



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. Karl⁴

Received 25 August 2008; revised 1 February 2009; accepted 16 February 2009; published 25 April 2009.

[1] Culture studies of denitrifying bacteria predict that denitrification will generate equivalent gradients in the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of deep ocean nitrate. A depth profile of nitrate isotopes from the Hawaii Ocean Time-series Station ALOHA shows less of an increase in $\delta^{18}\text{O}$ than in $\delta^{15}\text{N}$ 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- $\delta^{15}\text{N}$ signal of pelagic denitrification into waters well below and beyond the suboxic zone, whereas the nitrate $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate are elevated by pelagic denitrification, $\delta^{18}\text{O}$ is more elevated above background deep water than is $\delta^{15}\text{N}$ [Sigman *et al.*, 2005], while culture studies suggest that denitrification alone causes nearly equivalent increases in $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ [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 $\delta^{15}\text{N}$ of nitrate relative to its $\delta^{18}\text{O}$ – which we interpret with the help of a global ocean box model. As high- $\delta^{15}\text{N}$ nitrate from the ENP denitrification zone is converted to organic N and back to nitrate, the high- $\delta^{15}\text{N}$ 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- $\delta^{18}\text{O}$ 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: $\text{N}^* = [\text{NO}_3^-] - 16 * [\text{PO}_4^{3-}] + 2.9$ (in $\mu\text{mol kg}^{-1}$) [Deutsch *et al.*, 2001].

[4] The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate were measured using the denitrifier method [Casciotti *et al.*, 2002; Sigman *et al.*, 2001] ($\delta^{15}\text{N}_{\text{sample}} = ((^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference}} - 1) * 1000\text{‰}$; $\delta^{18}\text{O}_{\text{sample}} = ((^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{reference}} - 1) * 1000\text{‰}$). Measurements are referenced to air N_2 and VSMOW using the nitrate reference material IAEA-N3, with a $\delta^{15}\text{N}$ of 4.7‰ vs. air and a $\delta^{18}\text{O}$ of 25.6‰ vs. VSMOW [Böhlke *et al.*, 2003]. The nitrate $\delta^{18}\text{O}$ 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 $\pm 0.15\text{‰}$ for $\delta^{15}\text{N}$ and $\pm 0.35\text{‰}$ for $\delta^{18}\text{O}$.

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

¹Department of Geosciences, Princeton University, Princeton, New Jersey, USA.

²Institut für Geowissenschaften, Universität Potsdam, Potsdam, Germany.

³Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, California, USA.

⁴Department of Oceanography, University of Hawai'i, Honolulu, Hawaii, USA.

from Middelburg *et al.* [1996]. The model steady state output is tabulated in Table S1¹.

[7] Oceanic N₂ fixation is assumed to produce PN with a δ¹⁵N 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, ¹⁵ε, of a nitrate-consuming process is defined here as (k¹⁴/k¹⁵ − 1)*1000‰, where k¹⁴ and k¹⁵ are the rate coefficients of the consumption reactions for the ¹⁴N- and ¹⁵N-bearing forms of nitrate, respectively. Organic matter regeneration/nitrification is assumed to yield nitrate with the δ¹⁵N 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 δ¹⁸O 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 ¹⁵ε:¹⁸ε ratio of 1 for both nitrate assimilation and denitrification (¹⁸ε ≡ (k¹⁶/k¹⁸ − 1)*1000‰) [Granger *et al.*, 2004, 2008].

2.2. Isotope Terms

[9] Below, we refer to the derived parameter Δ(15,18), which quantifies deviations in the nitrate δ¹⁵N-to-δ¹⁸O relationship from that expected from a specific removal process [Sigman *et al.*, 2005]:

$$\Delta(15,18) \equiv (\delta^{15}\text{N} - \delta^{15}\text{N}_b) - ({}^{15}\epsilon : {}^{18}\epsilon) * (\delta^{18}\text{O} - \delta^{18}\text{O}_b) \quad (1)$$

where δ¹⁵N_b and δ¹⁸O_b represent the isotopic composition of the background nitrate supply to the system, and δ¹⁵N and δ¹⁸O are the measured isotopic composition of nitrate in a given sample. The ¹⁵ε:¹⁸ε is the N-to-O isotope effect ratio of the consuming process, taken to be 1. In this study, we define δ¹⁵N_b and δ¹⁸O_b as the mean values for our ALOHA samples below 3500 m, rounded to the nearest 0.1‰: δ¹⁵N_b = 5.0‰ vs. air, and δ¹⁸O_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 Δ(15,18) indicates a higher nitrate δ¹⁵N than expected from (1) the sample's nitrate δ¹⁸O, (2) the δ¹⁵N and δ¹⁸O of the nitrate supplied to the system, and (3) the ¹⁵ε:¹⁸ε of the consuming process.

3. Results

[10] Above the abyssal waters at ALOHA, there is an upward increase in both nitrate δ¹⁵N and δ¹⁸O into the depths corresponding to the isopycnals of the [O₂] 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 differ-

ence between δ¹⁵N and δ¹⁸O in terms of the amplitude of increase. In the 750–2000 m depth interval, nitrate δ¹⁵N is ~0.4‰ more elevated than is δ¹⁸O 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 δ¹⁸O of nitrate versus its δ¹⁵N: as one shoals gradually from 3600 m, the δ¹⁸O and δ¹⁵N increase in a ratio of ~0.7 (Figure 2). Upon reaching the denitrification-driven δ¹⁵N and δ¹⁸O maxima at 350–500 m, this trend is broken, with the δ¹⁸O and δ¹⁵N at these depths being equally elevated above abyssal nitrate (Figure 2a; see dashed reference line with slope of 1).

[11] Given only N₂ fixation (with nitrification to nitrate) and denitrification operating in the ocean N cycle, one would expect equivalent increases in nitrate δ¹⁸O and δ¹⁵N from regions of N₂ 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 δ¹⁸O-to-δ¹⁵N variation ratio (Δδ¹⁸O:Δδ¹⁵N) 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 δ¹⁸O and δ¹⁵N increase in a ratio of 0.72. Moreover, the deviation of Δδ¹⁸O:Δδ¹⁵N from 1 observed in the ALOHA data and the model is complemented by a similar measured deviation in the Δδ¹⁸O:Δδ¹⁵N of inter-basin gradients (Sigman *et al.*, submitted manuscript, 2008).

[12] The deviation in Δδ¹⁸O:Δδ¹⁵N 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 ¹⁵N and ¹⁸O. This nitrate is mixed or upwells into the North Pacific surface, where it is converted into high-δ¹⁵N PN, which sinks back into the interior, to be regenerated as high-δ¹⁵N 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 δ¹⁸O of nitrification, such that this cycled nitrate has lost the ¹⁸O 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 Δδ¹⁸O-to-Δδ¹⁵N decoupling is greatest there.

[13] This box model dynamic applies to the Station ALOHA data. The denitrification occurring in the eastern Pacific produces high-δ¹⁵N nitrate, and the entrainment of this nitrate leads to ¹⁵N enrichment of the sinking flux in the region [Altabet *et al.*, 1999], the regeneration of which spreads the nitrate δ¹⁵N 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 δ¹⁵N elevation by denitrification can be spread throughout the ocean by the assimilation of ¹⁵N-enriched nitrate at the surface, sinking, and remineralization in the interior, the δ¹⁸O elevation cannot, leading to a less regionally distributed denitrification-driven signal in nitrate δ¹⁸O than in δ¹⁵N. This can explain the mid-depth (750–1500 m) interval with Δ(15,18) > 0 (Figure 1c). Using a three end-member mixing model, we estimate that 45% (i.e.

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

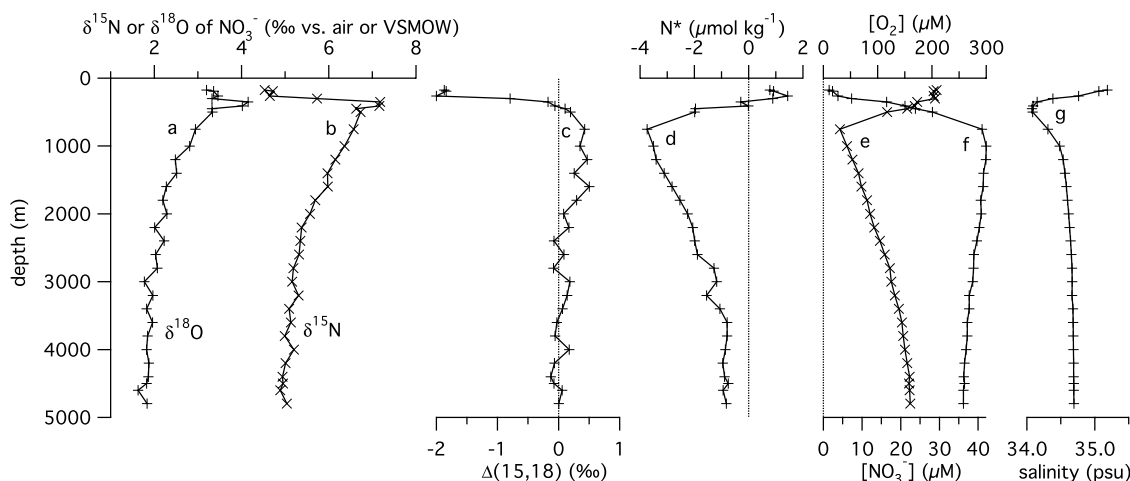


Figure 1. For a depth profile of samples collected as Hawaii Ocean Time-series Station ALOHA during HOT-120 in November 2000, (a) nitrate $\delta^{18}\text{O}$, (b) nitrate $\delta^{15}\text{N}$, (c) $\Delta(15,18)$, (d) N^* , (e) $[\text{O}_2]$, (f) $[\text{NO}_3^-]$, and (g) salinity.

half) of the $\delta^{15}\text{N}$ elevation at 1200 m (relative to abyssal nitrate with a $\delta^{15}\text{N}$ of 5.0‰) is due to the remineralization of organic matter derived from high- $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ by denitrification, then its $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$ 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 $\delta^{15}\text{N}$ of N export would be lower than that of the nitrate supply, which

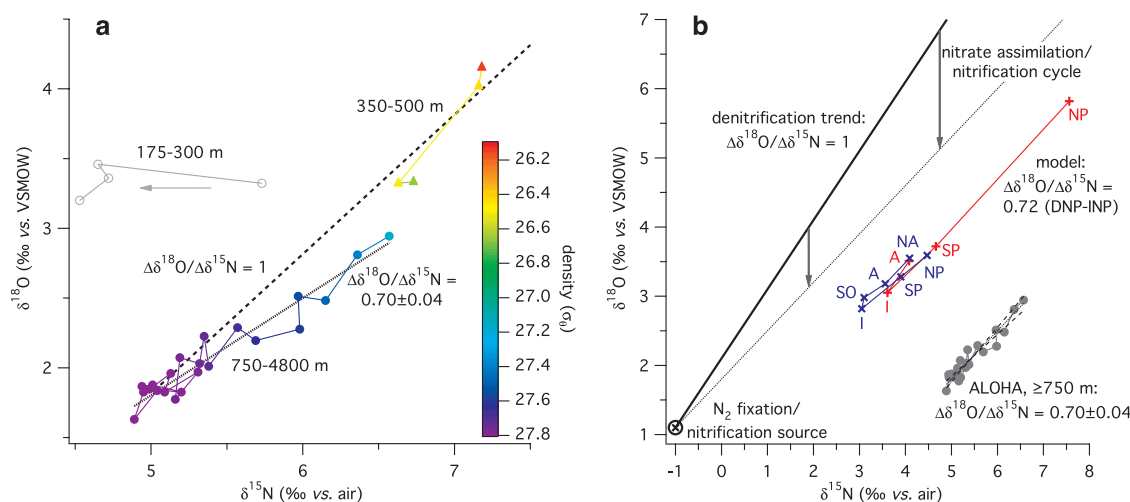


Figure 2. (a) Nitrate $\delta^{18}\text{O}$ versus nitrate $\delta^{15}\text{N}$ for the Station ALOHA data and (b) comparison of the deep data (750–4800 m) to output from the box model. In Figure 2a, samples at ≥ 350 m depth are color coded according to density; above this, a gray arrow indicates shoaling. Nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ increase upward from the base of the profile due to denitrification at mid-depths in the eastern Pacific. The upward increase in nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ from 4800 to 750 m has a $\Delta\delta^{18}\text{O}:\Delta\delta^{15}\text{N}$ 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 $\Delta\delta^{18}\text{O}:\Delta\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate deriving from N_2 fixation, and the black line shows the expected correlation between nitrate $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ 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 over-represent 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, $\Delta(15,18)$ 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 $\Delta(15,18)$) [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 $\Delta(15,18)$ in the ENP margin waters should work to raise the $\delta^{18}O$ of nitrate relative to its $\delta^{15}N$ (lower the $\Delta(15,18)$) at ALOHA, compensating for the high $\Delta(15,18)$ 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 $\Delta(15,18)$ 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ [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 $\delta^{18}\text{O}$ of nitrate relative to its $\delta^{15}\text{N}$ 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.

[22] **Acknowledgments.** We thank G. Cane and R. Ho for isotope analyses and two anonymous reviewers of the manuscript. This work was supported by the US NSF through grants OCE-0447570 (D. M. S.), OCE-0550771 (C.D.), OCE-0326616 (D. M. K.), and EF-04245599 (D. M. K.), by the Gordon and Betty Moore Foundation (D. M. K.), and by the Deutsche Forschungsgemeinschaft (M. P. H., through G. H. Haug).

References

- Altabet, M. A., et al. (1999), The nitrogen isotope biogeochemistry of sinking particles from the margin of the eastern North Pacific, *Deep Sea Res., Part I*, 46, 655–679.
- Böhlke, J. K., et al. (2003), Oxygen isotopes in nitrate: New reference materials for ^{18}O : ^{17}O : ^{16}O measurements and observations on nitrate-water equilibration, *Rapid Commun. Mass Spectrom.*, 17, 1835–1846.
- Brandes, J. A., and A. H. Devol (1997), Isotopic fractionation of oxygen and nitrogen in coastal marine sediments, *Geochim Cosmochim Acta*, 61, 1793–1801.
- Brandes, J. A., and A. H. Devol (2002), A global marine fixed nitrogen isotopic budget: Implications for Holocene nitrogen cycling, *Global Biogeochem. Cycles*, 16(4), 1120, doi:10.1029/2001GB001856.
- Brandes, J. A., et al. (1998), Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles, *Limnol. Oceanogr.*, 43, 1680–1689.
- Casciotti, K. L., et al. (2002), Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, *Anal. Chem.*, 74, 4905–4912.
- Casciotti, K. L., et al. (2008), Constraints on nitrogen cycling at the subtropical North Pacific Station ALOHA from isotopic measurements of nitrate and particulate nitrogen, *Deep Sea Res., Part II*, 55, 1661–1672.
- Deutsch, C., N. Gruber, R. M. Key, J. L. Sarmiento, and A. Ganachaud (2001), Denitrification and N_2 fixation in the Pacific Ocean, *Global Biogeochem. Cycles*, 15, 483–506.
- Deutsch, C., D. M. Sigman, R. C. Thunell, A. N. Meckler, and G. H. Haug (2004), Isotopic constraints on glacial/interglacial changes in the oceanic nitrogen budget, *Global Biogeochem. Cycles*, 18, GB4012, doi:10.1029/2003GB002189.
- Granger, J., et al. (2004), Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton, *Limnol. Oceanogr.*, 49, 1763–1773.
- Granger, J., et al. (2008), Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria, *Limnol. Oceanogr.*, 53, 2533–2545.
- Karl, D., et al. (2002), Dinitrogen fixation in the world's oceans, *Biogeochemistry*, 57/58, 47–98.
- Keir, R. S. (1988), On the late Pleistocene ocean geochemistry and circulation, *Paleoceanography*, 3, 413–445.
- Knapp, A. N., D. M. Sigman, and F. Lipschultz (2005), N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-Series Study site, *Global Biogeochem. Cycles*, 19, GB1018, doi:10.1029/2004GB002320.
- Lehmann, M. F., et al. (2004), Coupling the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of nitrate as a constraint on benthic nitrogen cycling, *Mar. Chem.*, 88, 1–20.
- Lehmann, M. F., et al. (2007), The distribution of nitrate $^{15}\text{N}/^{14}\text{N}$ in marine sediments and the impact of benthic nitrogen loss on the isotopic composition of oceanic nitrate, *Geochim Cosmochim Acta*, 71, 5384–5404.
- Liu, K. K., et al. (1996), The nitrogen isotopic composition of nitrate in the Kuroshio Water northeast of Taiwan: Evidence for nitrogen fixation as a source of isotopically light nitrate, *Mar. Chem.*, 54, 273–292.
- Middelburg, J. J., K. Soetaert, P. M. J. Herman, and C. H. R. Heip (1996), Denitrification in marine sediments: A model study, *Global Biogeochem. Cycles*, 10, 661–673.
- Montoya, J. P., et al. (2002), Nitrogen fixation and nitrogen isotope abundances in zooplankton of the oligotrophic North Atlantic, *Limnol. Oceanogr.*, 47, 1617–1628.
- Schmitz, W. J. (1995), On the interbasin-scale thermohaline circulation, *Rev. Geophys.*, 33, 151–173.
- Sigman, D. M., M. A. Altabet, D. C. McCorkle, R. Francois, and G. Fischer (1999), The $\delta^{15}\text{N}$ of nitrate in the Southern Ocean: Consumption of nitrate in surface waters, *Global Biogeochem. Cycles*, 13, 1149–1166.
- Sigman, D. M., et al. (2001), A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, *Anal. Chem.*, 73, 4145–4153.
- Sigman, D. M., J. Granger, P. J. DiFiore, M. M. Lehmann, R. Ho, G. Cane, and A. van Geen (2005), Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin, *Global Biogeochem. Cycles*, 19, GB4022, doi:10.1029/2005GB002458.

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.