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Sinking organic matter spreads the nitrogen isotope signal of pelagic denitrification in the North Pacific

Daniel M. Sigman,[1] Peter J. DiFiore,[1] Mathis P. Hain,[1,2] Curtis Deutsch,[3] and David M. Karl[4]

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[1] Culture studies of denitrifying bacteria predict that denitrification will generate equivalent gradients in the $\delta^{15}N$ and $\delta^{18}O$ of deep ocean nitrate. A depth profile of nitrate isotopes from the Hawaii Ocean Time-series Station ALOHA shows less of an increase in $\delta^{18}O$ than in $\delta^{15}N$ as one ascends from abyssal waters into the denitrification-impacted mid-depth waters. A box model of the ocean nitrate N and O isotopes indicates that this is the effect of the low latitude nitrate assimilation/regeneration cycle: organic N sinking out of the surface spreads the high-$\delta^{15}N$ signal of pelagic denitrification into waters well below and beyond the suboxic zone, whereas the nitrate $\delta^{18}O$ signal of denitrification can only be transmitted by circulation in the interior. **Citation:** Sigman, D. M., P. J. DiFiore, M. P. Hain, C. Deutsch, and D. M. Karl (2009), Sinking organic matter spreads the nitrogen isotope signal of pelagic denitrification in the North Pacific, *Geophys. Res. Lett.*, *36*, L08605, doi:10.1029/2008GL035784.

1. Introduction

[2] The N and O isotope ratios of nitrate (NO_3^-) provide information on the transformations of oceanic fixed N. In the suboxic thermocline waters of the eastern North Pacific (ENP) margin, where both the $\delta^{18}O$ and $\delta^{15}N$ of nitrate are elevated by pelagic denitrification, $\delta^{18}O$ is more elevated above background deep water than is $\delta^{15}N$ [*Sigman et al.*, 2005], while culture studies suggest that denitrification alone causes nearly equivalent increases in $\delta^{18}O$ and $\delta^{15}N$ [*Granger et al.*, 2008]. Plausible explanations for this field observation include (1) the input of nitrate from coupled N_2 fixation/nitrification and (2) the cycling of nitrate through a reduction/re-oxidation sequence [*Sigman et al.*, 2005]. Here, we report the opposite tendency in the deep to mid-depth open North Pacific waters off Hawaii – elevation of the $\delta^{15}N$ of nitrate relative to its $\delta^{18}O$ – which we interpret with the help of a global ocean box model. As high-$\delta^{15}N$ nitrate from the ENP denitrification zone is converted to organic N and back to nitrate, the high-$\delta^{15}N$ signal of denitrification is preserved and spread through the North Pacific Ocean, adding to the spreading of the isotope signal by circulation in the ocean interior. However, the O atoms of nitrate are removed upon conversion to organic N, to be added anew by subsequent nitrification, such that the high-$\delta^{18}O$ signal of denitrification is erased by the ocean's internal N cycling.

2. Methods

[3] Water samples were collected at the Hawaii Ocean Time-series Station ALOHA during HOT-120 in November 2000. Nitrate isotope samples were collected in pre-cleaned polyethylene bottles and stored frozen. The nutrient, O_2, and salinity data were generated as part of the HOT program (http://hahana.soest.hawaii.edu/). We use N* as a measure of the nitrate-to-phosphate relationship: $N^* = [NO_3^-] - 16^*[PO_4^{3-}] + 2.9$ (in μmol kg^{-1}) [*Deutsch et al.*, 2001].

[4] The $\delta^{15}N$ and $\delta^{18}O$ of nitrate were measured using the denitrifier method [*Casciotti et al.*, 2002; *Sigman et al.*, 2001] ($\delta^{15}N_{sample} = (({}^{15}N/{}^{14}N)_{sample}/({}^{15}N/{}^{14}N)_{reference} - 1) * 1000‰$; $\delta^{18}O_{sample} = (({}^{18}O/{}^{16}O)_{sample}/({}^{18}O/{}^{16}O)_{reference} - 1) * 1000‰$). Measurements are referenced to air N_2 and VSMOW using the nitrate reference material IAEA-N3, with a $\delta^{15}N$ of 4.7‰ vs. air and a $\delta^{18}O$ of 25.6‰ vs. VSMOW [*Böhlke et al.*, 2003]. The nitrate $\delta^{18}O$ data were updated from the referencing scheme of *Casciotti et al.* [2002] to a new scheme using the multiple nitrate isotope reference materials now available [*Böhlke et al.*, 2003] according to D. M. Sigman et al. (The dual isotopes of deep nitrate as a constraint on the cycle and budget of oceanic fixed nitrogen, submitted to *Deep Sea Research, Part I*, 2008). The isotope values for samples reported here derive from at least duplicate analyses, yielding standard errors of ±0.15‰ for $\delta^{15}N$ and ±0.35‰ for $\delta^{18}O$.

2.1. Box Model

[5] The nitrate isotopes were incorporated into the 'CYCLOPS' box model [*Keir*, 1988]. Relevant aspects of the nitrate isotope component are described by Sigman et al. (submitted manuscript, 2008). Essential information follows.

[6] The model's fixed N includes only nitrate and particulate organic N (PN). In the surface boxes, nitrate is assimilated into organic matter in a 16:1 ratio to phosphate, and organic N and P sink out of the surface ocean and are regenerated in this same ratio. N_2 fixation occurs to maintain P (rather than N) limitation of carbon fixation and export in the low latitude surface boxes. Denitrification occurs in the water column, through a routine that develops a suboxic domain within any given box on the basis of its O_2 concentration and demand for oxidant. Sedimentary denitrification rate is parameterized using a modified expression

[1]Department of Geosciences, Princeton University, Princeton, New Jersey, USA.
[2]Institut für Geowissenschaften, Universität Potsdam, Potsdam, Germany.
[3]Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, California, USA.
[4]Department of Oceanography, University of Hawai'i, Honolulu, Hawaii, USA.

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from *Middelburg et al.* [1996]. The model steady state output is tabulated in Table S1[1].

[7] Oceanic N_2 fixation is assumed to produce PN with a $\delta^{15}N$ of −1‰ [e.g., *Montoya et al.*, 2002]. The N isotope effects of nitrate assimilation and denitrification are assumed to be 5‰ and 25‰, respectively [e.g., *Brandes et al.*, 1998; *Sigman et al.*, 1999]; the N isotope effect, $^{15}\varepsilon$, of a nitrate-consuming process is defined here as $(^{14}k/^{15}k - 1)*1000‰$, where ^{14}k and ^{15}k are the rate coefficients of the consumption reactions for the ^{14}N- and ^{15}N-bearing forms of nitrate, respectively. Organic matter regeneration/nitrification is assumed to yield nitrate with the $\delta^{15}N$ of the organic matter. We assume that sedimentary denitrification consumes nitrate without isotope discrimination [*Brandes and Devol*, 1997; *Lehmann et al.*, 2004, 2007].

[8] In the model case used here, the nitrate O atoms are assumed to derive solely from ambient water [*Casciotti et al.*, 2002; Sigman et al., submitted manuscript, 2008]. The $\delta^{18}O$ of newly produced nitrate from nitrification is not well known. We preliminarily estimate that it is 1.15‰ greater than ambient water (Sigman et al., submitted manuscript, 2008), but with minimal significance for this study. We apply an $^{15}\varepsilon$:$^{18}\varepsilon$ ratio of 1 for both nitrate assimilation and denitrification ($^{18}\varepsilon \equiv (^{16}k/^{18}k - 1)*1000‰$) [*Granger et al.*, 2004, 2008].

2.2. Isotope Terms

[9] Below, we refer to the derived parameter $\Delta(15,18)$, which quantifies deviations in the nitrate $\delta^{15}N$-to-$\delta^{18}O$ relationship from that expected from a specific removal process [*Sigman et al.*, 2005]:

$$\Delta(15,18) \equiv (\delta^{15}N - \delta^{15}N_b) - (^{15}\varepsilon :^{18}\varepsilon) * (\delta^{18}O - \delta^{18}O_b) \quad (1)$$

where $\delta^{15}N_b$ and $\delta^{18}O_b$ represent the isotopic composition of the background nitrate supply to the system, and $\delta^{15}N$ and $\delta^{18}O$ are the measured isotopic composition of nitrate in a given sample. The $^{15}\varepsilon$:$^{18}\varepsilon$ is the N-to-O isotope effect ratio of the consuming process, taken to be 1. In this study, we define $\delta^{15}N_b$ and $\delta^{18}O_b$ as the mean values for our ALOHA samples below 3500 m, rounded to the nearest 0.1‰: $\delta^{15}N_b$ = 5.0‰ vs. air, and $\delta^{18}O_b$ = 1.8‰ vs. VSMOW. This depth interval is reasonably taken as reflecting the Southern Ocean-derived abyssal water that flows into the North Pacific, where it rises and flows back southward at ∼1–3 km depth while undergoing biogeochemical alteration [*Schmitz*, 1995]. A positive $\Delta(15,18)$ indicates a higher nitrate $\delta^{15}N$ than expected from (1) the sample's nitrate $\delta^{18}O$, (2) the $\delta^{15}N$ and $\delta^{18}O$ of the nitrate supplied to the system, and (3) the $^{15}\varepsilon$:$^{18}\varepsilon$ of the consuming process.

3. Results

[10] Above the abyssal waters at ALOHA, there is an upward increase in both nitrate $\delta^{15}N$ and $\delta^{18}O$ into the depths corresponding to the isopycnals of the $[O_2]$ and N* minima in the eastern North Pacific (Figure 1), presumably resulting from the influence of the denitrification zones of the eastern Pacific. However, there is an interesting difference between $\delta^{15}N$ and $\delta^{18}O$ in terms of the amplitude of increase. In the 750–2000 m depth interval, nitrate $\delta^{15}N$ is ∼0.4‰ more elevated than is $\delta^{18}O$ relative to their deep values at ALOHA (Figures 1a and 1b), yielding a maximum in Δ (15,18) of ∼0.4‰ (Figure 1c). This observation is also apparent in a plot of the $\delta^{18}O$ of nitrate versus its $\delta^{15}N$: as one shoals gradually from 3600 m, the $\delta^{18}O$ and $\delta^{15}N$ increase in a ratio of ∼0.7 (Figure 2). Upon reaching the denitrification-driven $\delta^{15}N$ and $\delta^{18}O$ maxima at 350–500 m, this trend is broken, with the $\delta^{18}O$ and $\delta^{15}N$ at these depths being equally elevated above abyssal nitrate (Figure 2a; see dashed reference line with slope of 1).

[11] Given only N_2 fixation (with nitrification to nitrate) and denitrification operating in the ocean N cycle, one would expect equivalent increases in nitrate $\delta^{18}O$ and $\delta^{15}N$ from regions of N_2 fixation (or from global mean deep water) toward a region of denitrification (bold black line in Figure 2b). However, this 'denitrification-only' behavior does not appear to fit our data from ALOHA. A similar deviation from the denitrification-driven $\delta^{18}O$-to-$\delta^{15}N$ variation ratio ($\Delta\delta^{18}O$:$\Delta\delta^{15}N$) appears among the boxes of the ocean model (blue crosses and red pluses in Figure 2b). Comparing deep and intermediate North Pacific boxes, the closest analogue to the ALOHA profile, nitrate $\delta^{18}O$ and $\delta^{15}N$ increase in a ratio of 0.72. Moreover, the deviation of $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ from 1 observed in the ALOHA data and the model is complemented by a similar measured deviation in the $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ of inter-basin gradients (Sigman et al., submitted manuscript, 2008).

[12] The deviation in $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ from 1 in the model arises from the regeneration and nitrification of sinking N. Denitrification in the model, which occurs most rapidly in the intermediate North Pacific, renders the nitrate in that box enriched in ^{15}N and ^{18}O. This nitrate is mixed or upwells into the North Pacific surface, where it is converted into high-$\delta^{15}N$ PN, which sinks back into the interior, to be regenerated as high-$\delta^{15}N$ nitrate in the underlying intermediate and deep boxes. This N cycling preserves the N isotope signal of denitrification and spreads it beyond the box hosting the denitrification by a means other than circulation. However, the regenerated nitrate has the $\delta^{18}O$ of nitrification, such that this cycled nitrate has lost the ^{18}O enrichment from denitrification (gray arrows in Figure 2b). Since the model assumes that most (84%) of the sinking flux is regenerated in the intermediate box, the $\Delta\delta^{18}O$-to-$\Delta\delta^{15}N$ decoupling is greatest there.

[13] This box model dynamic applies to the Station ALOHA data. The denitrification occurring in the eastern Pacific produces high-$\delta^{15}N$ nitrate, and the entrainment of this nitrate leads to ^{15}N enrichment of the sinking flux in the region [*Altabet et al.*, 1999], the regeneration of which spreads the nitrate $\delta^{15}N$ signal of denitrification into waters outside the zone of denitrification. The regenerated nitrate, however, has no surviving O isotope signal of denitrification. Thus, whereas the $\delta^{15}N$ elevation by denitrification can be spread throughout the ocean by the assimilation of ^{15}N-enriched nitrate at the surface, sinking, and remineralization in the interior, the $\delta^{18}O$ elevation cannot, leading to a less regionally distributed denitrification-driven signal in nitrate $\delta^{18}O$ than in $\delta^{15}N$. This can explain the mid-depth (750–1500 m) interval with $\Delta(15,18) > 0$ (Figure 1c). Using a three end-member mixing model, we estimate that 45% (i.e.

[1] Auxiliary materials are available in the HTML. doi:10.1029/2008GL035784.

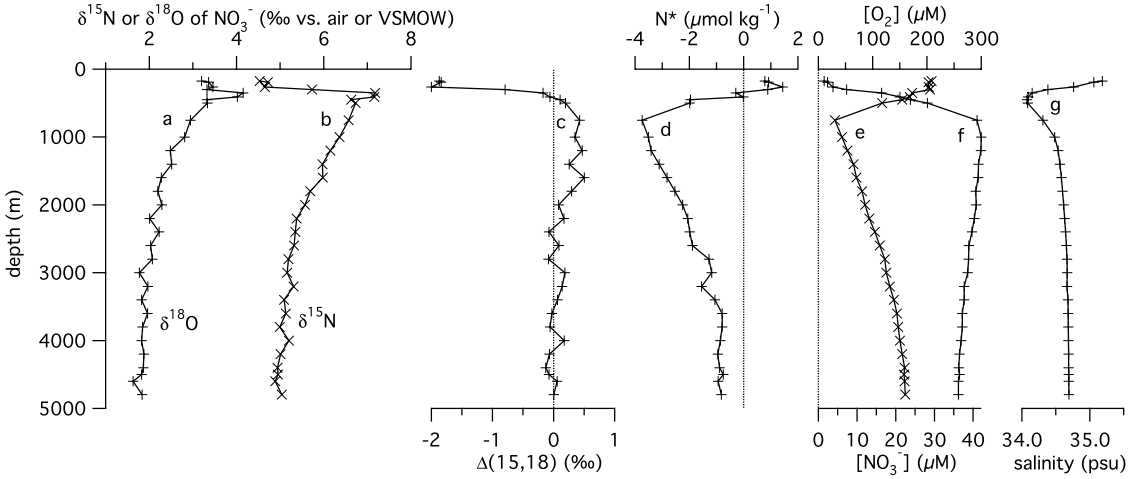


Figure 1. For a depth profile of samples collected as Hawaii Ocean Time-series Station ALOHA during HOT-120 in November 2000, (a) nitrate $\delta^{18}O$, (b) nitrate $\delta^{15}N$, (c) $\Delta(15,18)$, (d) N*, (e) $[O_2]$, (f) $[NO_3^-]$, and (g) salinity.

half) of the $\delta^{15}N$ elevation at 1200 m (relative to abyssal nitrate with a $\delta^{15}N$ of 5.0‰) is due to the remineralization of organic matter derived from high-$\delta^{15}N$ nitrate, the remainder coming from the circulation-driven input of nitrate from the ENP suboxic zone (see auxiliary material). However, this quantification must be considered preliminary, awaiting resolution of the additional considerations described next.

[14] If the regional nutrient supply to the surface ocean is elevated in nitrate $\delta^{15}N$ by denitrification, then its $[NO_3^-]$:$[PO_4^{3-}]$ ratio should also be reduced. If all of the phosphate is consumed in the surface, then either the N:P ratio of the export production must be below the canonical "Redfield" ratio of 16 for organic matter, or new N must be fixed in the surface. In the case of N_2 fixation, the $\delta^{15}N$ of N export would be lower than that of the nitrate supply, which

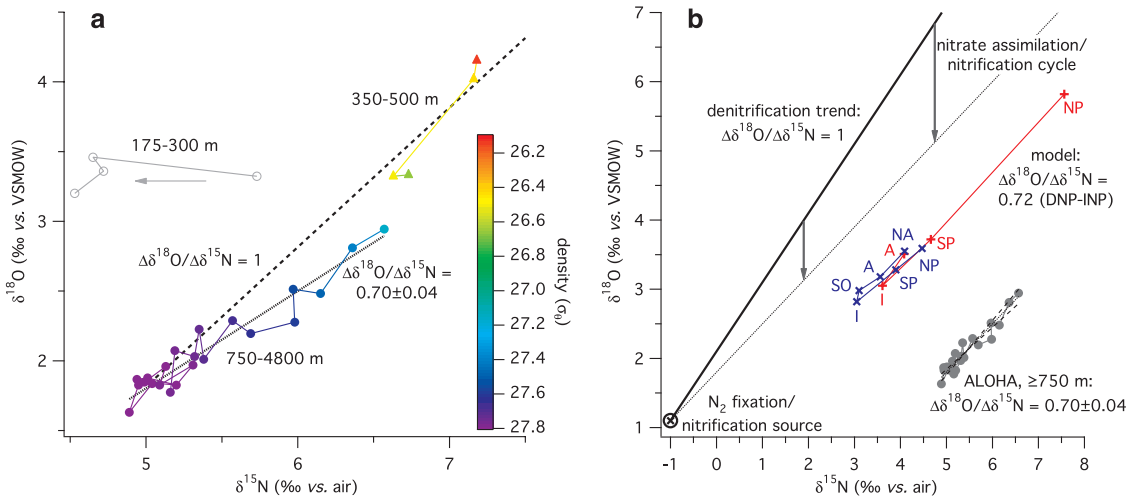


Figure 2. (a) Nitrate $\delta^{18}O$ versus nitrate $\delta^{15}N$ for the Station ALOHA data and (b) comparison of the deep data (750–4800 m) to output from the box model. In Figure 2a, samples at ≥350 m depth are color coded according to density; above this, a gray arrow indicates shoaling. Nitrate $\delta^{15}N$ and $\delta^{18}O$ increase upward from the base of the profile due to denitrification at mid-depths in the eastern Pacific. The upward increase in nitrate $\delta^{15}N$ and $\delta^{18}O$ from 4800 to 750 m has a $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ of 0.70 ± 0.04 (model-II least squares regression, with 95% confidence interval; see dotted line). In Figure 2b, the ALOHA data from 4800 to 750 m (gray symbols, with least-squares trend and 95% confidence interval plotted) are compared to the output from the box model. Blue crosses and red pluses indicate deep (bottom-1500 m) and intermediate (1500-150 m) boxes, respectively (NA, North Atlantic; A, Atlantic; SO, Southern Ocean; I, Indian; SP, South Pacific; and NP, North Pacific). The $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ slope defined by comparing intermediate and deep North Pacific boxes (INP-DNP) is 0.72. The circled cross in the lower left of Figure 2b indicates the estimated $\delta^{15}N$ and $\delta^{18}O$ of nitrate deriving from N_2 fixation, and the black line shows the expected correlation between nitrate $\delta^{18}O$ and $\delta^{15}N$ in a hypothetical ocean that includes only N_2 fixation (followed by regeneration and nitrification) and denitrification. The gray arrows then indicate the effect of including nitrate assimilation in the low latitude surface ocean followed by N export and regeneration/nitrification in the ocean interior.

would weaken the distinction between the N and O isotope dynamics of regeneration described above. Nevertheless, coupling of pelagic denitrification with N_2 fixation in a given ocean region works to raise the region's nitrate $\delta^{15}N$ [*Sigman et al.*, 2005], so the N-*vs.*-O isotope distinction would not be completely lost. Indeed, in our box model, in which N_2 fixation in the surface boxes compensates for any nitrate deficit in supply of nutrients from the subsurface, the deviation of $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ from 1 occurs and is comparable in amplitude to the data (Figure 2b). Assuming that sinking N has been supplemented by the full amount of N_2 fixation needed to completely remove the nitrate deficit upwelled in the eastern North Pacific, we recalculate that 58% of the $\delta^{15}N$ elevation measured at 1200 m derives from the regeneration of organic N, 13% more than without this consideration (see auxiliary material).

[15] As with denitrification in the ENP suboxic zones, partial nitrate assimilation in the surface formation regions of North Pacific Intermediate Water (which ventilates the ~450 m level at ALOHA; salinity minimum in Figure 1g) may also work to raise the $\delta^{15}N$ and $\delta^{18}O$ of nitrate in the upper kilometer of the water column relative to deeper water. The low latitude nitrate assimilation/nitrification cycle should alter any such partial nitrate assimilation isotope signal in the same manner as its effect on the denitrification signal: Complete nitrate assimilation in the low latitude surface, coupled with sinking PN and regeneration of nitrate in the interior, removes the partial nitrate assimilation signal from the $\delta^{18}O$ of nitrate but not from its $\delta^{15}N$. Moreover, the high-$\delta^{15}N$ thermocline nitrate, once assimilated and converted into sinking PN, can be distributed deeper into the water column. Thus, part of the deviation of the O-to-N isotope trend from the expected 1-to-1 behavior between 3600 m and 750 m at ALOHA may derive from low latitude processing of the high latitude partial nitrate assimilation isotope signal in preformed nitrate at shallow levels. In the box model, this dynamic causes 30–50% of the deviation in $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ from 1, depending on the diagnostic used (Sigman et al., submitted manuscript, 2008). This would lower our estimate of the nitrate $\delta^{15}N$ elevation at 1200 m originating from sinking N from 45–58% (see above) to 23–41%. We favor the higher end of this range, because the model appears to overrepresent the partial nitrate assimilation dynamic relative to the real ocean (Sigman et al., submitted manuscript, 2008).

[16] Above 750 m, nitrate $\delta^{18}O$ and $\delta^{15}N$ continue to increase, with a sharp maximum at 350–400 m. Over this depth interval, the $\delta^{18}O$ of nitrate increases upward more than does its $\delta^{15}N$, yielding nearly equal elevations in nitrate $\delta^{18}O$ and $\delta^{15}N$ at 350–400 m relative to >3500 m depth (in Figure 1, Δ(15,18) at 350–400 m is 0; in Figure 2a, see dashed line with slope of 1). These depths fall within the salinity minimum associated with North Pacific Intermediate Water (Figure 1g) and on the same density surfaces as waters from the eastern North Pacific margin suboxic zone region where both nitrate $\delta^{18}O$ and $\delta^{15}N$ are elevated due to denitrification and where there is a notable elevation in nitrate $\delta^{18}O$ relative to its $\delta^{15}N$ (i.e. a negative Δ(15,18)) [*Sigman et al.*, 2005]. At these depths, isopycnal communication of the isotope signal of denitrification is more important, in which case the denitrification signals in both $\delta^{15}N$ and $\delta^{18}O$ are transmitted. Moreover, the distinctly negative Δ(15,18) in the ENP margin waters should work to raise the $\delta^{18}O$ of nitrate relative to its $\delta^{15}N$ (lower the Δ(15,18)) at ALOHA, compensating for the high Δ(15,18) of any nitrate mixed up from below (auxiliary material Figure S1).

[17] Above 350 m, nitrate $\delta^{15}N$ decreases to 4.2‰, while its $\delta^{18}O$ decreases less, such that Δ(15,18) decreases sharply toward the surface. This upward decrease in nitrate $\delta^{15}N$ has been observed previously in both the Atlantic and the Pacific subtropical ocean [*Karl et al.*, 2002; *Knapp et al.*, 2005; *Liu et al.*, 1996] and in this specific region [*Casciotti et al.*, 2008], where it has been explained as the remineralization of low-$\delta^{15}N$ sinking N produced by N_2 fixation in the overlying surface ocean.

[18] A more general view of the discussion above is that the low latitude nitrate assimilation/regeneration cycle in the ocean tends to lower the $\delta^{18}O$ of nitrate from the 1-to-1 variation with $\delta^{15}N$ expected from an ocean with only N_2 fixation (followed by nitrification) and denitrification, leading to less inter-basin variation in nitrate $\delta^{18}O$ and a lower mean ocean nitrate $\delta^{18}O$ (downward gray arrows in Figure 2b; Sigman et al., submitted manuscript, 2008). Consistent with this view, the $\delta^{18}O$ of abyssal Pacific nitrate is itself below the expected 1-to-1 trend, and the $\Delta\delta^{18}O$:$\Delta\delta^{15}N$ from the abyssal to mid-depth Pacific is also less than expected from N_2 fixation and denitrification alone (Figure 2b). At the same time, in regions where N fluxes are more dominated by N_2 fixation, denitrification, and their interaction, we would expect nitrate $\delta^{18}O$ and $\delta^{15}N$ to converge toward the bold line in Figure 2b. This may explain the convergence of the nitrate isotopes toward the N_2 fixation/denitrification trend in the waters at 350–500 m that communicate directly with the eastern Pacific margin suboxic zones, where both denitrification and N_2 fixation may be important [*Sigman et al.*, 2005], and in the waters above 350 m in which newly fixed N may represent an unusually large fraction of the nitrate pool [*Casciotti et al.*, 2008] (Figure 2a).

4. Conclusions

[19] The nitrate N and O isotope signals of denitrification can both be transported out of the region of denitrification by ocean circulation. However, only the N isotope signal of denitrification can also be transported by organic matter. This difference between the N and O isotopes of nitrate appears to be realized in the nitrate isotopes in the mid-depth water column at Station ALOHA, where the upward nitrate $\delta^{15}N$ increase from the abyss toward the [O_2] minimum begins deeper than does the $\delta^{18}O$ increase. These data suggest that roughly a third of N isotope elevation at 1–2 km depth relative to abyssal nitrate derives from the dissemination of the denitrification signal through nitrate assimilation in the surface, the production of sinking organic matter, and its regeneration back to nitrate at depth.

[20] As ocean general circulation models are applied to study suboxic zones and their communication with the global ocean, it appears that the N and O isotopes of nitrate will provide a useful test of realism that is more stringent and mechanistically specific than the simulation of nutrient concentrations alone. Specifically, the deviation of the nitrate N and O isotopes from denitrification-only behavior puts a constraint on the rate of exchange of nitrate from the

denitrification zones with the rest of the Pacific interior, relative to the rate of internal N cycling (nitrate assimilation in the surface ocean and the regeneration of sinking N in the interior). Similar constraints arise from larger scale (e.g., interbasin) gradients and mean ocean values of nitrate $\delta^{15}N$ and $\delta^{18}O$ [*Brandes and Devol*, 2002; *Deutsch et al.*, 2004; Sigman et al., submitted manuscript, 2008].

[21] As with the isotope signal of denitrification from the eastern North Pacific suboxic zone, the coupled N and O isotope signal of partial nitrate assimilation in the subpolar surface, once subducted into the thermocline, should also be altered by the low latitude nitrate assimilation/nitrification cycle, also lowering the $\delta^{18}O$ of nitrate relative to its $\delta^{15}N$ in the low latitude water column (i.e. raising its $\Delta(15,18)$). The unknown importance of this process is a source of uncertainty in our interpretation of the ALOHA data. However, with more work, it too can yield constraints on the interaction between ocean circulation and biogeochemistry.

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C. Deutsch, Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA 90095-1565, USA.

P. J. DiFiore, M. P. Hain, and D. M. Sigman, Department of Geosciences, Princeton University, Princeton, NJ 08544, USA. (sigman@princeton.edu)

D. M. Karl, Department of Oceanography, University of Hawai'i, Honolulu, HI 96822, USA.

Auxiliary Material Text #1

Fraction of nitrate δ^{15}N elevation due to regeneration of sinking N vs. circulation: The mid-depth nitrate at ALOHA (e.g., in the 1200 m sample, with a δ^{15}N of 6.2‰ and a δ^{18}O of 2.5‰) can be treated as a mixture of three end-members: (1) abyssal nitrate, with a δ^{15}N of 5.0‰ and a δ^{18}O of 1.8‰ (Δ(15,18)$\equiv$ 0‰), (2) nitrate from the suboxic ENP, with a δ^{15}N of 11.4‰ and a δ^{18}O of 9.2‰ (Δ(15,18) = -1.1‰) [*Sigman et al.*, 2005], delivered through the interior circulation, and (3) nitrate from the regeneration/nitrification of sinking N that was produced from nitrate upwelled from the suboxic zones. The nitrate from nitrification is taken to have a δ^{18}O of 1.15‰, our preliminary estimate for the δ^{18}O of newly nitrified nitrate [*Sigman et al.*, in review]. Two values are considered for its δ^{15}N: (1) 11.4‰, identical to the nitrate in the suboxic ENP [*Sigman et al.*, 2005] (representing an input of nitrate with Δ(15,18) = 7.1‰), and (2) 8.3‰, which is the N-weighted mean of 75% suboxic zone nitrate with a δ^{15}N of 11.4‰ and 25% N from N_2 fixation with a δ^{15}N of -1‰, the latter being added to remove a ~25% deficit of nitrate relative to phosphate in ENP suboxic waters [*Sigman et al.*, 2005] (representing an input of nitrate with Δ(15,18) = 4.0‰). The system of equations is as follows:

$$\delta^{15}N = \frac{\delta^{15}N_{abyssal} * N_{abyssal} + \delta^{15}N_{suboxic} * N_{suboxic} + \delta^{15}N_{sinking} * N_{sinking}}{N_{abyssal} + N_{suboxic} + N_{sinking}}$$

$$\delta^{18}O = \frac{\delta^{18}O_{abyssal} * N_{abyssal} + \delta^{18}O_{suboxic} * N_{suboxic} + \delta^{18}O_{sinking} * N_{sinking}}{N_{abyssal} + N_{suboxic} + N_{sinking}}$$

$$1 = N_{abyssal} + N_{suboxic} + N_{sinking}$$

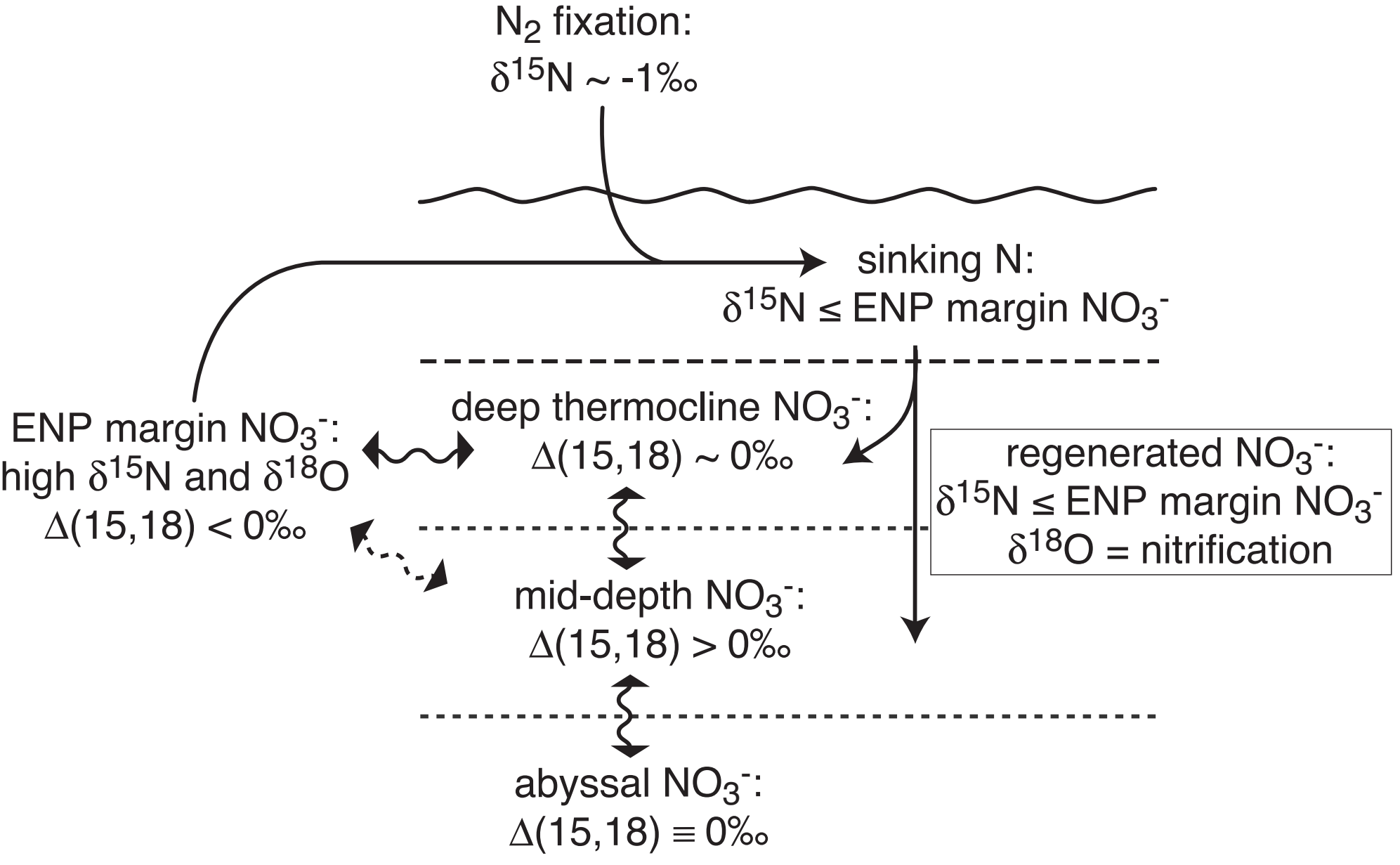
This system is fully determined. The end-member solution for these two cases yields: (1, without N_2 fixation) 82.0% from abyssal nitrate, 9.9% from circulation, and 8.1% from regeneration, and (2, with N_2 fixation) 74.9% from abyssal nitrate, 10.4% from circulation, and 14.7% from regeneration.

Auxiliary Material Table 1. Model standard case output

		conditions		concentrations			isotopes				fluxes			
Box level	Name	temp. (°C)	sal. (ppt)	NO_3^- (µmol/kg)	PO_4^{3-} (µmol/kg)	O_2 (µmol/kg)	NO_3^- $\delta^{15}N$ (‰ vs. air)	NO_3^- $\delta^{18}O$ (‰ vs. nitrif.)	H_2O $\delta^{18}O$ (‰ vs. SMOW)	O_2 $\delta^{18}O$ (‰ vs. SMOW)	export (Tg N/yr)	N_2 fixation (Tg N/yr)	w.c. denit. (Tg N/yr)	sed. denit. (Tg N/yr)
Surface	Atlantic	18.5	36.0	0.016	0.001	232.0	32.03	30.54	0.70	24.20	90.7	43.3	0.0	28.1
	Indian	18.5	35.0	0.016	0.001	233.6	34.95	33.40	0.17	24.20	72.7	22.9	0.0	12.2
	S. Pacific	18.5	35.0	0.016	0.001	233.6	38.50	36.72	0.17	24.20	79.7	28.2	0.0	13.8
	N. Pacific	18.5	34.5	0.016	0.001	234.4	33.82	31.72	-0.10	24.20	99.4	41.6	0.0	15.5
	Boreal (N. Atlantic)	4.0	35.0	7.3	0.55	320.7	4.19	2.27	0.17	24.20	1.0	0.0	0.0	0.0
	Open Antarctic	0.0	33.8	20.5	1.62	365.4	4.68	3.17	-0.47	24.20	83.5	0.0	0.0	0.0
	Subantarctic	5.0	34.0	14.1	1.22	314.2	6.31	4.80	-0.37	24.20	62.5	0.0	0.0	0.0
	Polar Antarctic	0.0	33.5	26.6	2.00	366.3	3.54	2.03	-0.63	24.20	22.5	0.0	0.0	0.0
Intermediate	Atlantic	8.3	34.5	23.8	1.78	168.2	4.08	2.13	-0.08	31.53	0.0	0.0	0.6	3.2
	Indian	7.5	34.3	29.7	2.18	136.2	3.61	1.67	-0.23	34.73	0.0	0.0	1.3	1.6
	S. Pacific	8.2	34.3	28.8	2.20	122.6	4.66	2.34	-0.22	34.11	0.0	0.0	2.2	1.9
	N. Pacific	10.0	34.3	32.3	2.74	22.1	7.56	4.44	-0.20	47.12	0.0	0.0	32.4	1.8
Deep	Boreal (N. Atlantic)	5.6	34.8	13.3	1.00	265.5	4.09	2.17	0.08	25.90	0.0	0.0	0.0	0.0
	Atlantic	5.5	34.7	19.5	1.45	227.7	3.56	1.80	-0.02	28.17	0.0	0.0	0.0	2.5
	Southern	4.0	34.2	29.1	2.16	203.8	3.10	1.60	-0.26	30.16	0.0	0.0	0.0	0.0
	Indian	4.6	34.2	31.6	2.36	164.7	3.05	1.44	-0.26	33.40	0.0	0.0	0.1	6.4
	S. Pacific	5.6	34.2	32.5	2.50	129.2	3.90	1.90	-0.25	34.85	0.0	0.0	0.3	11.1
	N. Pacific	6.3	34.3	33.6	2.61	101.7	4.47	2.21	-0.24	37.01	0.0	0.0	0.0	1.2

Auxiliary Material Text #2

Caption for Auxiliary Material Figure 1: Interpretation of the variations in $\Delta(15,18)$ below 350m at Station ALOHA. $\Delta(15,18)$ is a measure of the ratio of the enrichment in ^{15}N and ^{18}O of nitrate relative to abyssal nitrate (here, $\Delta(15,18) = (\delta^{15}N - \delta^{18}O) - (\delta^{15}N - \delta^{18}O)_{abyssal}$; derived from the complete expression in the text). In the suboxic zone of the eastern North Pacific (ENP) margin, where nitrate $\delta^{15}N$ and $\delta^{18}O$ are elevated by denitrification, $\Delta(15,18)<0$ ($\sim$-2‰; [*Casciotti and McIlvin*, 2007; *Sigman, et al.*, 2005]). N cycling – upwelling of ^{15}N- and ^{18}O-enriched nitrate across the North Pacific, incorporation into sinking N, and regeneration at depth – redistributes the ^{15}N-enriched nitrate through the water column, reaching below the thermocline. However, the regenerated nitrate has lost any denitrification-derived ^{18}O enrichment, increasing the $\Delta(15,18)$ in the waters where the regeneration occurs. N_2 fixation in the surface layer will tend to lower the $\delta^{15}N$ of the sinking N, weakening the decoupling between N and O isotopes of nitrate associated with the assimilation/sinking/regeneration cycle, but the qualitative decoupling persists. In deep thermocline waters (e.g. at 350-500m), this increase in $\Delta(15,18)$ is more strongly offset by exchange with the low-$\Delta(15,18)$ ENP margin. Like denitrification in the suboxic zones, partial nitrate assimilation in subpolar surface waters followed by subduction of the remaining nitrate into intermediate and mode waters would also introduce high-$\delta^{15}N$ and $\delta^{18}O$ nitrate into the low latitude thermocline. As with the denitrification isotope signal, the processing of this high-$\delta^{15}N$ and -$\delta^{18}O$ nitrate in the low latitudes by nitrate assimilaton, N export, and regeneration would then lower its $\delta^{18}O$ relative to its $\delta^{15}N$, raising mid-depth $\Delta(15,18)$ (see main text). The unknown importance of this process is a caveat in our quantitative interpretation of the data. This diagram does not show the relevant features and processes associated with shallow (<350m) subsurface at ALOHA. in particular, the low-$\delta^{15}N$, low-$\Delta(15,18)$ nitrate in the shallow thermocline, which presumably originates from local N_2 fixation [*Casciotti* et al., 2008], is not shown. Moreover, local N cycling (e.g., upward supply of nitrate to the euphotic zone coupled to downward flux of organic N) is not shown.


N_2 fixation:
$\delta^{15}N \sim -1‰$
sinking N:
$\delta^{15}N \leq$ ENP margin NO_3^-
ENP margin NO_3^-:
high $\delta^{15}N$ and $\delta^{18}O$
$\Delta(15,18) < 0‰$
deep thermocline NO_3^-:
$\Delta(15,18) \sim 0‰$
regenerated NO_3^-:
$\delta^{15}N \leq$ ENP margin NO_3^-
$\delta^{18}O$ = nitrification
mid-depth NO_3^-:
$\Delta(15,18) > 0‰$
abyssal NO_3^-:
$\Delta(15,18) \equiv 0‰$