more isolated from the effects of sedimentary denitrification. Looking at a still higher level of detail, stations 9 and 11, which are the furthest from the southern tip of Baja among the southernmost group of stations, appear to have a slightly lower δ^{15}N/ln(f) trend than the other stations in that group (bold magenta crosses). It may be that the lower trend indicates a somewhat greater role for sedimentary denitrification at these stations than slightly further south, which might be due to the southward decrease in the area of continental margin at the southern tip of Baja (Figure 1)]. Alternatively, one might infer that it indicates a higher absolute rate of water column denitrification toward the south and thus a smaller relative role for sedimentary nitrate consumption. Again, we emphasize that these observations are subtle, and our comments about them are strictly speculative. We wish only to make the point that subtle variations in

isotopic enrichment within and among denitrification zones may reflect variations in the relative importance of sedimentary denitrification.

5. Implications

[41] We can estimate absolute rates of denitrification for the sediments and water column of the SBB, although our sampling scheme was not designed for this purpose, making our estimates highly uncertain. Our data for 1999 suggest that roughly 19.5 μM nitrate was denitrified from the bottom ~50 meters of the SBB over the seven months following the springtime flushing event. This estimate is based solely on the nitrate de-crease and thus assumes that there was no additional denitrification by coupling to nitrification within the SBB (i.e., by anaerobic ammonium oxidation in the sediments or by O$_2$-based nitrification near the redoxcline). It also assumes that the deep SBB is a closed system subsequent to springtime flushing.

Thus our estimate of total denitrification rate is conservative. If 76% of the nitrate loss was due to sedimentary denitrification, it would suggest a rate of ~4.5 mmol N m^{-2} d^{-1} (basin volume and area from *Emery* [1960]). This estimated rate is high relative to other studies in the borderland basins, for instance, 1.5 mmol N m^{-2} d^{-1} measured by *Jahnke* [1990] in the Santa Monica Basin (bottom water [O$_2$] = 10 μM), 1.0 mmol N m^{-2} d^{-1} measured by *Berelson et al.* [1987] in the San Pedro Basin (bottom water [O$_2$] ~ 6 μM), and 0.6 mmol N m^{-2} d^{-1} measured by *Berelson et al.* [1987] in the San Nicolas Basin (bottom water [O$_2$] ~ 18 μM). If 24% of the nitrate loss was due to water column denitrification, it would suggest a rate of 0.02 μM N d^{-1}, similar to an estimate of 0.027 μM d^{-1} for the open eastern tropical south Pacific [*Codispoti and Christensen*, 1985].

[42] Thus, while our data imply typical rates for water column denitrification, they seem to suggest a somewhat higher rate for sedimentary denitrification than has been found in chamber and pore water studies from nearby basins. We reiterate that our estimate of absolute rates is uncertain and thus should not be over−interpreted. Nevertheless, if sedimentary denitrification is unusually rapid in the SBB, then an explanation is needed. We have considered four possibilities. First, primary productivity and the downward rain of organic carbon are approximately an order of magnitude greater in the SBB than in nearby basins [*Berelson et al.*, 1996; *Thunell*, 1998] and so should fuel a higher rate of denitrification. Second, the rapid sedimentation rate observed in the SBB may more efficiently drive organic matter to the seafloor and into the sediments, thus increasing respiration in the sediments at the expense of respiration in the water column. Third, the presence of *Beggiatoa* mats in the sediment of the SBB increase the porosity of the sediment [*Reimers et al.*, 1990], possibly allowing for higher rates of nitrate diffusion into the sediment and thus allowing for higher denitrification rates. Fourth, *Beggiatoa* may play an active role in accelerating denitrification in SBB sediments. *Beggiatoa* concentrates nitrate in a central vacuole to use in the oxidation of sulfur; this concentration is extreme, as high as 160 mM [*McHatton et al.*,

1996]. There is some question as to whether the product of the nitrate reduction is N$_2$ [*Fossing et al.*, 1995; *McHatton et al.*, 1996; *Sweerts et al.*, 1990] or NH$_4^+$ [*Zopfi et al.*, 2001]. If the main product is N$_2$, then *Beggiatoa* metabolism itself could explain a high sedimentary denitrificaton rate [*Sweerts et al.*, 1990]. If NH$_4^+$ is the main product, then its role in accelerating denitrification would be limited to concentrating ammonium for a sedimentary nitrification−denitrification couple.

[43] As indicated by the model comparison, the conditions of ocean mixing and nitrate supply in the water column are not particularly important in determining the isotopic enrichment caused by denitrification in the SBB. As a result, we were unable to identify a model of physical nitrate supply that would allow us to explain the low degree of isotopic enrichment associated with denitrification in the SBB without resorting to an isotope effect for denitrification in the SBB that is much lower than appears to apply in the open ETNP. However, at higher degrees of nitrate consumption, (lower values of "f", the fraction of the initial nitrate left unconsumed by denitrification), the models described above diverge, leading to very different predictions for the δ^{15}N/ln(f) relationship. Under higher degrees of nitrate consumption, resupply of nitrate, either by finite mixing events or in the context of a steady state model, can lead to very low degrees of isotopic enrichment. Thus, in suboxic basins where nitrate is nearly completely consumed by denitrification, such as the Cariaco Basin (R. Thunell et al., manuscript in preparation, 2003), water column denitrification alone can cause low degrees of isotope enrichment during nitrate consumption. In this light, the use of the nitrate nitrogen isotopes to resolve sedimentary and water column denitrification may be limited to high−[NO$_3^-$] environments, unless other constraints can be incorporated.

Acknowledgments

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