Deglacial nitrogen isotope changes in the Gulf of Mexico: Evidence from bulk sedimentary and foraminifera-bound nitrogen in Orca Basin sediments

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[1] Constraining variations in marine N_2-fixation over glacial-interglacial timescales is crucial for determining the role of the marine nitrogen cycle in modifying ocean productivity and climate, yet paleo-records from N_2-fixation regions are sparse. Here we present new nitrogen isotope ($\delta^{15}N$) records of bulk sediment and foraminifera test-bound (FB) nitrogen extending back to the last ice age from the oligotrophic Gulf of Mexico (GOM). Previous studies indicate a substantial terrestrial input during the last ice age and early deglacial, for which we attempt to correct the bulk sediment $\delta^{15}N$ using its observed relationship with the C/N ratio. Both corrected bulk and FB-$\delta^{15}N$ reveal a substantial glacial-to-Holocene decrease of $\delta^{15}N$ toward Holocene values of around 2.5 ‰, similar to observations from the Caribbean. This $\delta^{15}N$ change is most likely due to a glacial-to-Holocene increase in regional N_2-fixation. A deglacial peak in the FB-$\delta^{15}N$ of thermocline dwelling foraminifera *Orbulina universa* probably reflects a whole ocean increase in the $\delta^{15}N$ of nitrate during deglaciation. The $\delta^{15}N$ of the surface dwelling foraminifera *Globigerinoides ruber* and the corrected bulk $\delta^{15}N$ show little sign of this deglacial peak, both decreasing from last glacial values much earlier than does the $\delta^{15}N$ of *O. universa*; this may indicate that *G. ruber* and bulk N reflect the euphotic zone signal of an early local increase in N_2-fixation. Our results add to the evidence that, during the last ice age, the larger iron input from dust did not lead to enhanced N_2-fixation in this region. Rather, the glacial-to-Holocene decrease in $\delta^{15}N$ is best explained by a response of N_2-fixation within the Atlantic to the deglacial increase in global ocean denitrification.

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1. Introduction

[2] Fixed nitrogen is the major limiting nutrient for primary productivity in vast parts of the present-day ocean. Hence, the processes that govern the sources and sinks of this fixed marine nitrogen pool constitute a potentially important control on the strength of the ocean's biological pump and thus on the atmospheric concentration of CO_2, with implications for global climate [*Altabet et al.*, 1995; *Broecker and Henderson*, 1998; *Falkowski*, 1997; *Ganeshram et al.*,

1995; *Gruber*, 2004]. The major source of fixed nitrogen to the ocean is N_2-fixation by diazotrophic organisms, whereas denitrification and anammox are its most important sink processes [*Gruber and Galloway*, 2008]. Despite extensive research, it is still not clear whether the marine nitrogen budget is currently in balance [*Codispoti*, 2007; *Deutsch et al.*, 2007] and how much it has changed in the past [*Altabet*, 2007; *Deutsch et al.*, 2004; *Gruber*, 2004; *Gruber and Galloway*, 2008].

[3] Stable nitrogen isotopes provide an important tool for studying the sources and sinks of oceanic nitrogen. During N_2-fixation, little isotopic fractionation is observed [*Wada and Hattori*, 1991], resulting in a $\delta^{15}N$ for newly fixed N of -2 to 0 ‰ ($\delta^{15}N$ (‰) = (($^{15}N/^{14}N$ of sample / $^{15}N/^{14}N$ of air) -1) * 1000). On the other hand, denitrification preferentially removes light nitrogen, leaving ^{15}N-enriched nitrate behind [*Cline and Kaplan*, 1975; *Liu and Kaplan*, 1989]. As a result, water column denitrification in the oxygen minimum zones increases the local and global ocean $\delta^{15}N$ of nitrate. However,

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the enrichment is only expressed if some of the nitrate remains unconsumed by this process [*Thunell et al.*, 2004]. Hence, denitrification in sediments, where nitrate supply is limited by diffusion, does not appear to strongly elevate the $\delta^{15}N$ of marine nitrate [*Brandes and Devol*, 1997, 2002; *Lehmann et al.*, 2004; *Sebilo et al.*, 2003]. The isotopic fractionation of the anammox process and the isotope dynamics of partial nitrification coupled to denitrification are poorly known. However, these processes have often been tacitly included in estimates of the water column and sedimentary denitrification isotope effects (see discussion in the work of *Sigman et al.* [2003]). Moreover, ammonium and nitrite consumption are often complete where anammox appears to occur, probably leading to similar limitations on the expression of the isotope effects of anammox as described above for sedimentary denitrification. In steady state, then, the average isotopic composition of oceanic nitrate appears to be largely controlled by the relative global magnitude of water column versus sedimentary denitrification [*Brandes and Devol*, 2002], with some modulation by the completeness with which nitrate is consumed in zones of water column denitrification and how this signal is transported and mixed into the global nitrate pool [*Deutsch et al.*, 2004].

[4] In the oligotrophic regions of the ocean, such as most of the tropical and subtropical ocean, the $\delta^{15}N$ of the total organic nitrogen sinking out of the euphotic zone must be equal to the flux-weighted $\delta^{15}N$ of all "new" nitrogen that enters this zone. This is because the pool of fixed nitrogen in the euphotic zone is very small and turns over quickly. New sources of nitrogen include vertical input of subsurface nitrate from the thermocline, N_2-fixation, atmospheric deposition, and riverine input of organic and inorganic nitrogen. The $\delta^{15}N$ of the sinking flux will therefore be a combined (and thus potentially complex) signal of changes in the isotopic composition and/or relative importance of the various new nitrogen sources. Furthermore, the $\delta^{15}N$ of thermocline nitrate itself reflects the combined effect of changes in deep ocean nitrate $\delta^{15}N$ and the accumulated signal of regional processes such as N_2-fixation or water column denitrification.

[5] N isotope records from the major denitrification zones in the eastern tropical north and south Pacific and the Arabian Sea [e.g., *Altabet et al.*, 1995; *De Pol-Holz et al.*, 2006; *Emmer and Thunell*, 2000; *Ganeshram et al.*, 1995; *Pride et al.*, 1999] consistently reveal lower $\delta^{15}N$ of sinking organic matter during glacial times. This signal has been interpreted as reflecting a lower thermocline $\delta^{15}N$ of nitrate, which suggests decreased water column denitrification during the glacial period in these regions. This observed pattern led *Ganeshram et al.* [1995] and *Altabet et al.* [1995] to the hypothesis that an excess of N_2-fixation over denitrification in glacial times caused a larger global nitrate reservoir at that time, potentially fuelling higher primary productivity, and hence contributing to the lower CO_2 levels in the atmosphere. This would have been substantially reinforced by decreased sedimentary denitrification due to the lower sea level of the last ice age, which exposed large shelf areas [*Christensen*, 1994]. However, implicit in the hypothesis of *Ganeshram et al.* [1995] and *Altabet et al.* [1995] is the assumption that N_2-fixation remained approximately constant across the glacial-interglacial transition.

[6] However, two contrasting views are proposing glacial-to-Holocene changes in N_2-fixation as well, albeit in different directions. On the one hand, recent evidence of a relatively tight coupling between denitrification and N_2-fixation [*Deutsch et al.*, 2007] suggests that N_2-fixation would have responded to the observed changes in denitrification, leading to decreased N_2-fixation in glacial times, which would have kept the change in the inventory of fixed nitrogen small [*Haug et al.*, 1998; *Tyrrell*, 1999]. On the other hand, N_2-fixation was proposed to have been enhanced in glacial times in response to increased iron input by dust, increasing the marine nitrogen reservoir and hence productivity in glacial times [*Broecker and Henderson*, 1998; *Falkowski*, 1997]. The basis for this hypothesis is the high iron content of the enzyme nitrogenase [*Rueter et al.*, 1992], which is required for N_2-fixation. However, the regional and global role of iron limitation in setting the rate of N_2-fixation is still a matter of discussion [*Hood et al.*, 2000; *Kustka et al.*, 2003; *Lenes et al.*, 2001; *Mills et al.*, 2004; *Moore et al.*, 2009; *Sañudo-Wilhelmy et al.*, 2001]. It is possible that both mechanisms interact, such that changes in the strength or location of Fe sources influence where marine N_2 fixation responds to variations in global denitrification [*Galbraith et al.*, 2004].

[7] The assessment of past changes in N_2-fixation from $\delta^{15}N$ measurements in marine sediments tends to be more challenging than that of changes in water column denitrification, as the signal is often overprinted by other processes such as diagenetic alteration (especially at oligotrophic open ocean sites) and allochthonous nitrogen input (because the regions of interest tend to be characterized by sediments with low nitrogen content, which are easily contaminated). Furthermore, records from sites that are close to water column denitrification zones are challenging to interpret, as the latter process tends to dominate the changes in the isotopic signal. Recently, *Ren et al.* [2009] demonstrated that organic nitrogen bound in foraminifera tests can be used to obtain records from oligotrophic sites, thereby avoiding many of the issues associated with diagenetic alteration and allochthonous nitrogen input. But the labor-intensive nature of these measurements currently precludes records with the temporal resolution that is easily achieved through bulk sediment analysis. In order to obtain high-resolution bulk sedimentary $\delta^{15}N$ records from areas dominated by N_2-fixation, one seeks exceptional sites that are distant from major denitrification zones and yet characterized by good preservation of sedimentary organic matter.

[8] In this study, we analyze sediments from such a site in the oligotrophic Gulf of Mexico (GOM). In this region as well as in the open subtropical North Atlantic, nitrogen fixation is responsible for the low $\delta^{15}N$ of thermocline nitrate (~2.5‰) [*Knapp et al.*, 2005, 2008]. The importance of N_2-fixation is supported by elevated N/P ratios observed in the subtropical North Atlantic thermocline [*Gruber and Sarmiento*, 1997; *Karl et al.*, 2002; *Michaels et al.*, 1996] and by numerous studies on the abundances and N_2-fixation rates of diazotrophic organisms, such as *Trichodesmium*, in the Caribbean, GOM, and subtropical North Atlantic [*Capone et al.*, 2005; *Carpenter and Price*, 1977; *Carpenter and Romans*, 1991; *Carpenter et al.*, 2004; *Goering et al.*, 1966; *Lenes et al.*, 2001; *Montoya et al.*, 2007; *Moore et al.*, 2009; *Tyrrell et al.*, 2003]. Combined with the
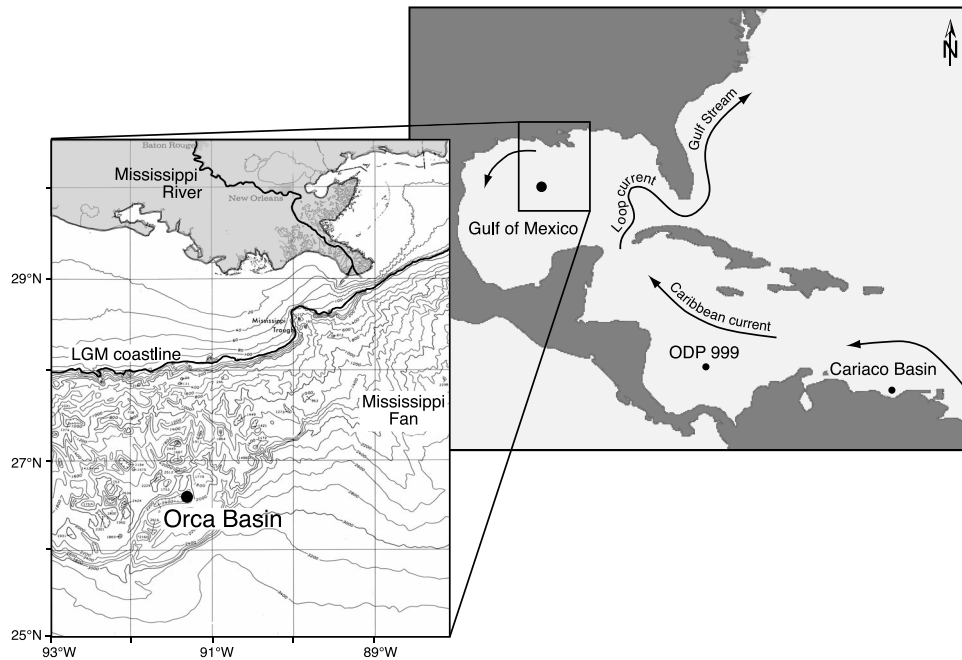
Figure 1. Map of the Gulf of Mexico showing the location of Orca Basin as well as the sites of δ^{15}N records in the Caribbean. Arrows indicate surface currents. The inset shows bathymetry of the Louisiana slope and Mississippi Fan. Approximate location of last glacial maximum (LGM) coastline is indicated. Core MD02–2550 was taken from the slope of Orca Basin, in a water depth of 2249 m at 26°56.77N and 91°20.74W. Isobath spacing is 20 m above 200 m and 200 m below.

absence of a major water column denitrification region, the elevated levels of N_2-fixation cause the Atlantic to be an overall net source of fixed nitrogen [*Gruber*, 2004], making it an ideal place to study how N_2-fixation might have changed in the past.

[9] Orca Basin is an intraslope basin off the coast of Louisiana and about 300 km southwest of the Mississippi mouth (Figure 1). The basin has a maximum depth of 2400 m and is surrounded by salt domes rising to 1800 m water depth [*Shokes et al.*, 1977]. Hence, the water column shallower than 1800 m overlying the Orca Basin is indistinguishable from the surrounding GOM. The lowermost 200 m of the basin are filled with dense, hypersaline brine [*Sackett et al.*, 1979], resulting in anoxic bottom water below the brine-seawater interface and leading to excellent preservation of organic matter in the sediments [*Meckler et al.*, 2008]. Although water column denitrification occurs in the basin at 2200 m depth [*Van Cappellen et al.*, 1998], this process is not recorded in the organic matter sinking out of the surface ocean and accumulating in the sediments. This is because of the large distance of the relatively minute denitrification zone from the surface ocean and from the strong subtropical thermocline. The brine probably built up around 8000 years before present (8 ka) due to lateral leakage from a salt deposit [*Addy and Behrens*, 1980]. Laminated sections of the sediment occurring deeper in the core indicate earlier sub- to anoxic intervals as well, and it is possible that the brine leakage has continuously supported low dissolved O_2 in the basin. Therefore, Orca Basin offers the unique combination of good organic matter preservation in an oligotrophic setting.

[10] A weakness of the location in the sense of this study is its proximity to the continental margin and to the mouth of the Mississippi River in particular (Figure 1). As a result of this proximity, input of terrestrial material can be large and numerous studies have shown that it has changed through time due to changes in sea level and meltwater inflow [*Jasper and Gagosian*, 1990, 1993; *Meckler et al.*, 2008; *Newman et al.*, 1973; *Northam et al.*, 1981]. Because terrigenous material has a different nitrogen isotopic composition to that of marine organic matter [*Calvert et al.*, 2001; *Meyers*, 1997; *Peters et al.*, 1978; *Schubert and Calvert*, 2001], the bulk δ^{15}N record can be significantly affected by this input. For this reason, we measured the FB-δ^{15}N at selected intervals of the core. As an autochthonous marine signal, FB-δ^{15}N should be insensitive to the input of allochthonous particulate nitrogen as long as it is not incorporated into the marine food web. We will discuss the bulk and FB-δ^{15}N data from Orca Basin regarding (1) local and regional changes in N_2-fixation at Orca Basin and in the tropical North Atlantic, respectively, and (2) the implications of our findings for the marine nitrogen cycle and its potential influence on global climate.

2. Material and Methods

[11] The 9.09 m long giant box core MD02–2550 was taken during IMAGES cruise VIII (PAGE) in 2002. Its chronology is based on 13 radiocarbon dates on foraminifera and has been described by *Meckler et al.* [2008]. In the Holocene section, a large hiatus of around 4.2 kyr (from 2.8 to 7.0 ka) is observed. The upper 232 cm of the core (back to 8.5 ka) consist of clearly laminated sediment colored

Table 1. FB-δ^{15}N Results From Core MD02–2550, Given as Averages and Their Standard Errors[a]

		G. ruber				O. universa				125–250 μm Size Fraction (mixed species)			
Depth (cm)	Age (yr BP)	Average	Standard Error	Number of Total Measurements	Number of Subsamples Prepared Separately	Average	Standard Error	Number of Total Measurements	Number of Subsamples Prepared Separately	Average	Standard Error	Number of Total Measurements	Number of Subsamples Prepared Separately
38	632	3.15	0.17	3	2	3.14	0.02	3	2	–	–	–	–
39	649	–	–	–	–	–	–	–	–	2.32	0.33	2	1
89	1481	–	–	–	–	–	–	–	–	2.97	0.34	2	1
90	1497	2.39	0.20	4	2	2.77	0.18	8	3	–	–	–	–
208	7832	2.62	0.12	4	2	3.75	0.15	4	1	3.52	0.36	2	1
287	10047	3.68	0.13	6	3	4.77	0.09	2	1	5.87	0.19	4	2
314	10808	3.69	0.12	6	3	6.75	0.46	3	1	6.01	0.23	2	1
423	14285	3.36	0.21	6	3	–	–	–	–	3.37	0.22	2	1
530	16298	4.20	0.19	6	2	5.22	0.17	2	1	4.22	0.19	2	1
715	19474	5.37	0.04	2	1	–	–	–	–	4.75	0.06	2	1
872	23121	4.76	0.05	2	1	–	–	–	–	5.36	–	1	1
896	23709	–	–	–	–	5.32	0.34	2	1	–	–	–	–
898	23758	5.00	0.11	5	2	–	–	–	–	5.68	0.14	2	1

[a]Missing data are due to insufficient abundance of foraminifera.

black by metastable iron sulfides, which accumulated under anoxic conditions in the brine layer [*Addy and Behrens*, 1980]. However, laminated sediment suggesting anoxic conditions can also be found below this depth. Below 567 cm (16.8 ka) the sediment appears mostly homogenous, except for several bundles of black layers in the bottom section of the core.

[12] Bulk sediment δ^{15}N was measured with a *Carlo-Erba CN2500* elemental analyzer online coupled to a *Thermo Finnigan DELTAplusXL* mass spectrometer at the GFZ. The core was sampled in 1 cm increments, corresponding to about 22 years on average, except for 0–150 cm and below 630 cm, where samples were taken every 10 cm. The freeze-dried and homogenized samples were analyzed without any further treatment. All samples were measured at least in duplicate and precision based on measurements of the reference standards IAEA N1 and N2 was better than 0.2‰. Total nitrogen (TN) and total organic carbon (TOC), measured on the same samples, as well as the resulting C/N ratios were published previously [*Meckler et al.*, 2008].

[13] The nitrogen isotopic composition of organic matter preserved in foraminiferal tests (FB-δ^{15}N) was measured in selected intervals. Where species abundance was sufficient, measurements were made both on *Globigerinoides ruber* and *Orbulina universa*, each picked from the >355 μm size fractions. In three samples, *G. ruber* was also picked from the 250–355 μm fraction. The results were indistinguishable from the larger size fraction and were therefore averaged. In addition, mixed (unpicked) foraminifera samples of the 125–250 μm size fractions were analyzed. This size fraction contained abundant *Globigerina bulloides*, but otherwise varied in species composition with depth (not quantified). All foraminifera-based samples were replicated (n = 2–8) including in most cases two or more subsamples which were prepared separately (see Table 1). Standard errors for the averages of all replicates ranged from 0.02 to 0.46‰ (mean = 0.19‰, Table 1).

[14] The protocol for measuring FB-δ^{15}N [*Ren et al.*, 2009] includes (1) chemical treatment of the foraminifera shells to remove external N contamination, followed by acid dissolution of the cleaned shells, (2) conversion of organic

N released into solution to nitrate by persulfate oxidation [*Knapp et al.*, 2005; *Nydahl*, 1978]; (3) measurement of nitrate concentration by chemiluminescence [*Braman and Hendrix*, 1989], and (4) bacterial conversion of nitrate to nitrous oxide [*Sigman et al.*, 2001], with measurement of the δ^{15}N of the nitrous oxide by gas chromatography-isotope ratio mass spectrometry using a modified *Thermo GasBench II* and *DeltaPlus* [*Casciotti et al.*, 2002].

[15] As the first step in cleaning the samples prior to FB-δ^{15}N analysis, 5 to 10 mg of foraminifera tests per sample were gently crushed, treated with 5 min of ultrasonication in 2% sodium hexametaphosphate (pH 8), then rinsed twice with deionized water (DI). To avoid any organic contamination associated with metal oxides, we conducted a reductive cleaning using sodium bicarbonate buffered dithionite-citrate reagent [*Mehra and Jackson*, 1958]. Samples were then soaked in 13% sodium hypochlorite ("bleach") for 6 h at room temperature, with several agitations to expose surfaces, and then rinsed with DI. The bleach treatment was previously compared with persulfate cleaning, which is likely a harsher treatment [*Brunelle et al.*, 2007]. The two cleaning methods yielded indistinguishable N content and δ^{15}N, indicating complete removal of external contamination and confirming the physically protected nature of shell-bound N. Following cleaning, the remaining 3 to 5 mg of cleaned foraminifera tests were completely dissolved in 6 N hydrochloric acid, releasing organic matter for analysis. After conversion of organic nitrogen to nitrate and prior to nitrate and δ^{15}N measurement, we centrifuged the solutions and removed the calcium precipitates generated during persulfate oxidation. This modification of the protocol reduces the influence of calcium ions and improves the precision of isotopic analysis by the denitrifier method [*Ren*, 2010].

3. Results and Discussion

[16] During the late Holocene, both bulk and FB-δ^{15}N show values of 2.2–3.2‰, which is much lower than the mean isotopic composition of oceanic nitrate (~5‰) [*Sigman et al.*, 2000]. The Orca Basin δ^{15}N values during this interval are, however, indistinguishable from the δ^{15}N of today's
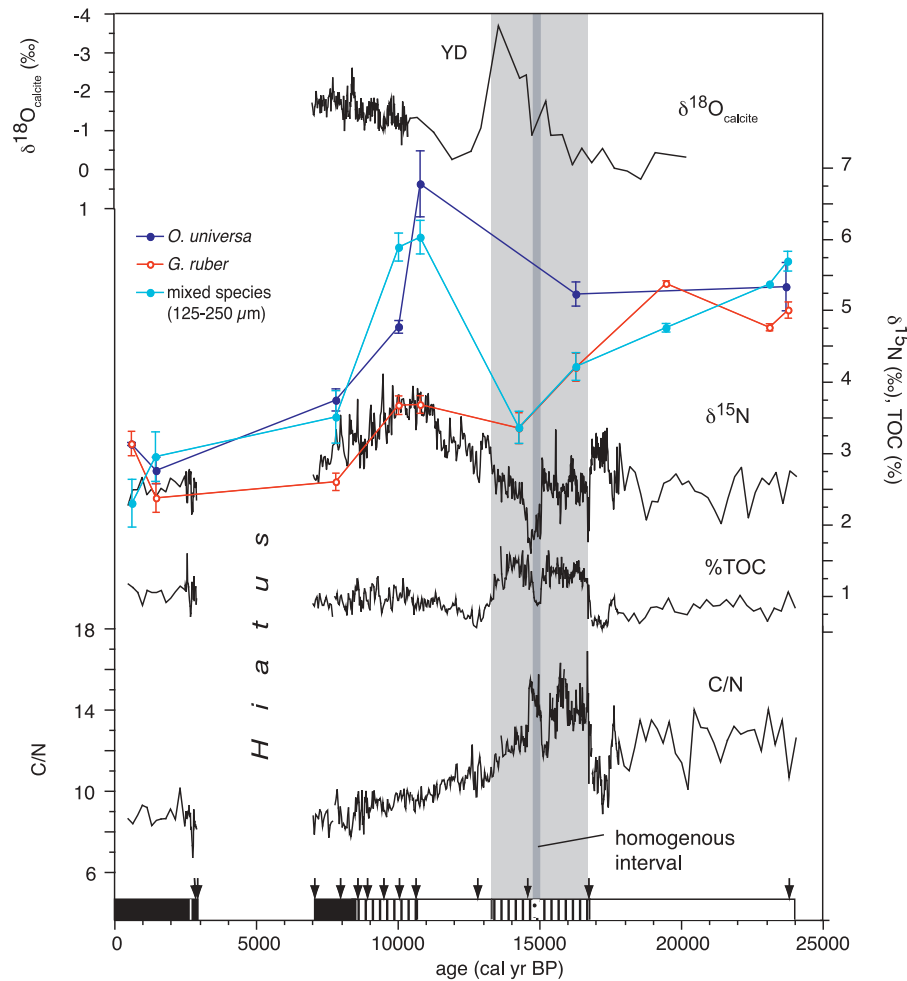
Figure 2. Bulk sediment and foraminifera-bound (FB) δ^{15}N records from Orca basin core MD02–2550 (this study) in comparison with %TOC, C/N and δ^{18}O from the same core [*Meckler et al.*, 2008]. Error bars on FB-δ^{15}N are 1 standard error of the mean where replicate analyses were performed (see Table 1). Lithology changes as described in the text are shown at the bottom (solid bar: black and laminated sediment, hatched bar: continuous laminations) and arrows specify depths of ^{14}C age control (see *Meckler et al.* [2008] for a description of the age model). Light shading indicates time of meltwater flow, corresponding to high %TOC and well-laminated sediment. YD signifies Younger Dryas.

nitrate in the thermocline of the subtropical Atlantic (around 2.6‰), likely reflecting the input and subsurface remineralization of newly fixed nitrogen [*Knapp et al.*, 2005, 2008]. While the hiatus between 2.8 and 7.0 ka prevents assessing the evolution of δ^{15}N through much of the Holocene, the early Holocene data before the hiatus suggest that the present-day low δ^{15}N values were almost reached by 7 ka. Thus, the substantial contribution of N_2-fixation to the thermocline nitrate pool in today's subtropical North Atlantic appears to have persisted for at least the last 3 kyr, if not through most of the Holocene.

[17] Further back in time, the different types of records have both similarities and differences. All three FB-δ^{15}N records, i.e., those of *G. ruber* and *O. universa* as well as that of the mixed species size fraction, show a clear difference between a glacial δ^{15}N of 4.8–5.7‰ and the lower Holocene values of 2.4–3.2‰ (Figure 2). But the different species diverge markedly during the deglaciation and early Holocene. The beginning of this species divergence occurs

around the time of peak deglacial meltwater input into the GOM, indicated by depleted δ^{18}O (Figure 2). In Orca Basin this interval is characterized by laminated sediments and elevated TOC concentrations (up to 1.6 wt%). Two of the FB-δ^{15}N records, the *O. universa* and the mixed species size fraction, exhibit a pronounced deglacial peak of δ^{15}N centered around 10 ka BP and reaching 6–7‰, whereas the deglacial peak is only very subtle in the *G. ruber* data. In contrast to FB-δ^{15}N, the bulk δ^{15}N record does not exhibit a clear glacial-to-Holocene difference. As in the FB-δ^{15}N data, a deglacial peak is apparent in the bulk δ^{15}N record centered at 9–11 ka. Maximum values during this peak (around 3.7‰) are much lower than peak δ^{15}N of *O. universa* and the mixed size fraction, but similar to the signal of *G. ruber*. During the meltwater interval, bulk δ^{15}N is similar to glacial and late Holocene values, except for a minimum of around 1.8 ‰ during and after the deposition of a homogenous interval in the core that is rich in terrigenous material [*Meckler et al.*, 2008].
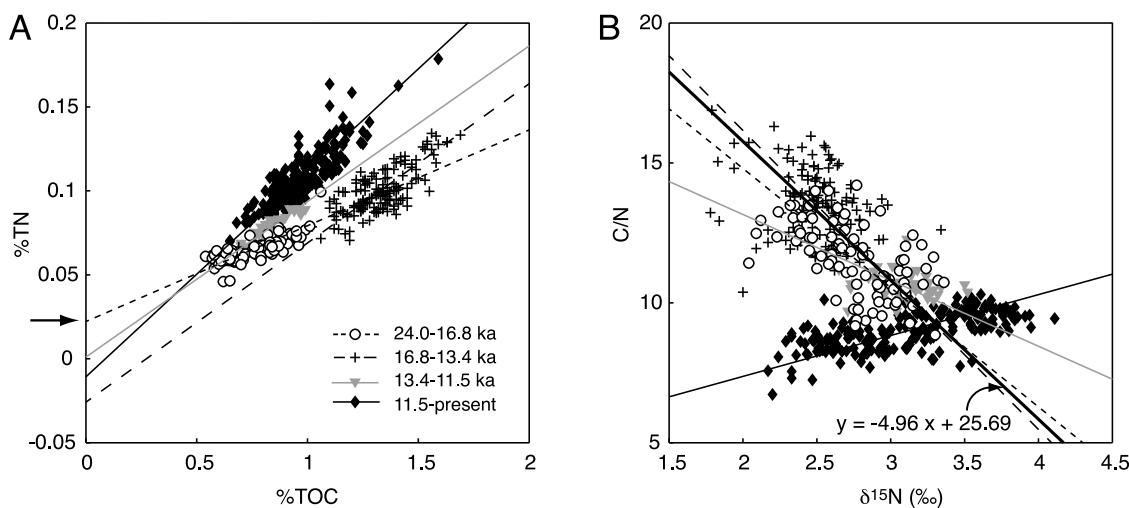
Figure 3. (a) Total nitrogen versus total organic carbon, grouped by age, and the respective regression lines (modified from *Meckler et al.* [2008]). Reduced Major Axis Regression was used instead of standard regression as in the work of *Meckler et al.* [2008], in order to minimize both y and x deviations from the regression line. Data from the homogenous interval (14.6–15.0 ka) are excluded. Only the oldest data group (24.0–16.8 ka) shows a significant positive intercept (arrow), indicating inorganic nitrogen contribution. (b) C/N versus bulk $\delta^{15}N$ for the four age groups with respective regression lines. Symbols as in Figure 3a. Also shown is the combined regression for all data older than 11.5 ka BP and its parameters. The slope of this line is used to correct bulk $\delta^{15}N$ for terrestrial inputs (see text and Figure 4).

[18] The potential reasons for the differences between the various records are manifold. Our working assumption is that the foraminifera-based $\delta^{15}N$ records are the most reliable recorders of the $\delta^{15}N$ of the nitrogen input to the euphotic zone, and that differences between the species reflect differences in their habitat, food, and trophic order. In contrast, we suspect that the bulk $\delta^{15}N$ was altered by the increased abundance of terrigenous organic matter prior to 11.5 ka. We furthermore suspect that greater concentrations of inorganic nitrogen in the glacial interval before around 17 ka further altered the bulk measurements. The most important lines of argument in support of this interpretation are that (1) bulk $\delta^{15}N$ is strongly negatively correlated with C/N (Figure 3b) in the glacial and deglacial part of the record before 11.5 ka, and that (2) a crossplot of TOC and TN has a positive intercept for the data prior to 13.4 ka (Figure 3a) [*Meckler et al.*, 2008]. High C/N ratios in organic matter are often a signal of terrestrial organic matter, whereas a positive intercept in the TOC-TN plot indicates the presence of inorganic nitrogen in the total nitrogen pool. Further support for the influence of terrestrial organic nitrogen on bulk $\delta^{15}N$ in the glacial and deglacial period comes from a correlation of $\delta^{13}C_{org}$ and $\delta^{15}N$ in these intervals (low $\delta^{13}C_{org}$ being another indication for terrestrial organic matter), although the smaller number of data points makes this relationship less clear (Figure S1 of the auxiliary material).[1] As both terrestrial organic nitrogen and inorganic nitrogen usually have a lower $\delta^{15}N$ than marine organic nitrogen [*Calvert et al.*, 2001; *Meyers*, 1997; *Peters et al.*, 1978; *Schubert and Calvert*, 2001], a larger contribution of these nitrogen sources would lower the bulk sediment $\delta^{15}N$, explaining the difference between bulk and FB-$\delta^{15}N$ before 11.5 ka. After

11.5 ka, in contrast, the negative correlation between $\delta^{15}N$ and C/N breaks down (Figure 3b). Instead, in this interval a slight positive correlation between $\delta^{15}N$ and C/N is observed, which is due to the Holocene $\delta^{15}N$ decrease coinciding with a subtle decrease in C/N. This subtle early to-late Holocene trend is also seen in $\delta^{13}C_{org}$ [*Meckler et al.*, 2008] and likely reflects a continued small decrease in the contribution of terrestrial organic matter. This reversed relationship of proxies for terrestrial organic matter and bulk $\delta^{15}N$ in the Holocene and the good correspondence of bulk $\delta^{15}N$ with FB-$\delta^{15}N$ of *G. ruber* argue that the Holocene decrease in bulk $\delta^{15}N$ from the deglacial maximum is not caused by changes in the input of terrestrial material.

[19] Other potential influences on bulk $\delta^{15}N$ that generally need to be considered, such as diagenetic alteration and variations in nutrient consumption, are unlikely to affect the Orca Basin record. Although the redox conditions in the water column varied in the course of the history of Orca Basin, lithologic changes (from bioturbated to laminated and to black sediment) in the core do not coincide consistently with shifts in $\delta^{15}N$, making such changes seem unlikely as a source of major artifacts. Rather, from the last ice age to the present, the Orca Basin seems to belong to the high-accumulation, organic-rich sites where little or no diagenetic alteration of the $\delta^{15}N$ record is observed [*Altabet et al.*, 1999; *Thunell et al.*, 2004]. Changes in the completeness of nitrate consumption are unlikely given the oligotrophic nature of the open GOM. Furthermore, this would have affected both bulk and FB-$\delta^{15}N$ in a similar manner.

3.1. Correction of the Bulk Sediment $\delta^{15}N$ Record

[20] The anti-correlation between bulk $\delta^{15}N$ and the C/N ratio in the older parts of the record provides a basis for correcting the bulk $\delta^{15}N$ record for terrestrial inputs and to estimate the $\delta^{15}N$ of marine organic matter. To this end,
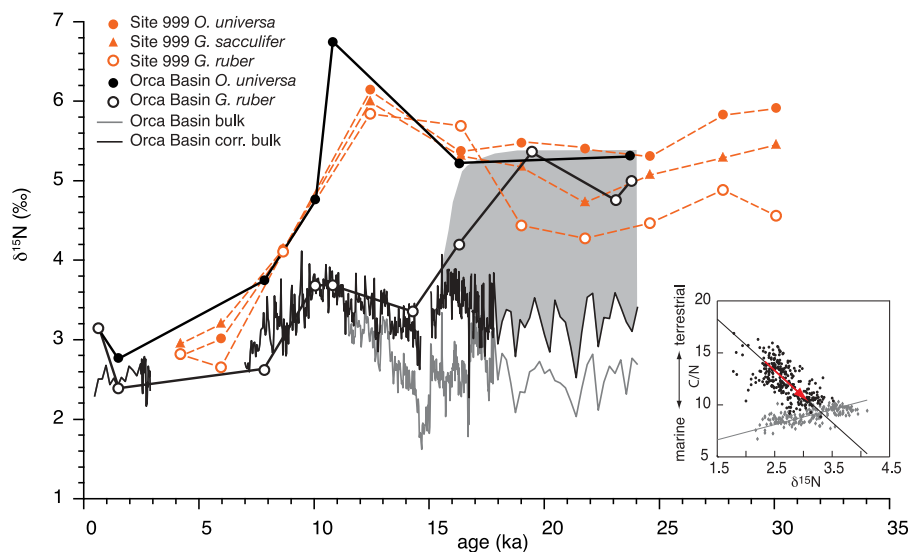
Figure 4. Comparison of Orca Basin FB-δ^{15}N, corrected bulk δ^{15}N from Orca Basin, and FB-δ^{15}N from ODP site 999 in the Caribbean Sea [*Ren et al.*, 2009]. The inset illustrates the correction of bulk δ^{15}N before 11.5 ka by shifting data along the regression line of C/N versus δ^{15}N to C/N = 9. For the correction, data from the homogenous interval (14.6–15.0 ka) were excluded. Grey shaded area depicts range of results of a sensitivity test for additional correction of bulk δ^{15}N for N_{inorg} (see auxiliary material).

we move the data points along the regression line for all data older than 11.5 ka to a C/N ratio of 9, the mean value of the Holocene data group ($\delta^{15}N_{corr} = ((9 - r_{C/N}) / -4.96) + \delta^{15}N$; Figure 4). Because using individual regression lines for different age groups does not change the general picture, we applied the same correction to all pre-11.5 ka data. A more thorough analysis would require determining the terrestrial end-member value and calculating the exact mixing line. However, as we do not have sufficient constraints for the nitrogen isotopic composition of the terrestrial end-member, we are using this linear approximation.

[21] The correction increases the δ^{15}N of bulk marine organic matter during the glacial by almost 1‰, suggesting that the "true" (i.e., marine) δ^{15}N values during the glacial period were about 1‰ more positive than during the Holocene, and as high as during the deglacial δ^{15}N peak observed in the uncorrected record (Figure 4). Hence, the corrected bulk δ^{15}N record supports the conclusions drawn from the FB-δ^{15}N data that the δ^{15}N of marine organic matter was significantly higher during the last glacial compared to the Holocene. Still, the bulk record shows a substantially smaller change than indicated by the FB-δ^{15}N data.

[22] However, the C/N ratio data suffer from ambiguities involving a possible inorganic nitrogen contribution. Inorganic nitrogen would work to lower the glacial C/N ratios to some extent, erasing the signal of terrestrial organic matter input while most likely contributing additional low-δ^{15}N nitrogen to the sediment [*Schubert and Calvert*, 2001]. Therefore, the correlation between δ^{15}N and C/N yields a conservative estimate for the impact of terrestrial inputs, especially in the glacial part of the record before 16.8 ka, when inorganic nitrogen seems to be present in significantly larger amounts. Since the estimate of N_{inorg} contribution from the intercept of the TOC-TN regression (Figure 3a) is only a rough approximation and depends on the definition of

group boundaries (Figure S2 of the auxiliary material), we did not correct C/N ratios for inorganic nitrogen. However, a sensitivity test using different possible ways for an N_{inorg} correction of C/N reveals that a bulk δ^{15}N record that is corrected for both terrestrial and inorganic nitrogen contributions can be as high as 5.5‰ in the glacial sediment (Figure S2 and gray shaded area in Figure 4), which would bring the bulk record into good agreement with FB-δ^{15}N. Hence, the divergence between bulk and FB-δ^{15}N in the glacial section of the core can be fully explained by the effects of significant terrigenous organic and inorganic nitrogen input. In the following, we only apply the C/N-based correction, as we regard the correction for the inorganic contribution as overly sensitive to assumptions.

3.2. Regional Comparison

[23] Comparison of the FB-δ^{15}N data from Orca Basin with a deglacial FB-δ^{15}N record from the close-by Ocean Drilling Program Site 999 in the Colombian Basin of the Caribbean Sea [*Ren et al.*, 2009] reveals very similar glacial and late Holocene values at the two sites (Figure 4). Furthermore, throughout the records, *O. universa* δ^{15}N is almost identical at the two locations, with a glacial-to-interglacial decrease of around 2.6‰ and a clear deglacial peak. The Caribbean and the GOM are located along the same path of surface and intermediate waters from the tropical to the subtropical North Atlantic, with the GOM being downstream of the Caribbean. The consistent glacial-to-interglacial decrease in FB-δ^{15}N therefore confirms the previous interpretation of a region-wide increase in N_2-fixation from the last ice age to the Holocene, lowering the thermocline nitrate δ^{15}N [*Ren et al.*, 2009]. The similarity of the *O. universa* signal at the two sites throughout the records suggests that this subsurface dwelling species is the best recorder of such changes in regional thermocline nitrate δ^{15}N. In addition to changes in regional N_2-fixation,

the subsurface nitrate $\delta^{15}N$ is influenced by variations in mean ocean nitrate $\delta^{15}N$, which is likely the cause for the observed deglacial peak in *O. universa* $\delta^{15}N$. Such a maximum has been proposed based on similar deglacial features in $\delta^{15}N$ records from diverse settings worldwide [e.g., *Altabet et al.*, 2002; *Galbraith et al.*, 2004; *Ganeshram et al.*, 2000; *Kao et al.*, 2008; *Meckler et al.*, 2007] and is predicted by models simulating the denitrification changes that occurred globally in sediments and the water column at the end of the last ice age [*Altabet and Curry*, 1989; *Deutsch et al.*, 2004].

[24] In contrast to *O. universa*, the FB-$\delta^{15}N$ of the mixed layer dwelling species *G. ruber* shows clear differences between Orca Basin and Site 999 until values converge in the late Holocene. While *G. ruber* $\delta^{15}N$ in the Orca Basin is slightly higher than at Site 999 during the last glacial maximum, the deglacial and early Holocene parts of the records from about 17 ka to 8 ka are characterized by much lower *G. ruber* $\delta^{15}N$ in the GOM compared to the Caribbean. The cause of this difference between the two sites and the divergence between species at Orca Basin during the deglacial period is as yet a mystery. One option is that the deglacial and early Holocene GOM was characterized by much stronger depth gradients in the $\delta^{15}N$ of particulate organic nitrogen (PON) compared to the Caribbean Sea. In addition, *G. ruber* lives near the sea surface and is therefore likely more susceptible than *O. universa* to local influences affecting the surface ocean.

[25] One difference between the two core sites is the proximity of Orca Basin to the Mississippi River, which was even greater when sea level was lower during the last ice age. Furthermore, large amounts of freshwater from the melting Laurentide ice sheet were delivered to the GOM during deglaciation. The potential influence of the Mississippi input on Orca Basin FB-$\delta^{15}N$ is twofold. First, input of isotopically light dissolved or small particulate nitrogen could have decreased the isotopic composition of surface plankton, and second, the freshwater input could have led to a stronger stratification of the water column compared to today. However, the timing of meltwater input and sea level rise likely caused these influences to decrease with time through the deglaciation. The (*G. ruber*-based) $\delta^{18}O$ record from Orca Basin (Figure 2) [*Flower et al.*, 2004; *Meckler et al.*, 2008] shows that the meltwater input was most pronounced before the Younger Dryas, i.e., before 12.9 ka, and mostly ceased afterwards due to rerouting of the meltwater toward the northern North Atlantic. In contrast, the largest inter-species divergence in $\delta^{15}N$ is observed after this input had declined. The deglacial rise in sea level continuously increased the distance between Mississippi river mouth and Orca Basin from 19 ka onwards, and the Orca Basin $\delta^{18}O_{seawater}$ record [*Flower et al.*, 2004] shows no sign of a substantial change in salinity after the Younger Dryas. Hence, the Mississippi-related influences might have contributed to the earlier part of the species divergence in FB-$\delta^{15}N$ at Orca Basin and the difference in *G. ruber* $\delta^{15}N$ between Orca Basin and Site 999, but they appear to have inappropriate timing to explain the long duration of this $\delta^{15}N$ difference through the Younger Dryas and into the Holocene.

[26] Another potential factor is a local increase in N_2-fixation confined to the GOM, affecting mostly the PON and recycled nitrogen in the surface mixed layer, while not

strongly altering the $\delta^{15}N$ of thermocline nitrate. The large-scale circulation in the region is dominated by the Caribbean Current, which brings waters from the tropical Atlantic into the Caribbean, and then flows around the Yucatan peninsula into the Gulf of Mexico as the Loop Current, before exiting again around the southern tip of Florida. Due to this surface-intensified circulation much of the isotopic imprint of N_2-fixation occurring in surface waters in the GOM might therefore be exported laterally into the North Atlantic instead of accumulating in the GOM thermocline, where it would be recorded by the thermocline dwelling *O. universa*. Thermocline nitrate $\delta^{15}N$ at Orca Basin instead likely reflects the integrated isotopic imprint of the N_2-fixation that occurs in tropical Atlantic waters as they flow northward [*Deutsch et al.*, 2007; *Knapp et al.*, 2008; *Moore et al.*, 2009], explaining the good correspondence of the $\delta^{15}N$ of *O. universa* at the Caribbean Site 999 and Orca Basin. *G. ruber* $\delta^{15}N$, in contrast, would be more sensitive to variations in local surface water N_2-fixation in such a system, and would be expected to reflect a combination of variations in thermocline nitrate $\delta^{15}N$ and local surface inputs of nitrogen. If this interpretation is correct, then the strength of local N_2-fixation should be reflected by the magnitude of the difference between *G. ruber* and *O. universa* $\delta^{15}N$, suggesting that N_2-fixation rates in the vicinity of Orca Basin peaked during deglaciation. During the early Holocene, in contrast, the difference between the two species stays approximately constant, suggesting that the decrease in FB- and bulk $\delta^{15}N$ during this time might be due to a combination of a more regional N_2-fixation increase further south and the proposed decrease in mean ocean nitrate $\delta^{15}N$ after the deglacial peak [*Deutsch et al.*, 2004]. It is important to note that at Site 999 in the Caribbean, the opposite trend in species differences has been observed, with records converging at around 16 ka. This discrepancy between the sites could be due to differences in the extent to which subsurface $\delta^{15}N$ variations are overprinted by local processes, or in the extent to which surface $\delta^{15}N$ changes penetrate through the euphotic zone. We hope to test our interpretation of inter-species differences in FB-$\delta^{15}N$ at both sites with further work in the Caribbean Sea and Gulf of Mexico as part of a broader effort to develop a mechanistic understanding of FB-$\delta^{15}N$ differences among species.

[27] A possible influence on FB-$\delta^{15}N$ that is difficult to constrain is a change in food source of the heterotrophic foraminifera. Since each trophic level is characterized by an increase in the $\delta^{15}N$ of organic tissue by about 3.5‰ [*Altabet*, 1988; *Deniro and Epstein*, 1981; *Montoya et al.*, 2002], a change in preference of phytoplankton versus zooplankton as food source, for example, would affect the $\delta^{15}N$ of foraminifera. However, the good regional correspondence of the *O. universa* records and the agreement of *G. ruber* $\delta^{15}N$ with corrected bulk $\delta^{15}N$ at Orca Basin argue for changes in the $\delta^{15}N$ of the nitrate and PON pools as discussed above as the primary reason for the observed variations in FB-$\delta^{15}N$.

[28] Together, the records from the Orca and Colombian Basins argue clearly for a higher glacial $\delta^{15}N$ of tropical Atlantic thermocline nitrate, indicating that the regional N_2-fixation rate was reduced during the last ice age. This result also suggests that Fe input is not the crucial factor determining the temporal changes in the N_2-fixation rates in this
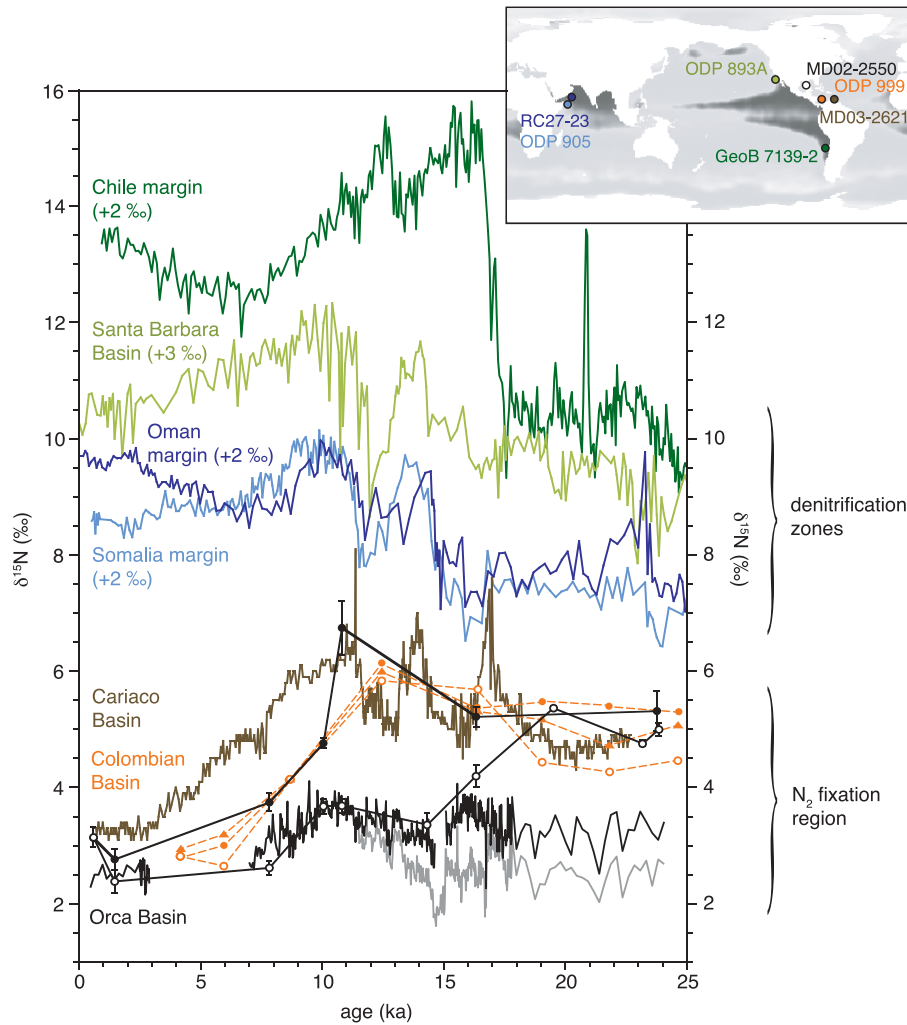
Figure 5. Global comparison of $\delta^{15}N$ records for Termination I. Shown are records from denitrification zones in the east Pacific off Chile [*De Pol-Holz et al.*, 2006] and off California (Santa Barbara Basin) [*Emmer and Thunell*, 2000], and the Arabian Sea off Oman [*Altabet et al.*, 2002] and off Somalia [*Ivanochko et al.*, 2005] in comparison with the data from Cariaco Basin off Venezuela [*Meckler et al.*, 2007], Colombian Basin [*Ren et al.*, 2009], and Orca Basin (this study). The uncorrected record from Orca Basin is shown in gray, and FB-$\delta^{15}N$ is shown by filled (*O. universa*) and open (*G. ruber*) circles. The inset shows the core locations on a map displaying the major oxygen minimum zones (dark gray), where most of the global water column denitrification is occurring. Some records are shifted for better comparison.

region and on the timescales we are investigating, since the likely greater ice age input of dust and iron to the tropical and subtropical Atlantic [*Mahowald et al.*, 1999] did not cause a corresponding increase in N$_2$-fixation rates. This might be due to the presently already high iron input into this region.

3.3. Global Implications

[29] With no evidence of glacial N$_2$-fixation having responded to increased inputs of atmospheric dust to the Atlantic, why then was N$_2$-fixation lower during glacial periods, and what is the temporal relationship of the changes in marine N$_2$-fixation in the Atlantic with the changes in water column denitrification in the Indo-Pacific? The Orca Basin record is from an oligotrophic regime that is distant from the Indo-Pacific regions of water column denitrification

in a region where N$_2$-fixation is the dominant control on the $\delta^{15}N$ difference of nitrate in the thermocline from that of mean ocean nitrate [*Knapp et al.*, 2008]. Hence, we can use the data in comparison with the other available records to assess the interplay of denitrification and N$_2$-fixation as well as changes in mean ocean nitrate $\delta^{15}N$.

[30] It is widely accepted that water column denitrification increased from lower glacial levels in the major water column suboxic zones of the eastern Pacific and Arabian Sea. This shift is well documented by several high-resolution nitrogen isotope records, showing a deglacial increase in $\delta^{15}N$, with a superimposed deglacial peak or double peak (Figure 5). In the Eastern North Pacific and the Arabian Sea, the strongest increase is observed at around 15 ka, the peak is interrupted by low Younger Dryas values, and the early Holocene decrease commences at around 10–9 ka [e.g.,

Altabet et al., 2002; *Emmer and Thunell*, 2000; *Ivanochko et al.*, 2005; *Pride et al.*, 1999]. In the Eastern South Pacific, the trends appear similar, but suggest a southern hemispheric timing, with the increase in $\delta^{15}N$ starting already at around 18–17 ka and a temporary minimum during the Antarctic cold reversal [*De Pol-Holz et al.*, 2006; *Higginson and Altabet*, 2004].

[31] The overall last glacial-to-Holocene decrease in the different $\delta^{15}N$ records from the Orca Basin and those from the Caribbean suggest that local to tropical Atlantic-scale N_2-fixation responded to this global increase in denitrification [*Meckler et al.*, 2007; *Ren et al.*, 2009]. If correct, this lends strong support to the proposed N/P ratio feedback [e.g., *Codispoti*, 1989; *Gruber*, 2004; *Haug et al.*, 1998; *Tyrrell*, 1999], which would work to stabilize the global marine nitrogen budget on glacial-interglacial timescales. The strength of the feedback and hence the timescale of the N_2-fixation response determines the amount of nitrogen that is lost from the ocean during deglaciation [*Deutsch et al.*, 2004]. The identification of the exact onset of N_2-fixation is hampered by the confounding imprint of the apparent deglacial peak in mean ocean nitrate on the records from the GOM and the Caribbean Sea. However, in the Orca Basin record, the divergence between the *O. universa* $\delta^{15}N$ (interpreted as being dominated by changes in thermocline nitrate $\delta^{15}N$) on the one hand, and the *G. ruber* and corrected bulk $\delta^{15}N$ (interpreted as including a shallow mixed layer signal) on the other hand, suggests an onset of N_2-fixation before 16 ka at this location. While a possible influence of meltwater-related nutrient input into GOM surface waters at the beginning of this divergence has to be acknowledged, the observed timing would suggest a tight coupling of N_2-fixation in the Atlantic to global changes in denitrification, minimizing the deglacial loss of fixed nitrogen from the ocean. In order to further investigate the question of glacial-interglacial changes in the marine nitrogen budget, an assessment of changes in N_2-fixation in the other ocean basins and their timing is necessary.

[32] In both Orca Basin and the Colombian Basin (Site 999), the overall decrease in $\delta^{15}N$ is largely completed in the early Holocene. In contrast, a $\delta^{15}N$ record from the Cariaco Basin off Venezuela shows a two-step decrease reaching into the late Holocene [*Meckler et al.*, 2007] (Figure 5). The second part of the decrease was interpreted to reflect a re-establishment of Saharan dust input after it had ceased in the early Holocene during the African Humid Period [*Adkins et al.*, 2006]. That this later decrease in $\delta^{15}N$ is not observed further north in the GOM and in the West Caribbean suggests that the inferred late increase in N_2-fixation is either local to the Cariaco Basin or confined to the tropical Atlantic. It is possible that the Intertropical Convergence Zone acted as a rain curtain for Saharan dust in the region of the Cariaco Basin until it migrated adequately southward over the course of the Holocene [*Haug et al.*, 2001]. Interestingly, several $\delta^{15}N$ records from various settings worldwide show late Holocene changes in $\delta^{15}N$ in either direction [e.g., *Altabet et al.*, 2002; *De Pol-Holz et al.*, 2006; *Emmer and Thunell*, 2000; *Kienast et al.*, 2008; *Pride et al.*, 1999] (Figure 5). The fact that not all records show such late changes might suggest that these are independent of the larger deglacial reorganizations in the marine nitrogen cycle

and instead confined to sites sensitive to Holocene variations in climatic forcing such as the Intertropical Convergence Zone migration.

4. Conclusions

[33] The Orca Basin data add to previous evidence for proposed feedbacks within the nitrogen cycle that stabilize the marine nitrogen budget on glacial-interglacial timescales [*Galbraith et al.*, 2004; *Haug et al.*, 1998; *Kienast*, 2000; *Meckler et al.*, 2007; *Ren et al.*, 2009; *Tyrrell*, 1999]. While the bulk sediment $\delta^{15}N$ record at face value exhibits similar values during the glacial and Holocene, the combined sediment data from the Orca Basin suggest that the bulk $\delta^{15}N$ was lowered by terrigenous nitrogen input during glacial times. When a C/N ratio-based correction is applied, marine $\delta^{15}N$ is found to have decreased by $\geq 1‰$ from the last glacial maximum to the late Holocene. The FB-$\delta^{15}N$ data support this evidence for a decrease in marine $\delta^{15}N$ since the last ice age. Together with FB-$\delta^{15}N$ data from the Colombian Basin and bulk sediment $\delta^{15}N$ data from the Cariaco Basin, these results argue against a strong sensitivity of N_2-fixation on dust input on glacial-interglacial timescales in the subtropical West Atlantic and support instead a view that the magnitude of N_2-fixation in the Atlantic is dominantly coupled to that of water column denitrification in the Indo-Pacific Ocean.

[34] The divergence of FB-$\delta^{15}N$ data from *G. ruber* and *O. universa* during the deglaciation and early Holocene is interpreted to reflect stronger vertical gradients in the $\delta^{15}N$ of PON during these times. While a meltwater-related input of low-$\delta^{15}N$ nitrogen and/or increase in stratification may affect this difference during the deglaciation, the persistence into the Holocene suggests that the divergence reflects an early increase in N_2-fixation affecting primarily the surface mixed layer where *G. ruber* dwells. Based on this interpretation, N_2-fixation would have started to increase sometime before 16 ka in the Gulf of Mexico, quickly after global sedimentary and water column denitrification are thought to have increased. Such a rapid response would suggest a strong feedback between denitrification and N_2-fixation, limiting nitrogen losses from the ocean during deglaciation.

[35] However, testing of this interpretation regarding the timing of the N_2-fixation increase will require further work on the controls of FB-$\delta^{15}N$. In particular, the divergence among different foraminifera species was not observed upon deglaciation in the Caribbean Sea [*Ren et al.*, 2009], where in fact a deglacial convergence of FB-$\delta^{15}N$ of various species was found. This difference between the two sites may result from a stronger local signal of N_2-fixation in the mixed layer of the Gulf of Mexico than in the open Caribbean, but this is only one of many possible interpretations.

[36] Bulk sedimentary $\delta^{15}N$ is the most widely used proxy for changes in the marine nitrogen cycle, as it very efficiently obtained. This study highlights one of the limitations of this proxy when applied in continental margin settings where terrestrial overprint is likely, while also suggesting the utility of correcting the isotopic data based on other bulk sediment parameters. Furthermore, the similarity of the bulk and foraminifera-bound $\delta^{15}N$ records in the Holocene suggests that the two proxies do converge under optimal conditions.

References

Addy, S. K., and E. W. Behrens (1980), Time of accumulation of hypersaline anoxic brine in Orca Basin (Gulf of Mexico), *Mar. Geol.*, *37*(3–4), 241–252, doi:10.1016/0025-3227(80)90104-8.

Adkins, J., P. deMenocal, and G. Eshel (2006), The "African humid period" and the record of marine upwelling from excess Th-230 in Ocean Drilling Program Hole 658C, *Paleoceanography*, *21*(4), PA4203, doi:10.1029/2005PA001200.

Altabet, M. A. (1988), Variations in nitrogen isotopic composition between sinking and suspended particles: Implications for nitrogen cycling and particle transformation in the open ocean, *Deep Sea Res.*, *35*(4), 535–554, doi:10.1016/0198-0149(88)90130-6.

Altabet, M. A. (2007), Constraints on oceanic N balance/imbalance from sedimentary N-15 records, *Biogeosciences*, *4*(1), 75–86, doi:10.5194/bg-4-75-2007.

Altabet, M. A., and W. B. Curry (1989), Testing models of past ocean chemistry using foraminifera 15N/14N, *Global Biogeochem. Cycles*, *3*(2), 107–119, doi:10.1029/GB003i002p00107.

Altabet, M. A., R. Francois, D. W. Murray, and W. L. Prell (1995), Climate-related variations in denitrification in the Arabian Sea from sediment N-15/N-14 ratios, *Nature*, *373*(6514), 506–509, doi:10.1038/373506a0.

Altabet, M. A., C. Pilskaln, R. Thunell, C. Pride, D. Sigman, F. Chavez, and R. Francois (1999), The nitrogen isotope biogeochemistry of sinking particles from the margin of the Eastern North Pacific, *Deep Sea Res., Part I*, *46*(4), 655–679, doi:10.1016/S0967-0637(98)00084-3.

Altabet, M. A., M. J. Higginson, and D. W. Murray (2002), The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO$_2$, *Nature*, *415*(6868), 159–162, doi:10.1038/415159a.

Braman, R. S., and S. A. Hendrix (1989), Nanogram nitrite and nitrate determination in environmental and biological-materials by vanadium (III) reduction with chemi-luminescence detection, *Anal. Chem.*, *61*(24), 2715–2718, doi:10.1021/ac00199a007.

Brandes, J. A., and A. H. Devol (1997), Isotopic fractionation of oxygen and nitrogen in coastal marine sediments, *Geochim. Cosmochim. Acta*, *61*(9), 1793–1801, doi:10.1016/S0016-7037(97)00041-0.

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.

Broecker, W. S., and G. M. Henderson (1998), The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO$_2$ changes, *Paleoceanography*, *13*(4), 352–364, doi:10.1029/98PA00920.

Brunelle, B. G., D. M. Sigman, M. S. Cook, L. D. Keigwin, G. H. Haug, B. Plessen, G. Schettler, and S. L. Jaccard (2007), Evidence from diatom-bound nitrogen isotopes for subarctic Pacific stratification during the last ice age and a link to North Pacific denitrification changes, *Paleoceanography*, *22*, PA1215, doi:10.1029/2005PA001205.

Calvert, S. E., T. F. Pedersen, and R. E. Karlin (2001), Geochemical and isotopic evidence for post-glacial palaeoceanographic changes in Saanich Inlet, British Columbia, *Mar. Geol.*, *174*(1–4), 287–305, doi:10.1016/S0025-3227(00)00156-0.

Capone, D. G., J. A. Burns, J. P. Montoya, A. Subramaniam, C. Mahaffey, T. Gunderson, A. F. Michaels, and E. J. Carpenter (2005), Nitrogen fixation by *Trichodesmium* spp.: An important source of new nitrogen to the tropical and subtropical North Atlantic Ocean, *Global Biogeochem. Cycles*, *19*, GB2024, doi:10.1029/2004GB002331.

Carpenter, E. J., and C. C. Price (1977), Nitrogen-fixation, distribution, and production of Oscillatoria (*Trichodesmium*) spp in western Sargasso and Caribbean seas, *Limnol. Oceanogr.*, *22*(1), 60–72, doi:10.4319/lo.1977.22.1.0060.

Carpenter, E. J., and K. Romans (1991), Major role of the cyanobacterium *Trichodesmium* in nutrient cycling in the North-Atlantic Ocean, *Science*, *254*(5036), 1356–1358, doi:10.1126/science.254.5036.1356.

Carpenter, E. J., A. Subramaniam, and D. G. Capone (2004), Biomass and primary productivity of the cyanobacterium *Trichodesmium* spp. in the

tropical N Atlantic Ocean, *Deep Sea Res., Part I*, *51*(2), 173–203, doi:10.1016/j.dsr.2003.10.006.

Casciotti, K. L., D. M. Sigman, M. G. Hastings, J. K. Bohlke, and A. Hilkert (2002), Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, *Anal. Chem.*, *74*(19), 4905–4912, doi:10.1021/ac020113w.

Christensen, J. P. (1994), Carbon export from continental shelves, denitrification and atmospheric carbon-dioxide, *Cont. Shelf Res.*, *14*(5), 547–576, doi:10.1016/0278-4343(94)90103-1.

Cline, J. D., and I. R. Kaplan (1975), Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean, *Mar. Chem.*, *3*, 271–299, doi:10.1016/0304-4203(75)90009-2.

Codispoti, L. A. (1989), Phosphorus vs. nitrogen limitation of new and export production, in *Productivity of the Ocean: Past and Present*, edited by W. H. Berger, V. S. Smetacek, and G. Wefer, pp. 377–394, John Wiley, Hoboken, N. J.

Codispoti, L. A. (2007), An oceanic fixed nitrogen sink exceeding 400 Tg Na-1 vs the concept of homeostasis in the fixed-nitrogen inventory, *Biogeosciences*, *4*(2), 233–253, doi:10.5194/bg-4-233-2007.

Deniro, M. J., and S. Epstein (1981), Influence of diet on the distribution of nitrogen isotopes in animals, *Geochim. Cosmochim. Acta*, *45*(3), 341–351, doi:10.1016/0016-7037(81)90244-1.

De Pol-Holz, R., O. Ulloa, L. Dezileau, J. Kaiser, F. Lamy, and D. Hebbeln (2006), Melting of the Patagonian Ice Sheet and deglacial perturbations of the nitrogen cycle in the eastern South Pacific, *Geophys. Res. Lett.*, *33*, L04704, doi:10.1029/2005GL024477.

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.

Deutsch, C., J. L. Sarmiento, D. M. Sigman, N. Gruber, and J. P. Dunne (2007), Spatial coupling of nitrogen inputs and losses in the ocean, *Nature*, *445*(7124), 163–167, doi:10.1038/nature05392.

Emmer, E., and R. C. Thunell (2000), Nitrogen isotope variations in Santa Barbara Basin sediments: Implications for denitrification in the eastern tropical North Pacific during the last 50,000 years, *Paleoceanography*, *15*(4), 377–387, doi:10.1029/1999PA000417.

Falkowski, P. G. (1997), Evolution of the nitrogen cycle and its influence on the biological sequestration of CO$_2$ in the ocean, *Nature*, *387*(6630), 272–275, doi:10.1038/387272a0.

Flower, B. P., D. W. Hastings, H. W. Hill, and T. M. Quinn (2004), Phasing of deglacial warming and Laurentide Ice Sheet meltwater in the Gulf of Mexico, *Geology*, *32*(7), 597–600, doi:10.1130/G20604.1.

Galbraith, E. D., M. Kienast, T. F. Pedersen, and S. E. Calvert (2004), Glacial-interglacial modulation of the marine nitrogen cycle by high-latitude O$_2$ supply to the global thermocline, *Paleoceanography*, *19*, PA4007, doi:10.1029/2003PA001000.

Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, and J. W. Murray (1995), Large changes in oceanic nutrient inventories from glacial to interglacial periods, *Nature*, *376*(6543), 755–758, doi:10.1038/376755a0.

Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, G. W. McNeill, and M. R. Fontugne (2000), Glacial-interglacial variability in denitrification in the world's oceans: Causes and consequences, *Paleoceanography*, *15*(4), 361–376, doi:10.1029/1999PA000422.

Goering, J. J., R. C. Dugdale, and D. W. Menzel (1966), Estimates of in situ rates of nitrogen uptake by *Trichodesmium* sp in tropical Atlantic Ocean, *Limnol. Oceanogr.*, *11*(4), 614–620, doi:10.4319/lo.1966.11.4.0614.

Gruber, N. (2004), The marine nitrogen cycle and atmospheric CO$_2$, in *Carbon-Climate Interactions*, edited by M. Follows and T. Oguz, pp. 97–148, John Wiley, New York.

Gruber, N., and J. N. Galloway (2008), An Earth-system perspective of the global nitrogen cycle, *Nature*, *451*(7176), 293–296, doi:10.1038/nature06592.

Gruber, N., and J. L. Sarmiento (1997), Global patterns of marine nitrogen fixation and denitrification, *Global Biogeochem. Cycles*, *11*(2), 235–266, doi:10.1029/97GB00077.

Haug, G. H., T. F. Pedersen, D. M. Sigman, S. E. Calvert, B. Nielsen, and L. C. Peterson (1998), Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr, *Paleoceanography*, *13*(5), 427–432, doi:10.1029/98PA01976.

Haug, G. H., K. A. Hughen, D. M. Sigman, L. C. Peterson, and U. Rohl (2001), Southward migration of the intertropical convergence zone through the Holocene, *Science*, *293*(5533), 1304–1308, doi:10.1126/science.1059725.

Higginson, M. J., and M. A. Altabet (2004), Initial test of the silicic acid leakage hypothesis using sedimentary biomarkers, *Geophys. Res. Lett.*, *31*, L18303, doi:10.1029/2004GL020511.

Hood, R. R., A. F. Michaels, and D. G. Capone (2000), Answers sought to the enigma of marine nitrogen fixation, *Eos Trans. AGU*, *81*(13), 133–139, doi:10.1029/00EO00086.

Ivanochko, T. S., R. S. Ganeshram, G. J. A. Brummer, G. Ganssen, S. J. A. Jung, S. G. Moreton, and D. Kroon (2005), Variations in tropical convection as an amplifier of global climate change at the millennial scale, *Earth Planet. Sci. Lett.*, *235*(1–2), 302–314, doi:10.1016/j.epsl.2005.04.002.

Jasper, J. P., and R. B. Gagosian (1990), The sources and deposition of organic-matter in the late Quaternary Pygmy Basin, Gulf of Mexico, *Geochim. Cosmochim. Acta*, *54*(4), 1117–1132, doi:10.1016/0016-7037(90)90443-O.

Jasper, J. P., and R. B. Gagosian (1993), The relationship between sedimentary organic-carbon isotopic composition and organic biomarker compound concentration, *Geochim. Cosmochim. Acta*, *57*(1), 167–186, doi:10.1016/0016-7037(93)90477-E.

Kao, S. J., K. K. Liu, S. C. Hsu, Y. P. Chang, and M. H. Dai (2008), North Pacific-wide spreading of isotopically heavy nitrogen during the last deglaciation: Evidence from the western Pacific, *Biogeosciences*, *5*(6), 1641–1650, doi:10.5194/bg-5-1641-2008.

Karl, D., A. Michaels, B. Bergman, D. Capone, E. Carpenter, R. Letelier, F. Lipschultz, H. Paerl, D. M. Sigman, and L. Stal (2002), Dinitrogen fixation in the world's oceans, *Biogeochemistry*, *57*(1), 47–98, doi:10.1023/A:1015798105851.

Kienast, M. (2000), Unchanged nitrogen isotopic composition of organic matter in the South China Sea during the last climatic cycle: Global implications, *Paleoceanography*, *15*(2), 244–253, doi:10.1029/1999PA000407.

Kienast, M., M. F. Lehmann, A. Timmermann, E. Galbraith, T. Bolliet, A. Holboum, C. Normandeau, and C. Laj (2008), A mid-Holocene transition in the nitrogen dynamics of the western equatorial Pacific: Evidence of a deepening thermocline?, *Geophys. Res. Lett.*, *35*, L23610, doi:10.1029/2008GL035464.

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.

Knapp, A. N., P. J. DiFiore, C. Deutsch, D. M. Sigman, and F. Lipschultz (2008), Nitrate isotopic composition between Bermuda and Puerto Rico: Implications for N-2 fixation in the Atlantic Ocean, *Global Biogeochem. Cycles*, *22*, GB3014, doi:10.1029/2007GB003107.

Kustka, A. B., S. A. Sañudo-Wilhelmy, E. J. Carpenter, D. Capone, J. Burns, and W. G. Sunda (2003), Iron requirements for dinitrogen- and ammonium-supported growth in cultures of *Trichodesmium* (IMS 101): Comparison with nitrogen fixation rates and iron: carbon ratios of field populations, *Limnol. Oceanogr.*, *48*(5), 1869–1884, doi:10.4319/lo.2003.48.5.1869.

Lehmann, M. F., D. M. Sigman, and W. M. Berelson (2004), Coupling the N-15/N-14 and O-18/O-16 of nitrate as a constraint on benthic nitrogen cycling, *Mar. Chem.*, *88*(1–2), 1–20, doi:10.1016/j.marchem.2004.02.001.

Lenes, J. M., et al. (2001), Iron fertilization and the *Trichodesmium* response on the west Florida shelf, *Limnol. Oceanogr.*, *46*(6), 1261–1277, doi:10.4319/lo.2001.46.6.1261.

Liu, K. K., and I. R. Kaplan (1989), The eastern tropical Pacific as a source of N-15-enriched nitrate in seawater off southern California, *Limnol. Oceanogr.*, *34*(5), 820–830, doi:10.4319/lo.1989.34.5.0820.

Mahowald, N., K. Kohfeld, M. Hansson, Y. Balkanski, S. P. Harrison, I. C. Prentice, M. Schulz, and H. Rodhe (1999), Dust sources and deposition during the last glacial maximum and current climate: A comparison of model results with paleodata from ice cores and marine sediments, *J. Geophys. Res.*, *104*(D13), 15,895–15,916, doi:10.1029/1999JD900084.

Meckler, A. N., G. H. Haug, D. M. Sigman, B. Plessen, L. C. Peterson, and H. R. Thierstein (2007), Detailed sedimentary N isotope records from Cariaco Basin for terminations I and V: Local and global implications, *Global Biogeochem. Cycles*, *21*, GB4019, doi:10.1029/2006GB002893.

Meckler, A. N., C. J. Schubert, P. A. Hochuli, B. Plessen, D. Birgel, B. P. Flower, K. U. Hinrichs, and G. H. Haug (2008), Glacial to Holocene terrigenous organic matter input to sediments from Orca Basin, Gulf of Mexico: A combined optical and biomarker approach, *Earth Planet. Sci. Lett.*, *272*(1–2), 251–263, doi:10.1016/j.epsl.2008.04.046.

Mehra, O. P., and M. L. Jackson (1958), Iron oxide removal from soils and clays by a dithionite citrate system buffered with sodium bicarbonate, *Clays Clay Miner.*, *7*, 317–327, doi:10.1346/CCMN.1958.0070122.

Meyers, P. A. (1997), Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes, *Org. Geochem.*, *27*(5–6), 213–250, doi:10.1016/S0146-6380(97)00049-1.

Michaels, A. F., D. Olson, J. L. Sarmiento, J. W. Ammerman, K. Fanning, R. Jahnke, A. H. Knap, F. Lipschultz, and J. M. Prospero (1996), Inputs, losses and transformations of nitrogen and phosphorus in the pelagic North Atlantic Ocean, *Biogeochemistry*, *35*(1), 181–226, doi:10.1007/BF02179827.

Mills, M. M., C. Ridame, M. Davey, J. La Roche, and R. J. Geider (2004), Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, *Nature*, *429*(6989), 292–294, doi:10.1038/nature02550.

Montoya, J. P., E. J. Carpenter, and D. G. Capone (2002), Nitrogen fixation and nitrogen isotope abundances in zooplankton of the oligotrophic North Atlantic, *Limnol. Oceanogr.*, *47*(6), 1617–1628, doi:10.4319/lo.2002.47.6.1617.

Montoya, J. P., M. Voss, and D. G. Capone (2007), Spatial variation in N_2-fixation rate and diazotroph activity in the tropical Atlantic, *Biogeosciences*, *4*(3), 369–376, doi:10.5194/bg-4-369-2007.

Moore, C. M., et al. (2009), Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability, *Nat. Geosci.*, *2*(12), 867–871, doi:10.1038/ngeo667.

Newman, J. W., P. L. Parker, and E. W. Behrens (1973), Organic carbon isotope rations in Quaternary cores from Gulf of Mexico, *Geochim. Cosmochim. Acta*, *37*(2), 225–238, doi:10.1016/0016-7037(73)90130-0.

Northam, M. A., D. J. Curry, R. S. Scalan, and P. L. Parker (1981), Stable carbon isotope ratio variations of organic-matter in Orca Basin sediments, *Geochim. Cosmochim. Acta*, *45*(2), 257–260, doi:10.1016/0016-7037(81)90171-X.

Nydahl, F. (1978), On the peroxodisulphate oxidation of total nitrogen in waters to nitrate, *Water Res.*, *12*, 1123–1130, doi:10.1016/0043-1354(78)90060-X.

Peters, K. E., R. E. Sweeney, and I. R. Kaplan (1978), Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic-matter, *Limnol. Oceanogr.*, *23*(4), 598–604, doi:10.4319/lo.1978.23.4.0598.

Pride, C., R. Thunell, D. Sigman, L. Keigwin, M. Altabet, and E. Tappa (1999), Nitrogen isotopic variations in the Gulf of California since the last deglaciation: Response to global climate change, *Paleoceanography*, *14*(3), 397–409, doi:10.1029/1999PA900004.

Ren, H. (2010), Development and paleoceanographic application of planktonic foraminifera-bound nitrogen isotopes, Ph.D. thesis, 248 pp, Princeton Univ., Princeton, N. J.

Ren, H., D. M. Sigman, A. N. Meckler, B. Plessen, R. S. Robinson, Y. Rosenthal, and G. H. Haug (2009), Foraminiferal isotope evidence of reduced nitrogen fixation in the Ice Age Atlantic Ocean, *Science*, *323*(5911), 244–248, doi:10.1126/science.1165787.

Rueter, J. G., D. A. Hutchins, R. W. Smith, and N. L. Unsworth (1992), Iron nutrition in *Trichodesmium*, in *Marine Pelagic Cyanobacteria: Trichodesmium and Other Diazotrophs*, edited by E. J. Carpenter, D. G. Capone, and J. G. Rueter, pp. 289–306, Kluwer Acad., Dordrecht, Netherlands.

Sackett, W. M., J. M. Brooks, B. B. Bernard, C. R. Schwab, H. Chung, and R. A. Parker (1979), Carbon inventory for Orca Basin brines and sediments, *Earth Planet. Sci. Lett.*, *44*(1), 73–81, doi:10.1016/0012-821X(79)90009-8.

Sañudo-Wilhelmy, S. A., A. B. Kustka, C. J. Gobler, D. A. Hutchins, M. Yang, K. Lwiza, J. Burns, D. G. Capone, J. A. Raven, and E. J. Carpenter (2001), Phosphorus limitation of nitrogen fixation by *Trichodesmium* in the central Atlantic Ocean, *Nature*, *411*(6833), 66–69, doi:10.1038/35075041.

Schubert, C. J., and S. E. Calvert (2001), Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: Implications for nutrient utilization and organic matter composition, *Deep Sea Res., Part I*, *48*(3), 789–810, doi:10.1016/S0967-0637(00)00069-8.

Sebilo, M., G. Billen, M. Grably, and A. Mariotti (2003), Isotopic composition of nitrate-nitrogen as a marker of riparian and benthic denitrification at the scale of the whole Seine River system, *Biogeochemistry*, *63*(1), 35–51, doi:10.1023/A:1023362923881.

Shokes, R. F., P. K. Trabant, B. J. Presley, and D. F. Reid (1977), Anoxic, hypersaline basin in northern Gulf of Mexico, *Science*, *196*(4297), 1443–1446, doi:10.1126/science.196.4297.1443.

Sigman, D. M., M. A. Altabet, D. C. McCorkle, R. Francois, and G. Fischer (2000), The delta N-15 of nitrate in the Southern Ocean: Nitrogen cycling and circulation in the ocean interior, *J. Geophys. Res.*, *105*(C8), 19,599–19,614, doi:10.1029/2000JC000265.

Sigman, D. M., K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J. K. Bohlke (2001), A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, *Anal. Chem.*, *73*(17), 4145–4153, doi:10.1021/ac010088e.

Sigman, D. M., R. Robinson, A. N. Knapp, A. van Geen, D. C. McCorkle, J. A. Brandes, and R. C. Thunell (2003), Distinguishing between water column and sedimentary denitrification in the Santa Barbara Basin using the stable isotopes of nitrate, *Geochem. Geophys. Geosyst.*, *4*(5), 1040, doi:10.1029/2002GC000384.

Thunell, R. C., D. M. Sigman, F. Muller-Karger, Y. Astor, and R. Varela (2004), Nitrogen isotope dynamics of the Cariaco Basin, Venezuela, *Global Biogeochem. Cycles*, *18*, GB3001, doi:10.1029/2003GB002185.

Tyrrell, T. (1999), The relative influences of nitrogen and phosphorus on oceanic primary production, *Nature*, *400*(6744), 525–531, doi:10.1038/22941.

Tyrrell, T., E. Maranon, A. J. Poulton, A. R. Bowie, D. S. Harbour, and E. M. S. Woodward (2003), Large-scale latitudinal distribution of *Trichodesmium* spp. in the Atlantic Ocean, *J. Plankton Res.*, *25*(4), 405–416, doi:10.1093/plankt/25.4.405.

Van Cappellen, P., E. Viollier, A. Roychoudhury, L. Clark, E. Ingall, K. Lowe, and T. Dichristina (1998), Biogeochemical cycles of manganese and iron at the oxic-anoxic transition of a stratified marine basin (Orca Basin, Gulf of Mexico), *Environ. Sci. Technol.*, *32*(19), 2931–2939, doi:10.1021/es980307m.

Wada, E., and A. Hattori (1991), *Nitrogen in the Sea: Forms, Abundances and Rate Processes*, CRC Press, Boca Raton, Fla.

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