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# Constraints on oceanic N balance/ imbalance from sedimentary $^{15}\text{N}$ records

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## Abstract

According to current best estimates, the modern ocean's N cycle is in severe deficit. N isotope budgeting provides an independent geochemical constraint in this regard as well as the only means for past reconstruction. Overall, it is the relative proportion of N<sub>2</sub> fixation consumed by water column denitrification that sets average oceanic  $\delta^{15}\text{N}$  under steady-state conditions. Several factors (conversion of organic N to N<sub>2</sub>, Rayleigh closed and open system effects) likely reduce the effective fractionation factor ( $\epsilon$ ) for water column denitrification to about half the inherent microbial value for  $\epsilon_{\text{den}}$ . If so, the average oceanic  $\delta^{15}\text{N}$  of  $\sim 5\text{‰}$  is consistent with a canonical contribution from water column denitrification of 50% of the source flux from N<sub>2</sub> fixation. If an imbalance in oceanic N sources and sinks changes this proportion then a transient in average oceanic  $\delta^{15}\text{N}$  would occur. Using a simple model, changing water column denitrification  $\pm 30\%$  or N<sub>2</sub> fixation by  $\pm 15\%$  produces detectable ( $> 1\text{‰}$ ) changes in average oceanic  $\delta^{15}\text{N}$  over one residence time period or more with corresponding changes in oceanic N inventory. Changing sedimentary denitrification produces no change in  $\delta^{15}\text{N}$  but does change N inventory.

Sediment  $\delta^{15}\text{N}$  records from sites thought to be sensitive to oceanic average  $\delta^{15}\text{N}$  all show no detectable change over the last 3 kyr or so implying a balanced marine N budget over the latest Holocene. A mismatch in time scales is the most likely meaningful interpretation of the apparent conflict with modern flux estimates. Decadal to centennial scale oscillations between net N deficit and net surplus may occur but on the N residence timescale of several thousand years, net balance is achieved in sum. However, sediment  $\delta^{15}\text{N}$  records from the literature covering the period since the last glacial maximum show excursions of up to several ‰ that are consistent with sustained N deficit during the deglaciation followed by readjustment and establishment of balance in the early Holocene. Since imbalance was sustained for one N residence time period or longer, excursions in ocean N inventory of 10 to 30% likely occurred. The climatic and oceanographic changes that occurred over this period evidently overcame, for a

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time, the capacity of ocean biogeochemistry to maintain N balance.

## 1 Introduction

At present, there is considerable uncertainty regarding the state of the oceanic combined N budget. This is particularly so with respect to quantification of fluxes and whether sources are in rough balance with sinks (Codispoti et al., 2001). With the possible exception of anammox (Kuypers et al., 2003), the microbial transformation pathways responsible for these fluxes, by contrast, have been well known for almost a century. Oceanic N<sub>2</sub> fixation is now widely acknowledged as the dominant source with significant but more minor contributions from riverine and atmospheric inputs (Capone et al., 1997; Gruber and Sarmiento, 1997; Karl et al., 2002). Denitrification in suboxic regions of the water column as well as in continental margin sediments is the predominant sink with very minor contributions from sediment burial (Christensen et al., 1987). The magnitude of total sources or total sinks are on the order of 200 to 400 Tg/yr. Given that current combined N inventory is  $6 \times 10^5$  Tg (>95% in the form of NO<sub>3</sub><sup>-</sup>), the residence time (inventory/flux) for combined N in the ocean is less than 3 kyr. In comparison, oceanic P residence time is about 5 to 10-fold longer (Ruttenberg and Berner, 1993; Benitez-Nelson, 2000).

Inference of a quasi-balanced biogeochemical system between N sources and sinks was first made by Brandt (1902). While it is a common geochemical approach to assume balanced budgets to facilitate flux calculations (e.g. Gruber and Sarmiento, 1997), the oceanic N cycle is distinguished from other marine geochemical cycles by its short residence time and that sources and sinks are largely biological processes occurring in the ocean proper. It has been argued, though, that the latter implies close coupling between N<sub>2</sub> fixation and denitrification to maintain the oceanic NO<sub>3</sub><sup>-</sup> inventory at the Redfield ratio to PO<sub>4</sub><sup>-3</sup> (Redfield, 1934). Codispoti et al. (2001), however, did not assume balance and concluded that the present-day oceanic N budget is in severe deficit. They estimated total denitrification to be ~450 Tg N/yr. Their increase in es-

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5 estimated water column denitrification is based on limited data showing the yield of  $N_2$  relative to observed negative  $NO_3^-$  anomaly to be up to 4-fold higher than calculated from canonical stoichiometry. Sediment denitrification was estimated to be higher than previously thought based on extension of the water column results and recent discovery of anammox and other pathways involving Mn (Anschutz et al., 2000).

10 Implications of these findings include whether the modern oceanic N inventory is stable or changing in response to anthropogenic and/or climate forcing. If sustained over a significant fraction of oceanic N residence time, a significant drop in inventory would take place that would likely impact marine ecosystems and coupled biogeochemical cycles. A sustained deficit in N budget further suggests looser coupling of the marine N cycle to P cycling than conceived of by Redfield (1934) and many marine geochemists since.  $N_2$  fixation and denitrification may thus have sufficiently weak feedbacks between them to permit significant oscillation in oceanic N inventory and N:P ratio.

15 Alternative explanations for Codispoti et al.'s (2001) findings that may allow for marine N budget balance include larger than identified uncertainty in flux estimates. The last 4 decades of oceanic N budget literature shows sources and sinks have been consistently underestimated. Even with recent recognition of the importance of  $N_2$  fixation, its accepted magnitude may still be too low due to previously unidentified or under appreciated sources (e.g. Zehr et al., 2001). Alternatively, observations made over the last few decades may have aliased natural decadal to centennial-scale variability in the magnitude of N sources and/or sinks. If so, the current "deficit phase" will be followed by a "surplus phase" such that over a residence time of the N cycle balance is achieved. The Redfield perspective of strong feedback maintaining the 16:1 N:P ratio would pertain. A decadal to centennial scale response time would be consistent with the time-scale of intermediate ocean circulation that would communicate the biogeochemical signals of  $NO_3^-$  concentration and N:P ratio between  $N_2$  fixation and denitrification zones.

25 Sedimentary N isotope composition ( $\delta^{15}N$ ) has been used as to reconstruct the history of marine N cycle processes on time scales from 100's to millions of years. It is

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likely the only means to address the question of N cycle balance both over its most recent residence time period as well as more distant past. The more successful applications have been reconstructions of past variation in regional processes such as water column denitrification (Ganeshram et al., 1995; Pride et al., 1999; Ganeshram et al., 2000; Altabet et al., 2002; Thunell and Kepple, 2004) and near-surface NO<sub>3</sub><sup>-</sup> drawdown (Francois et al., 1997; Sigman et al., 1999). Attempts have been made to reconstruct the average  $\delta^{15}\text{N}$  of marine N and a number of theoretical studies point to this parameter as reflecting the balance between the largest N flux terms (Brandes and Devol, 2002). Due to good organic matter preservation and a location remote from high-nutrient, low chlorophyll (HNLC) and denitrification regions, sediment records for  $\delta^{15}\text{N}$  from the South China Sea have been cited as evidence for little change in ocean average  $\delta^{15}\text{N}$  over the last glacial cycle (Kienast, 2000). This has led to the conclusion that either N<sub>2</sub> fixation changes compensated for any change in denitrification and/or there was no change in the proportioning of denitrification between the sediment and the water column (Brandes and Devol, 2002). However, subsequent work in this area has shown that significant deglacial variations in  $\delta^{15}\text{N}$  occurred in a nearby site (Higginson et al., 2003).

The next section presents an overview of these theoretical considerations to evaluate the magnitude of  $\delta^{15}\text{N}$  variations expected in response to significant N imbalance. Following sections present methodological information and data for marine  $\delta^{15}\text{N}$  variation over the last 5 kyr (latest Holocene) as well as the last deglaciation 20 to 10 kyr ago. Finally, these  $\delta^{15}\text{N}$  records are interpreted as reflecting recent balance in the marine N budget but imbalance across the last glacial to interglacial transition.

## 2 Controls on average oceanic $\delta^{15}\text{N}$

In parallel with an oceanic N budget, there must also be a  $^{15}\text{N}$  budget that controls the average  $\delta^{15}\text{N}$  of the ocean. Several recent papers have modeled oceanic  $\delta^{15}\text{N}$  including a rather sophisticated time-varying box model with reasonable ocean circula-

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tion and feedbacks between denitrification and N<sub>2</sub> fixation (Deutsch et al., 2004). Here we take a simplified (single box) approach considering N<sub>2</sub> fixation as the sole source and denitrification (water column and sediment) as the sole sink to illustrate the rough magnitude and time scale of δ<sup>15</sup>N changes in response to oceanic N cycle imbalance (Fig. 1). This exercise is useful only because removal processes alter (e.g. fractionate) N isotopic ratio, otherwise average oceanic δ<sup>15</sup>N would simply reflect the weighted average of sources regardless of the magnitude of oceanic N fluxes or their balance. The magnitude of isotopic fractionation for a process is given by the fractionation factor (ε), though as seen below there can be a substantial difference between an ‘effective’ or observed ε and the fractionation factor inherent to the process.

N<sub>2</sub> fixation has been widely observed to produce little isotopic fractionation (Mina-gawa and Wada, 1986; Macko et al., 1987; Carpenter et al., 1997; Delwiche and Steyn, 1970) such that combined N produced by this process has a δ<sup>15</sup>N value close to that of atmospheric N<sub>2</sub> (by definition δ<sup>15</sup>N=0‰). In the marine environment, N<sub>2</sub> fixers such as *Trichodesmium* typically have δ<sup>15</sup>N values between 0 and -2‰. Hence the average δ<sup>15</sup>N of N sources should average near -1‰, unless the much smaller contributions from riverine and atmospheric inputs are very enriched or depleted in <sup>15</sup>N. In reality, average oceanic δ<sup>15</sup>N is near 5‰ as measured in deep ocean NO<sub>3</sub><sup>-</sup> (Sigman et al., 1997), the result of isotopic fractionation during denitrification which preferentially removes <sup>14</sup>N by producing N<sub>2</sub> gas with low δ<sup>15</sup>N. The combined N remaining is thus <sup>15</sup>N enriched with an average δ<sup>15</sup>N higher than the N<sub>2</sub> fixation sources. Average oceanic δ<sup>15</sup>N (~average oceanic δ<sup>15</sup>NO<sub>3</sub><sup>-</sup>), though, is well below the one estimated from the known range in the ε<sub>den.</sub> inherent to the microbial process as estimated from bacterial cultures and/or from NO<sub>3</sub><sup>-</sup> removal: δ<sup>15</sup>NO<sub>3</sub><sup>-</sup> relationships; 20 to 30‰ (Wellman et al., 1968; Miyake and Wada, 1971; Cline and Kaplan, 1975; Brandes et al., 1998; Altabet et al., 1999; Voss et al., 2001) assuming the system is close to steady-state;

$$\text{Flux}_{\text{input}} \times \delta^{15}\text{N}_{\text{avg. input}} = \text{Flux}_{\text{denitrification}} \times \delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}} \quad (1)$$

at steady state  $\text{Flux}_{\text{input}} = \text{Flux}_{\text{denitrification}}$

$$\delta^{15}\text{N}_{\text{avg. input}} = \delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}} \quad (2)$$

$$\delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}} = \delta^{15}\text{N}_{\text{avg. ocean}} - \varepsilon_{\text{den.}} \quad (3)$$

$$\delta^{15}\text{N}_{\text{avg. input}} = \delta^{15}\text{N}_{\text{avg. ocean}} - \varepsilon_{\text{den.}} \text{ or } \delta^{15}\text{N}_{\text{avg. ocean}} = \delta^{15}\text{N}_{\text{avg. input}} + \varepsilon_{\text{den.}} \quad (4)$$

5 Average ocean  $\delta^{15}\text{N}$  should be much higher than observed; 20 to 30‰! However, Brandes and Devol (2002, hereafter B&D) have pointed out that lower than expected average  $\delta^{15}\text{N}$  can be accounted for by the nil effective  $\varepsilon_{\text{den.}}$  associated with sediment denitrification due to substrate transport limitation of overall rate. Average oceanic  $\delta^{15}\text{N}$  at steady state is thus largely dependent on the relative contributions of water  
10 column and sedimentary denitrification:

$$\delta^{15}\text{N}_{\text{avg. ocean}} = \delta^{15}\text{N}_{\text{avg. input}} + f_{\text{WC}} \times \varepsilon_{\text{WC den.}} + (1 - f_{\text{WC}}) \times \varepsilon_{\text{sed den.}} \quad (5)$$

where  $f_{\text{WC}}$  is the fraction of total denitrification occurring in water column suboxic zones and  $1 - f_{\text{WC}}$  the fraction in sediments. Considering  $\varepsilon_{\text{sed denitrification}}$  is close to 0:

$$\delta^{15}\text{N}_{\text{avg. ocean}} \sim \delta^{15}\text{N}_{\text{avg. input}} + f_{\text{WC}} \times \varepsilon_{\text{WC den.}} \quad (6)$$

15 It had previously been thought that water column and sedimentary denitrification each made roughly equal contributions to oceanic N loss. B&D conclude, though, that to achieve an average steady state  $\delta^{15}\text{N}$  of 5‰, sedimentary denitrification must dominate and account for about 80% of total oceanic denitrification.

The B&D model assumes that the appropriate value for  $\varepsilon_{\text{WC den.}}$  in Eq. (6) is the same  
20 as the value inherent to the microbial process such that  $\delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}}$  in the water column would be  $\sim -20$ ‰. However there are at least three factors which would in reality increase  $\delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}}$  above this value and alter the impact of water denitrification on the ocean's N isotope budget. The first takes into account the large

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fractional removal of  $\text{NO}_3^-$  within water column denitrification zones whose effect is given by the accumulated product Rayleigh equation:

$$\delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}} = \delta^{15}\text{NO}_{3(u=0)}^- + \varepsilon_{\text{den}} \times (1 - u)/u \times \ln(1 - u) \quad (7)$$

where  $u$  is the fraction of the original  $\text{NO}_3^-$  pool utilized.

$\text{NO}_3^-$  anomaly profiles from open ocean denitrification zones show that  $\text{NO}_3^-$  removal can reach 50%. Being more conservative and using a 40% removal, the  $\delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}}$  is increased by 5‰ to  $\sim -15$ ‰. Second, the nature of the physical flow through the suboxic zone also influences effective isotopic fractionation. At one extreme, water parcels can be imagined as being isolated from each other as they pass through (advect) through the denitrification zone and the closed system approach of Eq. (7) would be most accurate. Alternatively at the other extreme, mixing between parcels greatly exceeds advection and open system assumptions apply:

$$\delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}} = \delta^{15}\text{NO}_{3(u=0)}^- - \varepsilon_{\text{den}} \times (1 - u) \quad (8)$$

Applying the open system Eq. (8), would further increase  $\delta^{15}\text{N}_{\text{N}_2 \text{ lost via denitrification}}$  to about  $-10$ ‰. In models with circulation components, Rayleigh and open/closed system considerations would be implicit but sensitive to the accuracy of the physical model. For example, Deutsch et al.'s (2004) reference to dilution effects due to circulation through water column denitrification zones likely include these elements. They also pointed out that Rayleigh effects may change with denitrification intensity through increasing the relative removal of  $\text{NO}_3^-$ . The result would be an otherwise counterintuitive result in which more intense water column denitrification reduces effective  $\varepsilon_{\text{den}}$  and lower oceanic average  $\delta^{15}\text{N}$ . However, increasing water column denitrification is just as likely to expand the volume of the suboxic zone such that the greater integrated denitrification is occurring over a larger volume with similar fractional removal. Only a 10 to 15% increase in fractional removal is needed to produce the observed deglacial  $\delta^{15}\text{N}$  records from water column denitrification zones.

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Finally, canonical denitrification stoichiometry has 16% of the  $N_2$  produced as actually derived from organic matter since no  $NH_4^+$  is apparently released (Richards, 1965). In water column denitrification regions, organic N has a  $\delta^{15}N$  between 8 to 10‰ due to the elevated  $\delta^{15}N$  of upwelled  $NO_3^-$ .

$$\delta^{15}N_{N_2 \text{ lost via denitrification}} = 0.84 \times [\delta^{15}NO_{3(u=0)}^- - \varepsilon_{\text{den.}} \times (1 - u)] + 0.16 \times 9 \quad (9)$$

Organic N conversion to  $N_2$  thus further raises  $\delta^{15}N_{N_2 \text{ lost via denitrification}}$  in the water column to about  $-7\%$ , or  $-12\%$  relative to  $\delta^{15}N_{\text{avg}}$  which would be the effective value of  $\varepsilon_{\text{den.}}$  for use in Eq. (6). Applying all three conditions and using  $-12\%$  for  $\varepsilon_{\text{den.}}$  produces a steady state balance in which total oceanic denitrification is close to being equally apportioned between water column and sedimentary denitrification (Fig. 2). The lower overall magnitude of sedimentary denitrification called for also makes more likely that a near-steady state in the ocean N budget exists assuming greater certainty in estimates for water column denitrification. Overall, though, steady state oceanic  $\delta^{15}N$  is a function of the relative partitioning between water column and sediment denitrification or more generally the fraction of  $N_2$  fixation that is removed via water column denitrification. The greater that fraction, the higher oceanic  $\delta^{15}N$ .

The effects of non-steady or imbalanced N fluxes on ocean N inventory or  $\delta^{15}N$  would be manifest on the residence time scale. For example, a 20% deficit sustained over the last 3 kyr would roughly result in a 20% decrease in N inventory and average oceanic  $NO_3^-$  concentration. Average oceanic  $\delta^{15}N$  may respond similarly to unsteady conditions on this time scale. Altabet and Curry (Altabet and Curry, 1989) showed theoretically that during periods of increasing N inventory that  $\delta^{15}N$  decreases during the transition regardless of whether the cause is an increase in  $N_2$  fixation or a decrease in denitrification. The magnitude of different perturbations to oceanic N budget can be examined using a time-varying version of the simplified model presented above. Initial conditions are those of balance with 50% partitioning between water column and sedimentary denitrification. Effective  $\varepsilon_{\text{wc den.}}$  is set to 12‰ as discussed. Figures 3 to 5 show the effects of  $\pm 10$ , 20, and 30% changes either water column or sediment

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denitrification and  $\pm 5$ , 10, and 15% changes in  $\text{N}_2$  fixation. Not surprisingly, a reduction (increase) in  $\text{N}_2$  fixation produces decreases (increases) in N inventory of  $\pm 40\%$  and increases (decreases) in  $\delta^{15}\text{N}$  of  $\pm 1\text{‰}$  over a period of 1 to 3 N residence time periods (9 kyr; Fig. 3). This magnitude of  $\delta^{15}\text{N}$  change could be detectable in high quality records. Changes in water column denitrification produces inverse effects with  $\delta^{15}\text{N}$  changes of  $\pm 2\text{‰}$  which would be readily detectable in reliable records (Fig. 4). If the actual contribution from water column denitrification was lower at the initial steady state, then the subsequent changes in oceanic N inventory would be proportionally smaller. However, the changes in oceanic  $\delta^{15}\text{N}$  would be of the same magnitude since for smaller initial water column denitrification, effective  $\varepsilon_{\text{wc den.}}$  would need to be larger to obtain the same initial steady value for oceanic  $\delta^{15}\text{N}$ . Interestingly, a change in sediment denitrification alone produces no change in oceanic  $\delta^{15}\text{N}$  because of the relative lack of isotopic fractionation, despite the corresponding excursions in N inventory (Fig. 5). Thus it is not the fraction of total denitrification that takes place in the water column per se that controls oceanic  $\delta^{15}\text{N}$  but its fraction relative to total inputs.

This theoretical exercise demonstrates that detectable variations in average oceanic  $\delta^{15}\text{N}$  would be produced in response to moderate N cycle imbalance if caused by fluctuations in either  $\text{N}_2$  fixation or water column denitrification. Though there has been speculation on possible variation in  $\text{N}_2$  fixation and sediment denitrification in response to climate forcing, there is clear evidence for water column denitrification (e.g. Altabet et al., 2002). The next section lays out the strategy for determining if there has been significant change in average oceanic  $\delta^{15}\text{N}$  over the latest Holocene (last 5 kyr), the period pertinent to the question of whether the modern oceanic N budget is in balance.

### 3 Site selection and analytical methods

To examine Holocene variations in marine  $\delta^{15}\text{N}$ , sites were chosen with the following criteria: 1) Sufficiently high accumulation rate to resolve any centennial or greater temporal scale variability ( $>20\text{ cm/kyr}$ ). 2) Sufficiently good preservation of sedimentary

organic matter to prevent diagenetic alteration of  $\delta^{15}\text{N}$  (Altabet, 2005). 3) A location not directly influenced by water column denitrification or HNLC conditions. Under HNLC conditions,  $\text{NO}_3^-$  is only partially utilized by phytoplankton in surface waters which can impose a separate isotopic fractionation effect typically rendering the organic matter produced depleted in  $^{15}\text{N}$  relative to the  $\text{NO}_3^-$  source (Altabet and Francois, 1994). Figure 6 shows the locations of the sites chosen for this study which generally are at margin locations of moderate depth which satisfy these criteria. Data from Chesapeake Bay is from the literature (Bratton et al., 2003) with the remaining sites analyzed as part of this study. In the last section, possible average oceanic  $\delta^{15}\text{N}$  changes across the last deglaciation and early Holocene are considered using available data from deep-ocean sites that fulfill criteria#3 with locations also noted in Fig. 6. Most of the near-shore and margin sites used for late Holocene reconstruction are not suitable for these earlier time periods as a result of sea level change. They were either exposed during the LGM, had changes in depositional environment, and/or in source waters. While most of the deep-ocean sites are likely influenced by diagenetic alteration of  $\delta^{15}\text{N}$ , a common pattern of variation will be shown to exist for them.

In many cases, individual sediment core age models were available from the literature. Where noted,  $^{14}\text{C}$  dating was carried out on bulk organic C with conversions from  $^{14}\text{C}$  age to calendar age using a marine reservoir age of about 500 years. The dating strategy was geared to identify which portions of the cores corresponded to later Holocene and not to develop precise age models. For  $\delta^{15}\text{N}$  analysis, aliquots of sediment core material were freeze dried and packed in tin foil cups. The analytical system was an elemental analyzer coupled by He continuous carrier flow to an isotope ratio mass spectrometer (EA-CF-IRMS). Samples were run either on a Europa/EuroboPrep-Finigan MAT 251 or EuroVector-GV Isoprime system.  $\delta^{15}\text{N}$  values are referenced to atmospheric  $\text{N}_2$  and have a reproducibility of better than  $\pm 0.2\%$ .

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## 4 Holocene $\delta^{15}\text{N}$ records

The  $\delta^{15}\text{N}$  record for Chesapeake Bay reported by Bratton et al. (2003) covers the last 3 kyr or 1 residence time of the marine N cycle. While these authors focused on the anthropogenic increase in  $\delta^{15}\text{N}$  due to land use changes and increasing eutrophication over the last 300 years, there is remarkably little change prior to this point. The average  $\delta^{15}\text{N}$  of the pre-colonial record is about 5‰ and indistinguishable from the modern oceanic average suggesting that this estuary was dependent on marine  $\text{NO}_3^-$  as its primary nitrogen source. Pertinent to the question of oceanic N balance this records also suggests, though not conclusively, that average oceanic  $\delta^{15}\text{N}$  did not change over the last few kyr.

Long Island Sound is another anthropogenically impacted estuary along the Mid-Atlantic coast of the US. Similar to Chesapeake Bay, the history of that impact is marked by increasing  $\delta^{15}\text{N}$  values, in this instance over the last 150 years (Fig. 7). The prior 4 kyr also show no trend in  $\delta^{15}\text{N}$  with values in this case averaging 2‰ higher (7‰) with variations of about  $\pm 0.5$ ‰. While consistent with stable late Holocene oceanic  $\delta^{15}\text{N}$ , the offset gives caution regarding local influences on N isotope composition. The most obvious one would be input of terrestrial N, but this would most likely lower  $\delta^{15}\text{N}$  relative to marine values. Alternatively, strong salinity stratification, warm summer bottom temperatures, and limited exchange with the open ocean may produce seasonally suboxic conditions and thereby stimulate local water column denitrification.

Going offshore of these estuaries to a continental slope site seaward of Chesapeake Bay, practically eliminates the likelihood of terrestrial or estuarine influences. Core CH07-98 GGC-19 from 1100 m depth on the Delmarva peninsula also shows very little variation in N isotopic composition over the latest Holocene (Fig. 8).  $\delta^{15}\text{N}$  has varied between 5.5 and 6‰ for the last 8 kyr. As for Chesapeake Bay and Long Island Sound, the Delmarva site most likely has slope water as it source of marine  $\text{NO}_3^-$ . This water mass has been shown to have a  $\delta^{15}\text{N}$  for deep water  $\text{NO}_3^-$  equivalent to the oceanic average (Sigman et al., 1997). It sits between the coast and the Gulf Stream off the

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Mid-Atlantic region of eastern N. America and is hydrographically connected to deep N. Atlantic water masses. Offshore subtropical waters of the Sargasso Sea are 1 to 3‰ lower in  $\delta^{15}\text{NO}_3^-$  due to the influence of  $\text{N}_2$  fixation in these waters (Knapp et al., 2005). Certainly, subtropical sources never had influence at this site over the last few thousand years.

By contrast, the Cariaco Basin is influenced by N. Atlantic subtropical waters and hence has a core top  $\delta^{15}\text{N}$  of 3.5‰ (Fig. 9). With respect to paleoceanographic records, it has the unique advantages of high accumulate rate and anoxic deep waters due to a sill at 150 m that restricts ventilation below this depth. A 580 kyr-long, lower-resolution record showed a persistent pattern of high glacial and low interglacial  $\delta^{15}\text{N}$  that was thought to reflect changes in  $\text{N}_2$  fixation in this region (Haug et al., 1998). However, these variations are now known to be due to sea level forcing of sill depth and water mass source to this site. Hence, we can only be confident in the  $\delta^{15}\text{N}$  record reflecting N cycling processes (regional or global) only during periods of stable sea level which, for the purposes of this paper, pertains to the last 6 to 8 kyr. While the data are at lower temporal resolution than at the estuarine and margin sites, very stable  $\delta^{15}\text{N}$  is apparent for the last 4 kyr at the lower value of 3.5‰. Decreasing  $\delta^{15}\text{N}$  prior to this period will be discussed in the next section.

The last site examined is distinguished by being at the eastern end of the equatorial Pacific on the Ecuadorian margin (W7706-77K, 540 m water depth) but well north of the Peru denitrification zone (Fig. 10). It covers that last 4 kyr and has a sedimentation rate of 50 cm/kyr permitting centennial scale sampling resolution. Its location implies Equatorial Underwater as the source of new  $\text{NO}_3^-$  for export production. The core top  $\delta^{15}\text{N}$  value of 6‰ is consistent with measurements made for this water mass made to the west at 140° latitude (Altabet, 2001). The 1‰ higher than oceanic average  $\delta^{15}\text{N}$  value probably represents a small contribution from recirculation of intermediate waters of the denitrification zones found to the north and south. At first glance, lower sediment  $\delta^{15}\text{N}$  values would be expected since the equatorial Pacific is one of the three major HNLC regions of the world's oceans in which Fe limitation prevents complete surface

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utilization of  $\text{NO}_3^-$ . However, HNLC conditions would be expected to be fully relieved near-shore due to Fe enrichment of upwelling waters by contact with slope and lower shelf sediments (Bruland et al., 2005). This record also shows very little variation in  $\delta^{15}\text{N}$ , values are  $5.5 \pm 0.5\text{‰}$  for the last 4 kyr. Modest centennial scale variability is suggested by the  $\pm 0.5$  swings in  $\delta^{15}\text{N}$ .

## 5 Implications of stable late Holocene oceanic $\delta^{15}\text{N}$

The 5 records, taken together, indicate no detectable secular change in oceanic  $\delta^{15}\text{N}$  over the last residence time period of the marine N cycle and perhaps somewhat longer. A secular change of at least  $1\text{‰}$  would have been readily detectable. Given the qualitative and quantitative considerations presented above regarding oceanic  $\delta^{15}\text{N}$  response to marine N cycle processes, the simplest explanation is that there has been relative steady state over the last few thousand years. There are several concerns that must be considered before this conclusion is accepted unequivocally.

First, only the Chesapeake Bay record has values equivalent to the oceanic average  $\delta^{15}\text{N}$  of near  $5\text{‰}$ . The others have values higher or lower due to some degree of regional influence such as  $\text{N}_2$  fixation in the case of Cariaco Basin or denitrification in the case of Ecuador despite the criteria listed in Sect. 3.0. At any one site it is possible, though unlikely, that regional or local variability occurred opposite in sign to global variability, canceling each other. To happen at all sites, though, is very remote indeed. Nevertheless, additional  $\delta^{15}\text{N}$  records at margin sites more strictly meeting criteria#s 1–3 need to be obtained to firmly demonstrate the global nature of these observations.

Second, oceanic  $\delta^{15}\text{N}$  is not sensitive to all modes of N cycle imbalance as noted above. Specifically, excursion in  $\delta^{15}\text{N}$  occurs only in response to sustained changes in the ratio of the global rates of water column denitrification to  $\text{N}_2$  fixation given some initial steady state. Changes in sedimentary denitrification alone would alter N cycle balance without affecting  $\delta^{15}\text{N}$ . However such a phenomena on a global scale is difficult

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to imagine particularly during the latest Holocene. Global sedimentary denitrification is a function of the area of shelf and upper slope sediments, the organic flux reaching these sediments, and the oxygenation of overlying waters (partially oxygenated bottom waters actually stimulate sedimentary denitrification by promoting coupled nitrification-denitrification). The first factor is a function of sea level which changed dramatically between 10 and 20 ka but not over the last 6 kyr. Other factors are coastal upwelling intensity and the nutrient and O<sub>2</sub> content of intermediate waters. If these were altered globally, changes in water column denitrification would have surely occurred in parallel making highly unlikely independent variations (Christensen et al., 1987), though not all analyses agree in this respect (Middleburg et al., 1996). The other mode of N isotope insensitivity would be parallel changes in N<sub>2</sub> fixation and water column denitrification that maintain their ratio while leaving sedimentary denitrification unchanged. Such a possibility implies a tight feedback mechanism between N<sub>2</sub> fixation and water column denitrification but not with sedimentary denitrification. Since feedbacks likely include seawater NO<sub>3</sub><sup>-</sup> content and N:P ratio which are influenced by denitrification wherever it occurs, this too seem unlikely. However, margin sediments are also where most of the loss of oceanic PO<sub>4</sub><sup>-3</sup> occurs via the formation of authigenic minerals (Ruttenberg and Berner, 1993). If a quantitative link between sediment denitrification and PO<sub>4</sub><sup>-3</sup> sequestration was shown then differentiation in how water column vs. sedimentary denitrification feedback on N<sub>2</sub> fixation could occur.

## 6 Reconciliation with modern observations

The down core  $\delta^{15}\text{N}$  data presented strongly support the case for a near steady-state oceanic N budget for the last few thousand years or so. How is this squared with the conclusions of Codispoti et al. (2001)? A simple (but not provable at this time) assertion is that major flux terms continue to be insufficiently accurate or precise. In particular, N<sub>2</sub> fixation may still be underestimated. Perhaps just as likely if not more so is a mismatch in time scale. The  $\delta^{15}\text{N}$  records presented have centennial to millennial scale

5 resolution while the modern flux estimates have, at their broadest, decadal resolution. Both sets of observations can be fundamentally correct without contradiction. The implication is that the oceanic N cycle can undergo periods of net inventory gain and loss that are up to centennial in scale but average into a balanced state on the millennial scale. The  $\pm 0.5\%$  variations in  $\delta^{15}\text{N}$  seen in the Ecuadorian margin core (Fig. 10) may represent such a phenomenon. It is also sensible with respect to the circulation time of the ocean. While the circulation time of abyssal oceanic waters have a thousand year time scale, intermediate waters have a decadal to centennial scale circulation time. Biogeochemical feedbacks must exist between denitrification and  $\text{N}_2$  fixation zones to maintain any control on the marine M cycle. Since these processes are geographically remote from each other (e.g. Gruber and Sarmiento, 1997), these feedbacks must be communicated through the intermediate water circulation of the ocean. Hence perturbations in sources or sinks and N inventory imbalance can occur on shorter timescale but are attenuated through negative back on longer time scales. Since the residence time scale of marine N is much longer, no significant changes in inventory or average  $\delta^{15}\text{N}$  can occur. However, as discussed in the next section, large-scale forcing associated with climate change can disrupt this balance and force the marine N cycle into longer time-scale imbalance and readjustment.

## 7 Deglacial and early Holocene changes in oceanic $\delta^{15}\text{N}$

20 Good to excellent  $\delta^{15}\text{N}$  records from the three major open ocean suboxic zones all show increases in denitrification intensity during the last deglaciation (20 to 10 kyr bp). In isolation, marine combined N inventory would decline and oceanic  $\delta^{15}\text{N}$  would increase given that modern open oceanic denitrification is 25 to 50% of total denitrification. A South China Sea record (Kienast, 2000) showing no change in  $\delta^{15}\text{N}$  across this time interval was used as evidence that compensating changes such as increased  $\text{N}_2$  fixation that would mute excursion in oceanic combined N inventory. Of course, given the theoretical considerations above, the ensemble of changes would have had

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to maintain a consistent ratio of water column denitrification to  $N_2$  fixation. However, there is evidence that sediment transport processes have made age model construction problematic for these sites in the South China Sea (Higginson et al., 2003). Another approach is to consider all published records from regions that are neither directly influenced by water column denitrification nor are within HNLC regions, regardless of organic matter preservation, to detect common trends (Fig. 6; Table 1).

While each of these records could individually be questioned as to the influence of local processes or diagenesis, a consistent picture is apparent in aggregate in which there is a 2 to 3‰ increase in  $\delta^{15}N$  from the last glacial maximum (LGM) to early Holocene and a subsequent 1 to 2‰ decrease to the late Holocene. The Cariaco basin record (Fig. 9) clearly shows this latter signal. The earlier part of this record as well as the one on Delmarva margin (Fig. 8) appear to contradict the tabulated results, but these sites are likely strongly influenced by sea level change during the last deglaciation. Qualitatively, the literature  $\delta^{15}N$  records supports a global oceanic impact from changes in water column denitrification; increasing (as a fraction of  $N_2$  fixation) upon deglaciation with subsequent decrease perhaps due to a “slow” feedback mechanism increasing  $N_2$  fixation or climatological forcing that decreases again water column denitrification. Peru margin  $\delta^{15}N$  records support the latter (Higginson and Altabet, 2004). If Fig. 4 is used to estimate the magnitude of these changes, water column denitrification varied by up to 30% between the LGM and present if effective  $\epsilon_{den.}$  is about half the fractionation factor inherent to the microbial process. The relative change in flux would scale down if effective  $\epsilon_{den.}$  is higher. Alternatively,  $N_2$  fixation could have decreased upon deglaciation by >15%. However at present, water column denitrification records as well as tentative  $\delta^{15}N$ -based  $N_2$  fixation record from the Sargasso Sea (Altabet, 2005) favor the first view. These changes would have resulted in significant variations in oceanic combined N inventory. For example a 15 % increase in denitrification relative to  $N_2$  fixation over 5 kyr would decrease total ocean inventory by about 25%. Of course, this perspective assumes no insidious compensation by opposite and equal changes in sedimentary denitrification.

In addition to transient imbalance in the ocean N budget during the last deglaciation, the literature  $\delta^{15}\text{N}$  records also suggests a late Holocene reorganization of oceanic N cycling relative to the LGM. LGM  $\delta^{15}\text{N}$  is 1 to 2‰ lower than during the late Holocene. If the LGM was also near-steady-state, water column denitrification stably accounted for a reduced proportion of total losses as supported by the denitrification zone records. Examining Fig. 2, that difference appears to be about 10%.

## 8 Summary and conclusions

The major microbial transformation pathways within the marine N cycle have been well known for about a century including the inference of long-term balance between sources and sinks (Brandt, 1902). Within the last 3 decades, serious and credible efforts have been made to quantify global ocean N fluxes and that with more detailed study estimates have almost been steadily revised upward. It is not clear if there is modern balance between sources (primarily  $\text{N}_2$  fixation) and losses (sedimentary and water denitrification). N isotope budgeting offers both geochemical constraints on considerations of the modern oceanic N cycle as well as the only means for past reconstruction. There is a large effective isotopic fractionation for water column denitrification as opposed to the nil effect for sedimentary denitrification. As a result, it is the relative proportion of the source flux from  $\text{N}_2$  fixation consumed by water column denitrification that sets average oceanic  $\delta^{15}\text{N}$  under steady state conditions. If an imbalance in oceanic N sources and sinks change this proportion, then a transient in average oceanic  $\delta^{15}\text{N}$  will occur. Given the modern average  $\delta^{15}\text{N}$  of near 5‰ for deepwater  $\text{NO}_3^-$ , inherent  $\epsilon_{\text{den.}}$  of about 20 to 30‰ for denitrification, and the  $\delta^{15}\text{N}$  for fixed N of 0 to -2, water column denitrification would appear to account for about 25% of the total sink assuming steady state. However, several factors (conversion of organic N to  $\text{N}_2$ , Rayleigh closed and open system effects) likely reduce the effective  $\epsilon$  for water column denitrification by half implying a more canonical contribution for water column denitrification of 50%. Examining non-steady conditions, changing water column denitrifica-

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tion  $\pm 30\%$  and  $N_2$  fixation by  $\pm 15\%$  produces detectable ( $>1\%$ ) changes in average oceanic  $\delta^{15}N$  over one residence time period or more with corresponding changes in oceanic N inventory. Changing sedimentary denitrification produces no change in  $\delta^{15}N$  but does change N inventory.

Sediment  $\delta^{15}N$  records from high accumulation-rate estuarine and continental margin sites not directly influenced by either water column denitrification or HNLC conditions all show no detectable change over the last 3 kyr or so. Given the level of sensitivity of average oceanic  $\delta^{15}N$  to imbalances caused by variations in water column denitrification and/or  $N_2$  fixation, the simplest and most likely interpretation is a steady and in balance marine N budget over the latest Holocene. The best estimates for modern fluxes, in contrast, indicate losses well in excess of sources. It would be facile to point to the modern flux estimates as insufficiently accurate. However, calling upon a mismatch in time scales is a likely more meaningful interpretation. Decadal to centennial scale oscillations between net N deficit and net surplus occur in response to periods of perturbation and readjustment through biogeochemical feedback. This feedback is likely transmitted through the intermediate circulation of the ocean which occurs on these timescales. If so, current imbalance is creating biogeochemical signals (reduced  $NO_3^-$  and N:P) that should either increase oceanic  $N_2$  fixation or reduce denitrification over the next century. On the N residence timescale of several thousand years, net balance is achieved as the sum of the swings between surplus and deficit as recorded by the average oceanic  $\delta^{15}N$  record.

Though not ideal, sediment  $\delta^{15}N$  records from the literature covering the period since the last glacial maximum indicate a 2 to 3‰ increase during the deglacial period and subsequent  $\sim 1\%$  decrease in the early Holocene. Combined with the  $\delta^{15}N$  records from water column denitrification zones, these changes are consistent with sustained N deficit during the deglaciation followed by readjustment and establishment of balance. Since imbalance was sustained for time periods on order of the N residence time or longer, excursions in ocean N inventory of 10 to 30% likely occurred. The climatic and oceanographic changes that occurred over this period (e.g. in water mass

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ventilation, sea level, coastal upwelling intensity) evidently overcame for a time, ocean biogeochemistry's feedback mechanisms for maintaining N balance. This change ultimately produced a reorganized late Holocene oceanic environment with proportionally greater water column denitrification.

5 Future progress in making use of N isotope biogeochemistry to understand the ocean's N cycle (past, present, and future) requires better and more widely distributed  $\delta^{15}\text{N}$  records that are likely to accurately reflect changes in oceanic average  $\delta^{15}\text{N}$  as well as those from regions sensitive to  $\text{N}_2$  fixation intensity. Quantitative interpretation of those records would also require development of sufficiently realistic, coupled  
10 physical-biogeochemical models to simulate the relationships in water column denitrification zones between water mass ventilation and circulation, organic matter flux, denitrification intensity, and isotopic signal generation as well as the transmittal of the biogeochemical feedbacks created to sites of  $\text{N}_2$  fixation.

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**Table 1.** Summary of  $\delta^{15}\text{N}(\text{‰})$  changes at oceanic sites which are neither within an HNLC or denitrifying region for the time periods indicated. These are generally sites with low accumulation rate (<5 cm/kyr) and sufficiently poor N preservation that diagenetic effects make any individual record suspect. However in aggregate, global signals are apparent. LGM (last glacial maximum) to early Holocene refers to the period from 20 to 10 kyr b.p. Early to late Holocene refers to the period from 10 to 5 kyr b.p. Data sources are <sup>1</sup>Altabet (2005), <sup>2</sup>Holmes et al. (1997), <sup>3</sup>Schubert et al. (2001), <sup>4</sup>Martinez et al. (2000), <sup>5</sup>Nakatsuka et al. (1995b), <sup>6</sup>Nakatsuka et al. (1995a).

Region	Early to Late Holocene	LGM to Early Holocene
Bermuda Rise <sup>1</sup>	−1	2.5
Bahama Outer Bank <sup>1</sup>	−1	3
Benguela <sup>2</sup>	−0.5	2
Arctic Ocean <sup>3</sup>	−1	3
NW Africa <sup>4</sup>	−1	3
W. Eq. Pacific <sup>5</sup>	−1.5	3.5
Bering Sea <sup>6</sup>	−1.5	1.5

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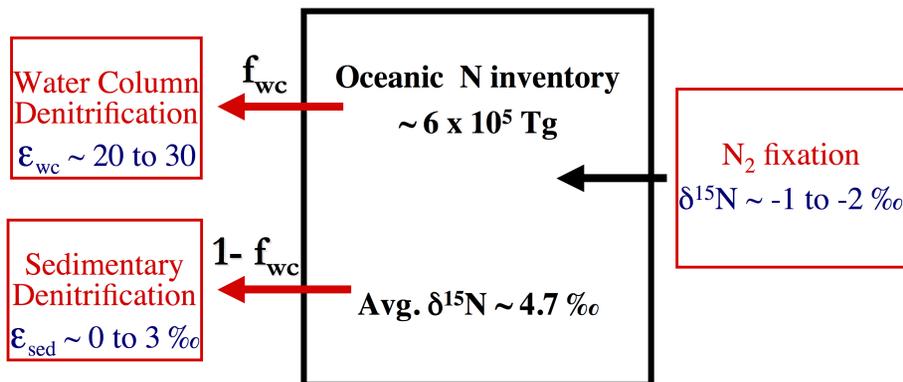
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**Fig. 1.** Schematic of the simple box model used to explore the influence on average oceanic  $\delta^{15}\text{N}$  and the relative proportions of N sources and sinks as well as variations in the effective N isotopic fractionation ( $\epsilon_{\text{den.}}$ ) associated with water column denitrification. The model is used under both steady and non-steady conditions. Accepted values for isotopic composition, fractionation effect, N inventory, and N fluxes are shown for reference.

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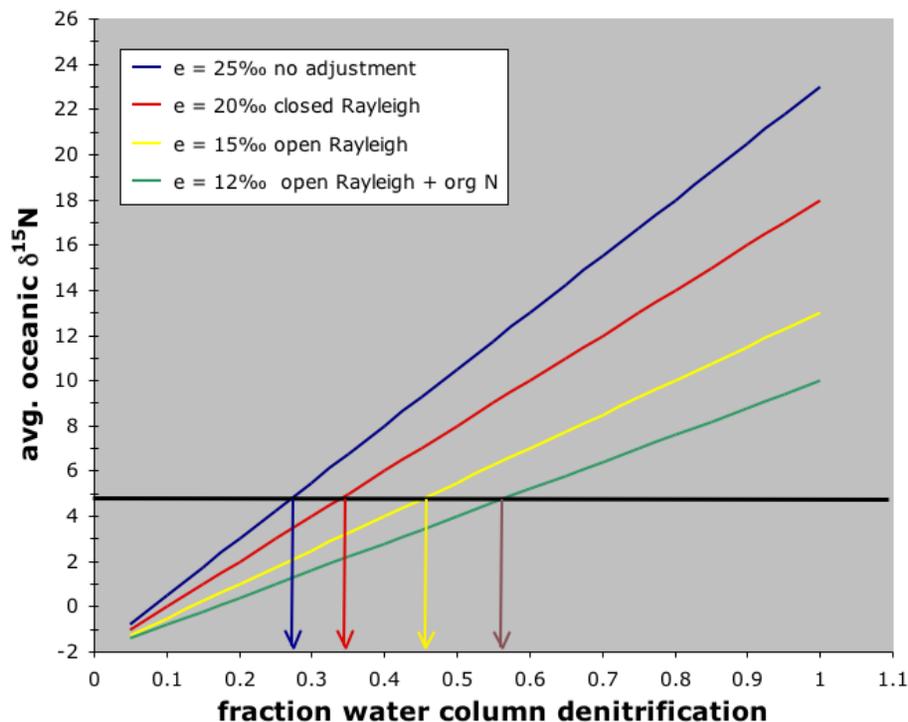
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**Fig. 2.** Steady state relationship between average oceanic  $\delta^{15}\text{N}$  and the fractional contribution from water column denitrification for several values of effective isotopic fraction factor ( $\epsilon_{\text{den.}}$ ). The largest value is the inherent value of  $\epsilon_{\text{den.}}$  associated with the microbial process. This value is reduced as discussed in the text. The horizontal line corresponds to the observed modern value for oceanic  $\delta^{15}\text{N}$ .

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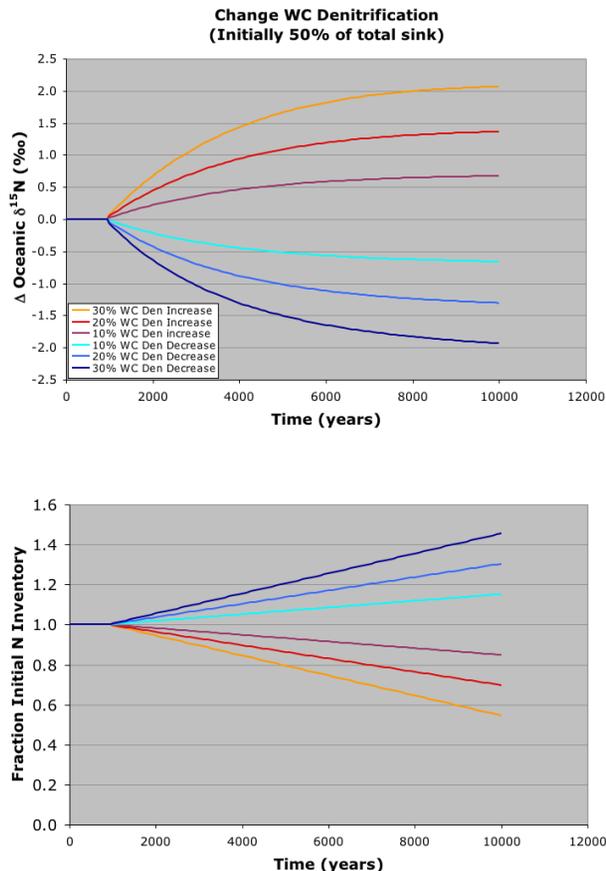
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**Fig. 3.** Temporal evolution of oceanic  $\delta^{15}\text{N}$  (top) and N inventory (bottom) with up to  $\pm 15\%$  changes in total  $\text{N}_2$  fixation (assumed to be sole source). Initial conditions are of steady state and 50% contributions from water column and sedimentary denitrification respectively. The value for  $\epsilon_{\text{den.}}$  (effective) is 12‰. Sedimentary denitrification is considered non-fractionating.

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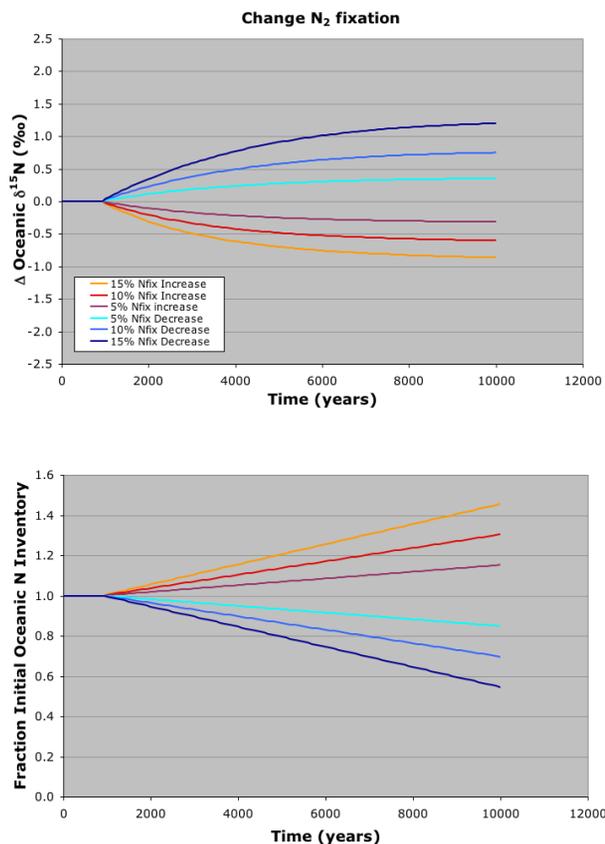
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**Fig. 4.** Temporal evolution of oceanic  $\delta^{15}\text{N}$  (top) and N inventory (bottom) with up to  $\pm 30\%$  changes in water column denitrification. Initial conditions are of steady state and 50% contributions from water column and sedimentary denitrification respectively. The value for  $\epsilon_{\text{den}}$  (effective) is 12‰. Sedimentary denitrification is considered non-fractionating.

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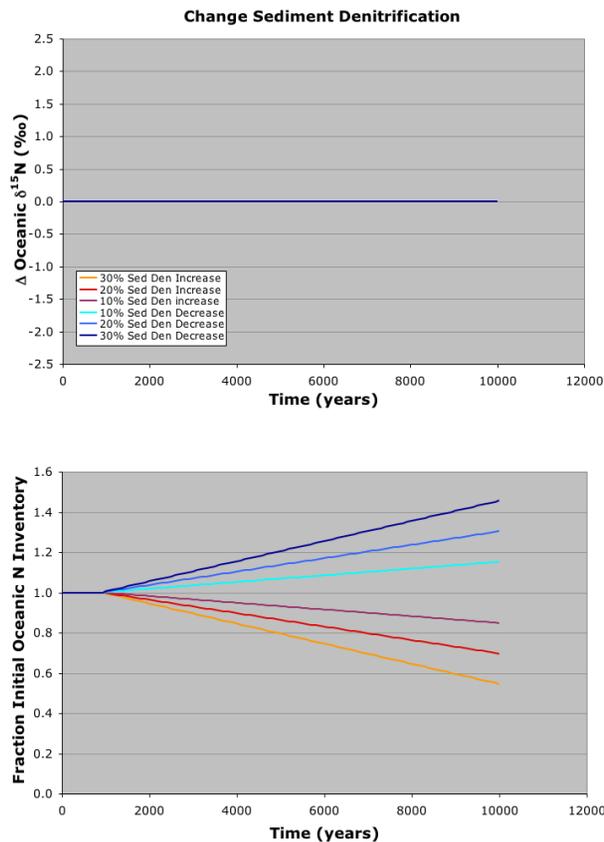
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**Fig. 5.** Temporal evolution of oceanic  $\delta^{15}\text{N}$  (top) and N inventory (bottom) with up to  $\pm 30\%$  changes in sedimentary denitrification. Initial conditions are of steady state and 50% contributions from water column and sedimentary denitrification respectively. The value for  $\epsilon_{\text{den}}$  (effective) for water column denitrification is 12‰. Because sedimentary denitrification is considered non-fractionating, no change in  $\delta^{15}\text{N}$  occurs despite changes in N inventory.

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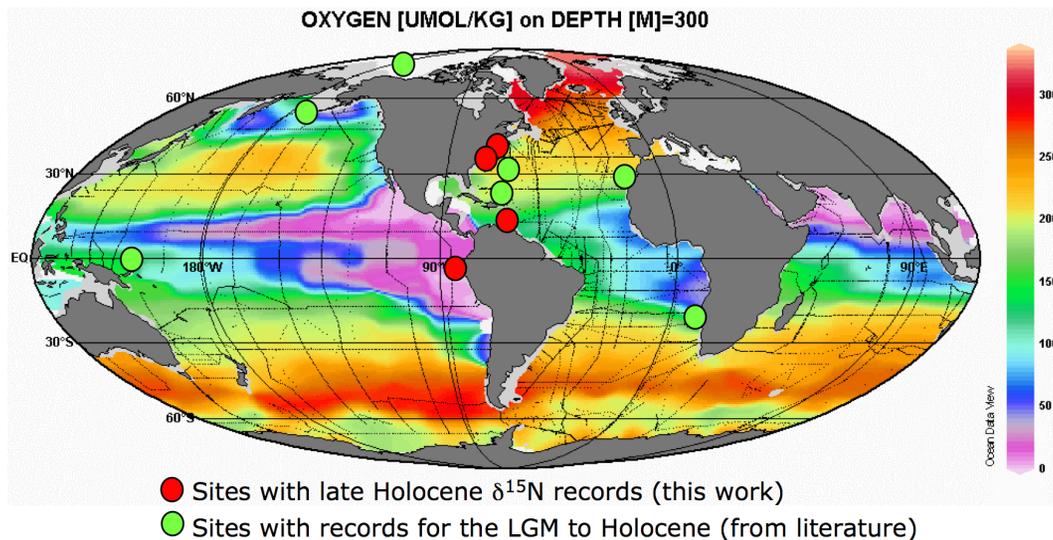
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**Fig. 6.** Location map for sediment  $\delta^{15}\text{N}$  records discussed in this paper. High-resolution, good fidelity records spanning the late Holocene are distinguished from those that cover the last glacial maximum but have poor temporal resolution and likely diagenetic influence. Oxygen at 300 m is contoured for reference to show locations of subsurface suboxic zones which sustain water column denitrification (data from the eWOCE database).

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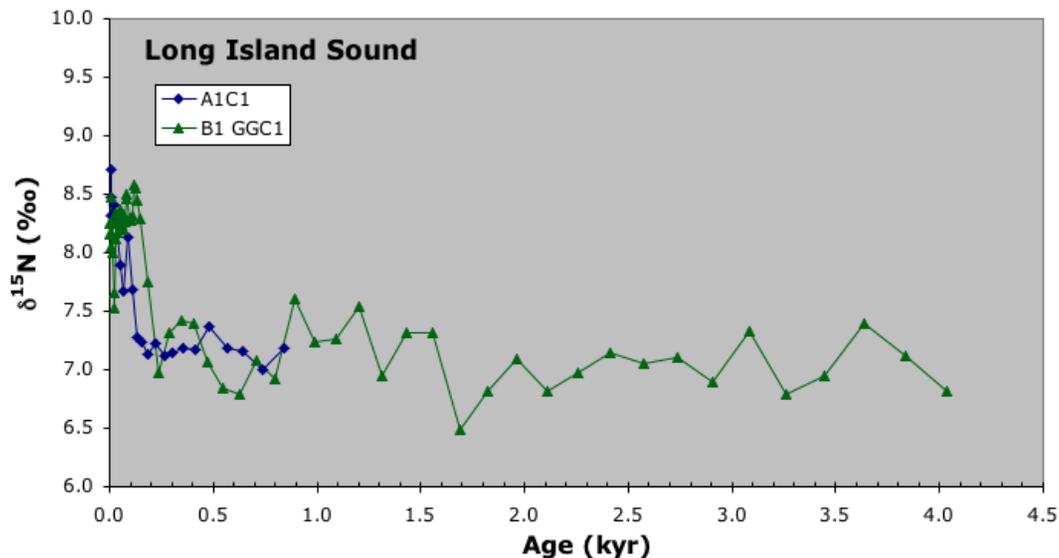
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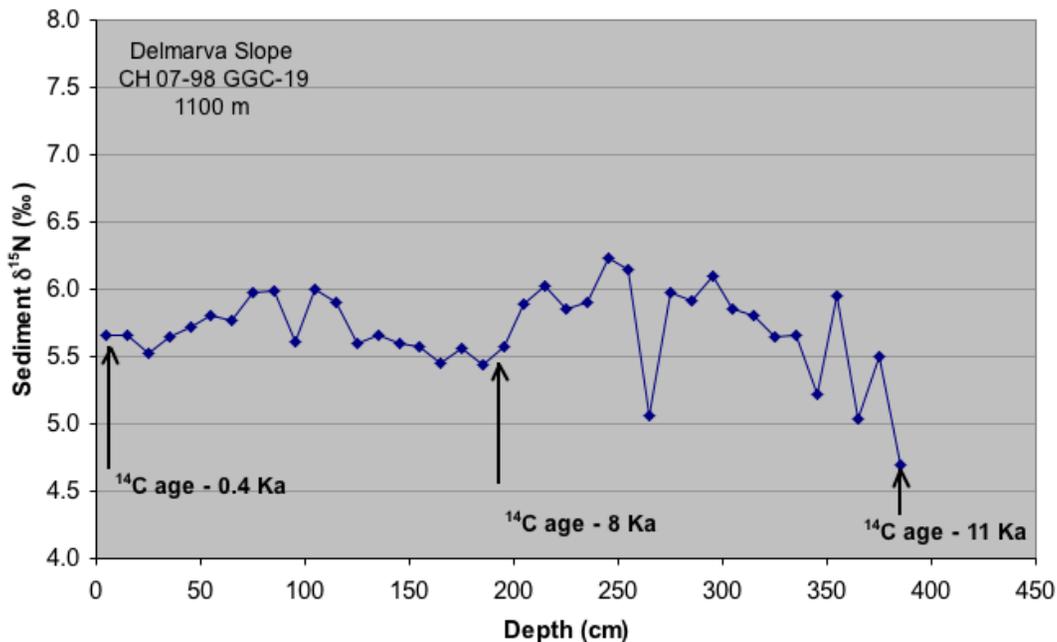


**Fig. 7.** Long Island Sound sediment  $\delta^{15}\text{N}$  records spanning the last 4 kyr. Age model established from  $^{14}\text{C}$  dating, and known pollen and contaminant horizons. The increase in  $\delta^{15}\text{N}$  within the last 200 years corresponds to the onset of anthropogenic eutrophication.

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**Fig. 8.** Sediment  $\delta^{15}\text{N}$  record from a site on the continental slope opposite the mouth of Chesapeake Bay (Delmarva) spanning the last 11 kyr. Due to the few  $^{14}\text{C}$  dates, the x-axis is depth in core and the dates are noted on the figure. The last 6 or 7 kyr are considered to be reliable for indicating oceanic  $\delta^{15}\text{N}$  with lower sea level influencing the earlier period.

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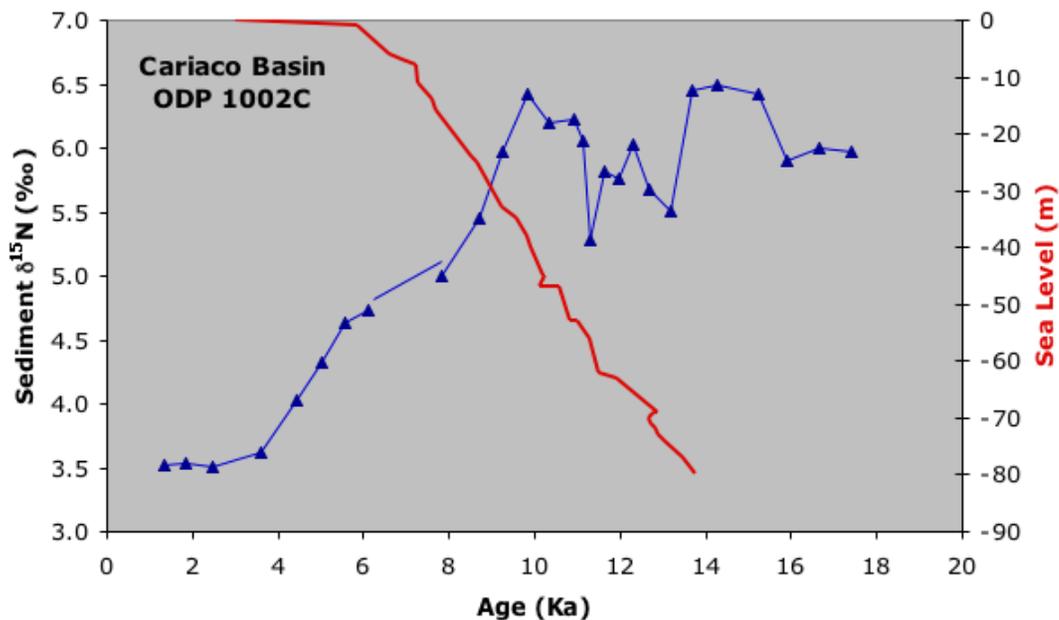
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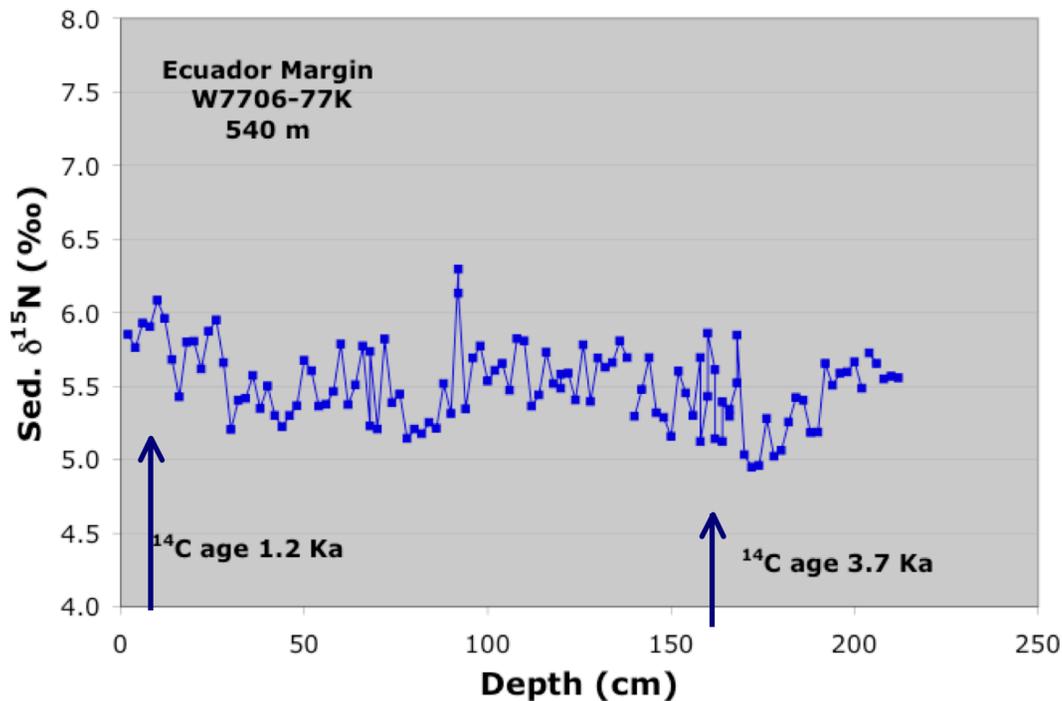


**Fig. 9.** Sediment  $\delta^{15}\text{N}$  record from the Cariaco Basin covering the last 20 kyr. Sea level change is shown for reference. Age model is based on a combination of  $^{14}\text{C}$  dating and foraminifera  $\delta^{18}\text{O}$ . The last 6 or 7 kyr are considered to be reliable for indicating oceanic  $\delta^{15}\text{N}$  (though regional influence from  $\text{N}_2$  fixation is apparent) with lower sea level influencing the earlier period.

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**Fig. 10.** Sediment  $\delta^{15}\text{N}$  record from a site on the Ecuadorian continental margin. Due to the few  $^{14}\text{C}$  dates, the x-axis is depth in core and the dates are noted on the figure.

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