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Anna Nele Meckler (2006): Late Quaternary changes in nitrogen fixation and climate variability recorded by sediments from the Gulf of Mexico and the Caribbean Sea

Chapter 4

Detailed sedimentary N isotope records from Cariaco Basin for Terminations I and V: Local and global implications*

Abstract

For the last deglaciation and Termination V (the initiation of MIS 11 at around 430 ka), we report high-resolution sedimentary nitrogen isotope ($\delta^{15}N$) records from Cariaco Basin in the Caribbean Sea. During both terminations, the previously reported interglacial decrease in $\delta^{15}N$ clearly lags local changes such as water column anoxia as well as global increases in denitrification by several thousand years. On top of the glacial-interglacial change, several $\delta^{15}N$ peaks were observed during the last deglaciation. The deglacial signal in Cariaco Basin can be best explained as a combination of 1) local variations in suboxia and water column denitrification as the reason for the millennial-scale peaks, 2) a deglacial maximum in mean ocean nitrate $\delta^{15}N$, and 3) increasing N_2 fixation in response to globally increased denitrification causing the overall deglacial $\delta^{15}N$ decrease. In the Holocene, much of the decrease in $\delta^{15}N$ occurred between 6 and 3 ka, coinciding with an expected precession-modulated increase in African dust transport to the (sub)tropical North Atlantic and the Caribbean. This begs the hypothesis that N_2 fixation in this region increased in response to interglacial maxima in denitrification elsewhere but that this response strengthened with increased mid-Holocene iron input. It remains to be seen whether the data for MIS 11 support this interpretation.

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1. Introduction

In many parts of the ocean, the availability of nitrogen is an important control on primary productivity. Marine productivity, in turn, influences the atmospheric CO_2 content and therefore indirectly global climate. With regard to the large glacial-interglacial variations in atmospheric CO_2, the question of whether the size of the marine nitrogen pool varied on these timescales therefore becomes important.

The main source of nitrogen to the ocean is N_2 fixation, whereas denitrification is its largest sink. Denitrification occurs both in the water column where it is suboxic, such as in the Eastern Tropical North and South Pacific and the Arabian Sea, and in sediments. The current understanding of the nitrogen budget and its regulation is still limited, as several factors potentially affect the individual processes. Globally, denitrification rates depend on organic matter fluxes as well as the ventilation of intermediate waters and probably the areal extent of the shelves [*Christensen*, 1994]. Diazotrophic (N_2 fixing) organisms, on the other hand, seem to depend on the availability of iron and/or phosphorus [*Sanudo-Wilhelmy et al.*, 2001; *Kustka et al.*, 2003; *Mills et al.*, 2004; *Deutsch et al.*, 2007], besides requiring specific light and temperature conditions [*LaRoche and Breitbarth*, 2005]. In addition, it has been proposed that the two processes constitute a feedback: When global denitrification increases, the availability of nitrogen with respect to phosphate decreases, which might make diazotrophic organisms more competitive, leading to an increase in N_2 fixation [*Redfield et al.*, 1963; *Haug et al.*, 1998; *Tyrrell*, 1999; *Galbraith et al.*, 2004].

Both denitrification and N_2 fixation can be traced back in time using the isotopic composition of organic nitrogen in sediments. Denitrification results in the preferential loss of ^{14}N, with a fractionation factor of roughly 25 ‰ [*Barford et al.*, 1999], causing the remaining nitrate pool to become progressively enriched in ^{15}N. In systems where some nitrate remains (i.e., most water column settings), the enriched nitrate is consumed by phytoplankton so that the denitrification signal is recorded in the sediments. The preferential loss of ^{14}N during water column denitrification results in a mean oceanic nitrate $\delta^{15}N$ that is around 5 ‰ [*Sigman et al.*, 2000], i.e. greater than that of atmospheric N_2, which is 0 ‰ by definition ($\delta^{15}N$ (‰) = (($^{15}N/^{14}N$ of sample / $^{15}N/^{14}N$ of air) – 1) * 1000). The mean oceanic nitrate $\delta^{15}N$ appears to be mainly controlled by the relative importance of water column and sedimentary denitrification (the latter being associated with little isotopic fractionation), with the ratio of these two fluxes currently estimated to be 1:4 [*Brandes and Devol*, 2002] to 1:3 [*Deutsch et al.*, 2004]. N_2 fixation introduces fixed N with a $\delta^{15}N$ of ~0-2‰ [*Wada and Hattori*, 1991], i.e. lower than that of mean ocean nitrate, so that local to regional N_2 fixation inputs may also be recorded in sediments.

A number of high-resolution sedimentary nitrogen isotope records for the last deglaciation exist from denitrification zones, displaying increases in $\delta^{15}N$ after the last glacial maximum *[e.g., Altabet et al., 1995; Ganeshram et al., 1995; Pride et al., 1999; Emmer and Thunell,* *2000; De Pol-Holz et al., 2006]*, which suggests that the global rate of water column denitrification is stronger during interglacials. In contrast, low-resolution records from the South China Sea do not exhibit glacial-interglacial variability and have been interpreted to reflect an unchanged isotopic composition of mean ocean nitrate [*Kienast*, 2000]. These observations can only be explained if feedback mechanisms prevent large changes in the marine nitrogen budget [*Deutsch et al.*, 2004]. One possibility is the N_2 fixation feedback mentioned above. The other potential feedback involves denitrification itself, an increase in which could reduce nitrate supply to the surface ocean and thus primary productivity, leading to decreased oxygen demand for organic matter remineralization [*Codispoti*, 1989]. To assess the importance of these proposed feedbacks, records from N_2 fixation areas are needed. However, diagenetic overprints have been reported from sediments in low-accumulation rate settings with oxygenated bottom waters [*Altabet and Francois*, 1994]. Unfortunately, such conditions characterize most regions where N_2 fixation is prominent and the signal not overprinted by denitrification. However, there are a few exceptions, such as Cariaco Basin in the Caribbean Sea, which is characterized by anoxic bottom water while being located in a region with current N_2 fixation (Figure 1). The present N cycle and N isotope dynamics of this basin have been studied [*Richards and Vaccaro*, 1956; *Thunell et al.*, 2004], providing a basis for assessing past changes.

2. Study site

Cariaco Basin is a semi-enclosed coastal basin that is up to 1400 m deep, separated from the open Caribbean by a sill with a maximum depth of 145 m. The bottom water of the basin is anoxic below around 300 m, and strong denitrification occurs in the water column just above this depth [*Richards and Vaccaro*, 1956; *Richards and Benson*, 1961; *Thunell et al.*, 2004] (Figure 2). The oxic/anoxic interface is sharp, leading to very slow exchange with overlying waters. As a result, nitrate is nearly completely consumed at the interface, such that minimal ^{15}N-enriched nitrate is mixed into the overlying thermocline. Sinking flux and surface sediments record a $\delta^{15}N$ of 3-3.5‰, similar to thermocline nitrate and sinking N in the subtropical North Atlantic [*Altabet*, 1988; *Knapp et al.*, 2005], the deviation from a mean ocean nitrate of ~5‰ presumably reflecting the importance of N_2 fixation in the region and/or the Cariaco Basin itself.

The geographic location of Cariaco Basin at the current northern boundary of the seasonal movement of the Intertropical Convergence Zone (ITCZ) results in two distinct seasons: a rainy season in late summer/fall and a dry season with strong, trade wind-induced upwelling in winter/spring. The nutrient supply during the upwelling season stimulates high productivity dominated by diatoms [*Woodworth et al.*, 2004].

The conditions in Cariaco Basin were very different during glacial times, when sea level was up to 120 m lower than today. Under such circumstances, only a shallow connection re-

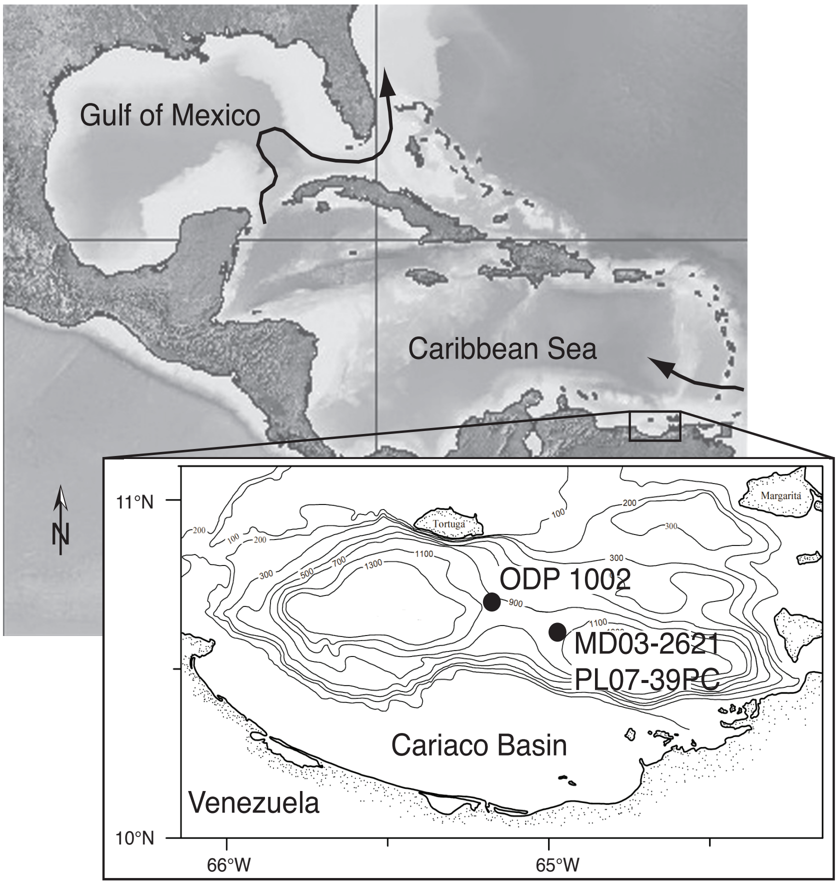


Figure 1. Map of the Cariaco Basin, located off Venezuela in the Caribbean Sea. Arrows depict major surface currents. Closed symbols correspond to the locations of the cores used for this study. Isobaths are in meter below sea level.

mained to the open Caribbean, isolating the basin from the dense and nutrient-rich thermocline water outside. Bioturbated sediments and benthic fauna are found in those intervals, indicating oxygenated bottom waters [*Peterson et al.*, 1991] and implying that there was probably little to no water column denitrification in the basin during glacial times.

In an earlier study on sedimentary N isotope variations in Cariaco Basin [*Haug et al.*, 1998], lower $\delta^{15}N$ was observed in interglacial sections as compared to sediments from glacial times. It was suggested that the low interglacial values are caused by increased N_2 fixation in response to increased denitrification. A question remaining in that study was, however, whether such a feedback worked locally or globally, i.e. whether the local or the global deglacial increase in denitrification triggered N_2 fixation in the basin and/or the surrounding area. In order to address this question, we focus on two terminations in detail, namely the last deglaciation (Termination I) and Termination V at approximately 430 kyrs before present (ka). Thereby, we assess details of the deglacial decreases in $\delta^{15}N$ and, for Termination I, compare those changes to the large body of other proxy data available for Cariaco Basin.

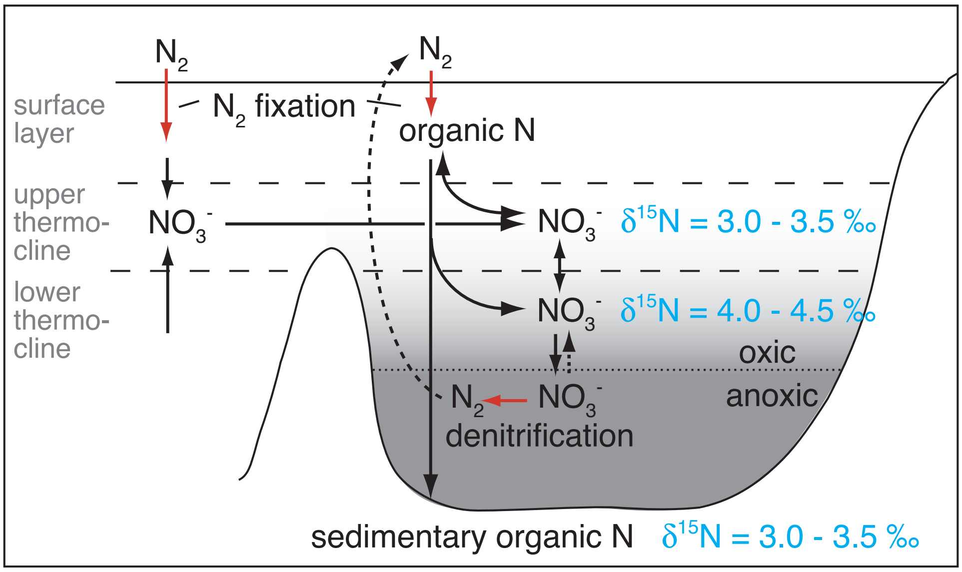


Figure 2. Simplified sketch of the present-day nitrogen cycle in Cariaco Basin (not to scale; see text for details). Isotopic composition of nitrate and surface sediments are taken from *Thunell et al.* [2004].

3. Materials and Methods

For this study we used two cores from Cariaco Basin. To examine Termination V, samples were taken from the deep part of ODP core 1002C (119-123 m composite depth) every 2 cm. This core was taken from the western side of the central ridge in the basin at around 900 m depth (Figure 1). For the last deglaciation, we used core MD03-2621, obtained in 2003 during IMAGES cruise XI (PICASSO) from the eastern side of the central ridge (10°40.69 N, 64°58.29 W) at a water depth of around 850 m. Samples were taken every 2 cm in the upper 12 m of the core.

The sediment in the sampled sections of core MD03-2621 looks very similar to that from other Cariaco Basin cores. In the glacial sections, the sediment appears homogenous and shows signs of bioturbation. A bright blue clay layer occurs from 8.8-8.3 m depth (centered around 16 ka). The abrupt onset of distinct laminations was observed at 7.9 m depth (14.5 ka), with subsequently lighter sediment color and increased varve thickness between 6.6 m and 5.0 m (corresponding to the Younger Dryas period). Above 5.0 m, the again darker varves become thinner and less distinct, although laminations are present until the top of the core.

Total nitrogen (TN) content and $\delta^{15}N$ were measured with a *Carlo-Erba CN2500* elemental analyzer coupled to a *Thermo-Finnigan DELTAplusXL* mass spectrometer, using the reference standards IAEA N1 and N2. For core MD03-2621, roughly one quarter of the samples were measured at least twice, whereas for core 1002, all samples were measured in duplicate. Precision was in most cases better than ± 0.2 ‰ (1 SD) for $\delta^{15}N$ and better than ± 5% of the mean value for TN. In core MD03-2621, concentrations of total organic carbon (TOC, in weight percent) were determined by HCL addition to samples weighed into silver cups, which were dried subsequently at 70°C without rinsing. The samples were measured on a *Eurovector* elemental analyzer with a precision of ± 5 % of the mean.

The age model for ODP core 1002C was constructed by correlating *G. ruber* $\delta^{18}O$ from this core [*Peterson et al.*, 2000] to a global stack of benthic foraminiferal $\delta^{18}O$ [*Lisiecki and Raymo*, 2005]. The data and tie-points are shown in Figure 3. For the investigated sections of MD03-2621, the age model is based on visual correlation of several parameters to well-dated neighboring cores using the software AnalySeries V2.0 [*Paillard et al.*, 1996]: Shipboard-obtained lightness data and Ti content measured by XRF-scanning were correlated to grayscale and Ti, respectively, from core 1002, and TOC was correlated to TOC from core PL07-39PC.

4. Results

The TOC record from core MD03-2621 (Figure 3) agrees very well with that obtained previously for core PL07-39PC [*L. Peterson*, unpublished data], which allowed using it for constructing the age model. After 20 ka, TOC decreases from its glacial value of 3 % to a minimum of 0.5 %, which coincides with the blue clay layer. At 14.5 ka, the onset of the Bølling period, a rapid increase to ~ 5.5 % can be seen, concurrent with the onset of clear laminations in the core. TOC stays high, although variable, until the onset of the Younger Dryas period, when it suddenly drops to 2.5 %. However, as earlier studies showed [*Peterson et al.*, 1991; *Hughen et al.*, 1996], sedimentation rates triple during the Younger Dryas, leading to a peak in organic carbon accumulation rates, which will be discussed later. The end of the Younger Dryas coincides again with a rapid increase of TOC to values similar to the Bølling/Allerød interval, staying high until about 9 ka. A minimum with TOC concentrations around 4.0 % is observed for the early Holocene until around 6.5 ka, after which concentrations steadily increase to a present-day value of 5.8 %.

Like TOC, $\delta^{15}N$ is relatively constant until 20 ka (Figure 3), with values between 4.5 and 5.0 ‰. After 20 ka, a peak occurs with maximum $\delta^{15}N$ values of 7.5 ‰ at 17 ka, the increase being first gradual and then abrupt. Following a rapid decrease to glacial values in the clay layer, $\delta^{15}N$ increases again sharply with the onset of laminations to around 6.5 ‰. Values are lower during the Younger Dryas, with lowest values (around 5.0 ‰) in the first half of this interval and a step-like increase to 5.5 ‰ in the second half. At the end of the Younger Dryas, $\delta^{15}N$ increases to a third peak of around 6.4 ‰ in the Preboreal (11.5-10 ka), with a very short maximum of 8.0 ‰ at 11.4 ka. Afterwards, a stepwise decrease is observed during the Holocene. Between 7.5 and 6 ka, a plateau with values similar to those from the glacial (around 4.8 ‰) can be noticed. Since around 3 ka, $\delta^{15}N$ has been steady at 3.3 ‰.

Due to the peaks in both TOC and $\delta^{15}N$ during the Bølling/Allerød and the Preboreal/early Holocene, it is not clear exactly where the deglacial increase in TOC and the decrease in $\delta^{15}N$ begin. Nonetheless, it becomes obvious that the $\delta^{15}N$ decrease occurs several thousand years later than the TOC increase and certainly much later than the onset of laminations, which indicate the deglacial turning point in local hydrographic conditions.

For Termination V, the onset of the deglacial changes is easier to determine because superimposed peaks are much less pronounced (Figure 3). TN (which covaries with TOC) starts to increase around 6 kyrs before the decrease of $\delta^{15}N$. In these sections of core 1002C, laminations are less developed than for the last deglaciation, which makes a comparison of the $\delta^{15}N$ signal to periods of anoxia more difficult. However, it seems that during this termination, laminations begin before the increase in TOC and are interrupted by short non-laminated intervals during the interglacial. Compared to Termination I, $\delta^{15}N$ is around 1 ‰ lower, but both the magnitude and the duration of the deglacial $\delta^{15}N$ decrease are surprisingly similar during the two terminations. Features analogous to the mid-Holocene plateau and the constant late Holocene $\delta^{15}N$ are apparent during marine isotope stage (MIS) 11 as well.

5. Discussion

5.1. Glacial-interglacial variability

Since local conditions changed dramatically with sea level, the glacial-interglacial $\delta^{15}N$ variations in Cariaco Basin could potentially be caused by a number of different factors, which will be briefly discussed in the following. However, available constraints for the last deglaciation show that the long-term changes in $\delta^{15}N$ are unlikely to be due to local influences associated with sea level rise and anoxia but are instead probably caused by changes in N_2 fixation.

Better-ventilated bottom water in glacial times could have influenced $\delta^{15}N$ through decreased denitrification strength or stronger diagenetic alteration. The heavier glacial $\delta^{15}N$ could be due to incomplete denitrification (compared to complete denitrification in interglacials). However, although denitrification occurs under suboxic conditions (below 1-2 mg/l) [*Codispoti*, 1995], signs of bioturbation and the presence of benthic fauna make it unlikely that oxygen became adequately depleted in the water column to sustain significant denitrification throughout the glacial periods. Diagenetic enrichments of up to 5 ‰ have been observed at sites with well-ventilated bottom water [*Altabet and Francois*, 1994], whereas usually very little alteration is seen in anoxic settings [*Pride et al.*, 1999; *Emmer and Thunell*, 2000; *Thunell et al.*, 2004]. However, the onset of anoxia clearly preceded the $\delta^{15}N$ decrease in Cariaco Basin. Moreover, it was associated with a sudden increase in $\delta^{15}N$.

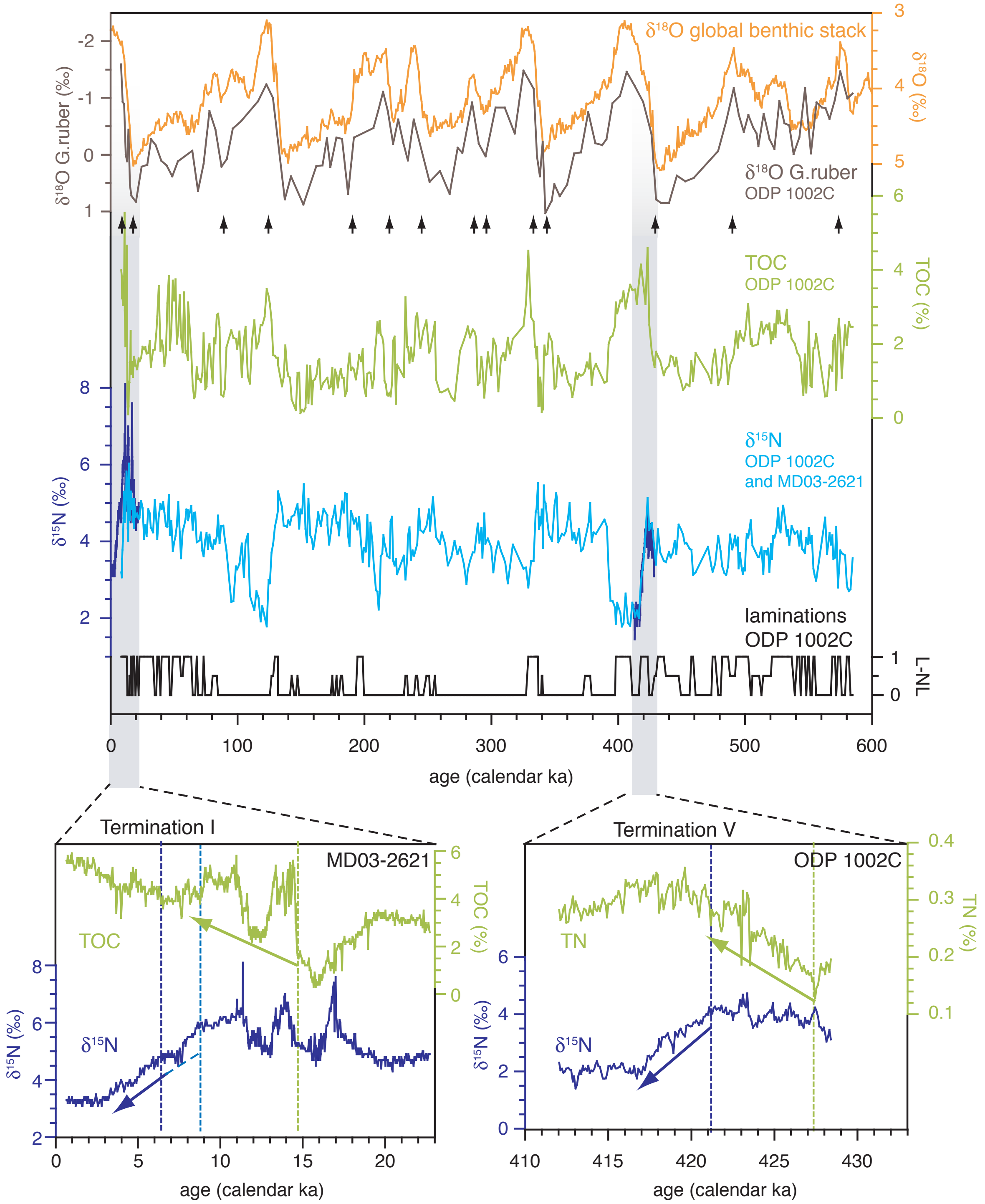


Figure 3. Cariaco Basin low- and high-resolution records. Upper panel: $\delta^{18}O$ of *G. ruber* [*Peterson et al.,* 2000] and global benthic $\delta^{18}O$ stack [*Lisiecki and Raymo*, 2005] used for tuning (black arrows are tiepoints). Low-resolution TOC and $\delta^{15}N$ records and lamination data (1 = laminated) are from *Haug et al.* [1998]. Lower panels: High-resolution data from core MD03-2621 and ODP core 1002C. Dashed lines indicate onset of deglacial change (ambiguous for $\delta^{15}N$ during Termination I).

Incomplete nutrient utilization enriches the nitrate pool in ^{15}N due to preferential uptake of ^{14}N by phytoplankton [e.g., *Farrell et al.*, 1995; *Wu et al.*, 1997; *Sigman et al.*, 1999]. If glacial upwelling was stronger, delivering more nitrate to the surface outside the basin that was not immediately consumed, the water advected inside could have contained enriched nitrate. In contrast, in interglacials upwelling of thermocline waters occurs in the basin, and all nitrate is consumed during the upwelling season. Hence, this difference could result in higher glacial $\delta^{15}N$ values in the sinking organic matter. However, one would again expect to see the decrease when the thermocline connection became established, i.e. probably at 14.5 ka. Instead, $\delta^{15}N$ increases at that time and the decrease occurs much later.

Contribution of terrigenous organic matter could alter the bulk sedimentary $\delta^{15}N$ signal, usually decreasing the values *[e.g., Peters et al., 1978; Calvert et al., 2001]*. However, no significant trend in the abundance of terrestrial biomarkers has been observed for the last 14 kyrs [*Werne et al.*, 2000]. Similarly, C/N values obtained in this study do not show a significant difference between glacial and Holocene values, except for the Younger Dryas and the blue clay layer, which will be discussed later.

Finally, the low Holocene $\delta^{15}N$ in Cariaco Basin (compared to mean ocean nitrate $\delta^{15}N$) suggests an influence of regional and/or local N_2 fixation. As proposed earlier [*Haug et al.*, 1998], a stronger contribution of this process could lower the sinking flux $\delta^{15}N$ in interglacial times. This is the most likely cause for the decreasing $\delta^{15}N$, whereby the time lag is an indication that it is not (or not alone) triggered by local denitrification.

When comparing the low-resolution Cariaco Basin $\delta^{15}N$ data to long records from other areas (Figure 4), a significant time lag can also be observed between rapid deglacial increases in global denitrification and the $\delta^{15}N$ decreases in Cariaco Basin. Both the $\delta^{15}N$ record from the Arabian Sea (ODP core 722; Figure 4) [*Altabet et al.*, 1999] and that from the Eastern Tropical North Pacific (ODP core 1012; not shown) [*Liu et al.*, 2005] show consistent patterns of elevated $\delta^{15}N$ in interglacials, reflecting increased denitrification. Thereby, $\delta^{15}N$ increases coincide with decreases in global ice volume as indicated by foraminiferal $\delta^{18}O$ in the respective cores. In core 722, even a slight lead of $\delta^{15}N$ with respect to $\delta^{18}O$ has been observed [*Altabet et al.*, 1999]. As a way to circumvent age model artifacts, we therefore compare the $\delta^{15}N$ and $\delta^{18}O$ records from Cariaco Basin to assess the relative timing of N_2 fixation changes and global denitrification. In some cases, the changes in $\delta^{18}O$ (and denitrification zone $\delta^{15}N$) occur much earlier than the decreases in $\delta^{15}N$ in Cariaco Basin. For example, during Termination V, the shift in $\delta^{18}O$ of planktic foraminifera in Cariaco Basin coincides with the increase in TN, around 6 kyrs before the $\delta^{15}N$ decrease (Figure 3). At Termination II (around 130 ka), the lag of $\delta^{15}N$ to $\delta^{18}O$ in Cariaco Basin is around 4-5 kyrs. Since estimates of the residence time of nitrate in the ocean currently range between 1.5 to 3.0 kyrs [*Gruber and Sarmiento*, 1997; *Brandes and Devol*, 2002], the time lags at these deglaciations seem too long to explain the $\delta^{15}N$ signal with a simple response of regional N_2 fixation to globally increased denitrification. There are two possible explanations. First, the signal of an earlier N_2 fixation increase could be masked by a second process, such as a change in the mean isotopic composition of oceanic nitrate. Second, another stimulating factor for N_2 fixation (besides low N:P ratios) could cause the delayed response, which will be further discussed in the context of the Holocene $\delta^{15}N$ decrease (section 5.3).

The mean N isotopic composition of oceanic nitrate is supposed to be reflected in $\delta^{15}N$ records from the South China Sea [*Kienast*, 2000], the longest of which covers the last 200 kyrs (Figure 4). Interestingly, in glacial times both the absolute values and the variability of the Cariaco Basin record are similar to those in the South China Sea. Only the negative excursions during the Holocene and the last interglacial stand out with significantly lower values. This suggests that in glacials at least the longer-term signal is mainly affected by the global mean isotopic composition of nitrate. Although the low resolution of the records and the limitations of the age models hamper a more detailed comparison, it is interesting to note that a peak can be observed in the South China Sea record just before the last interglacial (MIS 5), which is also present in the Cariaco record. A deglacial peak in the mean isotopic composition of oceanic nitrate has also been suggested for the last deglaciation and is probably related to transient changes in the relative importance of water column and sedimentary denitrification [*Deutsch et al.*, 2004]. It is therefore possible that part of the deglacial signal in Cariaco Basin reflects such temporary changes in global nitrate isotopic composition.

The high-resolution records from Cariaco Basin allow for a more detailed assessment of this potential influence and the relative timing of the interglacial $\delta^{15}N$ decreases. The records also reveal additional millennial-scale features, such as three peaks during the last deglaciation. We discuss these signals first before returning to the timing of the N_2 fixation increase.

5.2. Millennial-scale variations during the last deglaciation

During the deglaciation, large changes occurred both within Cariaco Basin (related to sea level rise) and in the global nitrogen cycle (through increasing global denitrification). The complicated signal of $\delta^{15}N$ during the last deglaciation could therefore either be caused by local changes or be related to global N cycle changes. Most likely, it reflects a combination of these influences.

Due to the specific bathymetry of the Cariaco Basin, we have to distinguish between two different regimes (Figure 5): 1) glacial conditions with an isolated basin and (mostly) oxygenated bottom water and 2) deglacial to interglacial conditions characterized by a thermocline connection to the open Caribbean and anoxic bottom water (after 14.5 ka). In the first regime, before 14.5 ka, the shallow sill depth of 25-40 m restricted the exchange between Cariaco Basin and the open Caribbean, allowing only mixed layer water to enter the basin. The result was probably a decreased density gradient within the basin, potentially amplified by more vigorous mixing caused by stronger winds. In addition, climate reconstructions from terrestrial archives indicate that the last glacial maximum was drier than today [*Bradbury et al.*, 1981], implying decreased freshwater input to the basin, which would have further reduced stratification. Fi-

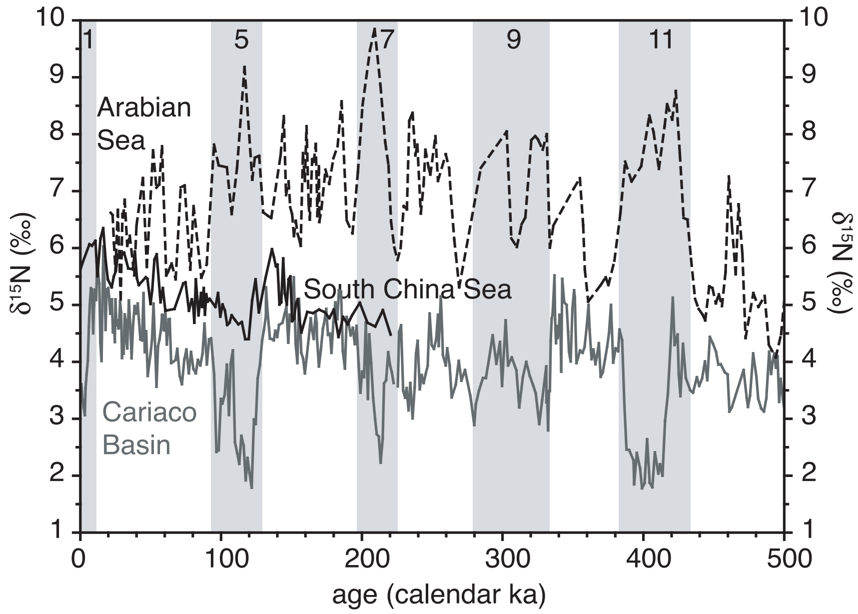


Figure 4. The long $\delta^{15}N$ record from Cariaco Basin [*Haug et al.*, 1998] in comparison with records from the Arabian Sea (ODP core 722) [*Altabet et al.,* 1999] and the South China Sea (core 17954) [*Kienast*, 2000]. Shaded bars indicate interglacials and numbers are marine isotope stages.

nally, local productivity might have been reduced due to decreased input of thermocline nutrients (see discussion below). These changes in local conditions prevented the deep basin from turning anoxic. The first peak in $\delta^{15}N$ occurs under these glacial conditions, which is at first surprising. However, several other local proxies indicate an event at the same time. After 17.5 ka, proxies for terrestrial material (e.g. Ti [*Haug et al.*, 2001, and unpublished data] and detrital mass accumulation rates [*L. Peterson*, unpublished data]; Figure 6) indicate a large pulse of terrigenous input, which also encompasses the blue clay layer, represented by the minimum in sediment lightness (L*).

One possibility to explain the large input of terrestrial material is the first flushing of previously exposed shelf area due to the beginning sea level rise, which might have been abrupt [*Clark et al.*, 2004]. The other option is increased freshwater input, which is supported by more negative $\delta^{18}O$ values of planktic foraminifera [*Lin et al.*, 1997]. This would also explain the event character of the terrigenous input, which did not continue with further sea level rise. Interestingly, a similar blue clay layer was observed off the Amazon River mouth at around the same time [*Hemming et al.*, 1998], suggesting a larger-scale hydrologic anomaly. The reason for a freshwater pulse is currently unclear. Around this time, summer insolation increased in the northern hemisphere and northern hemispheric glaciers started to melt. However, this is also the time of Heinrich event 1, and a profound reduction in the formation rate of North Atlantic Deep Water [*McManus et al.*, 2004] and therefore winter cooling. The effect of such increased seasonality [*Denton et al.*, 2005] in the tropics is an open question.

A pulse of freshwater into the well-mixed Cariaco Basin might have led to transient stratification, resulting in suboxic conditions and denitrification in the water column. If denitrification was incomplete, the associated ^{15}N enrichment of subsurface nitrate could explain the high $\delta^{15}N$ of up to 7.5 ‰. The sudden decrease in $\delta^{15}N$ afterwards coincides with the blue clay layer and a drop in C/N values to around 4. In face of the evidence for large terrigenous input, these unusually low C/N ratios can only be explained by an increased proportion of clay-bound inorganic nitrogen due to low TOC concentrations and high abundance of clay. If so, the light isotopic composition commonly observed for inorganic nitrogen could add to the rapid decrease after the $\delta^{15}N$ peak ~17 ka, enhancing the effect of an expected decrease in denitrification strength. Since, in all other parts of the core, C/N ratios are at values that would be expected for sedimentary organic matter, a significant influence of inorganic nitrogen on bulk $\delta^{15}N$ is likely limited to the blue clay layer.

2) After 14.5 ka, at the onset of the Bølling period, the sediment suddenly became laminated, indicating permanent anoxia in the deep basin. The reason was probably that sea level rise during meltwater pulse 1A allowed thermocline waters to enter the basin. Since %TOC

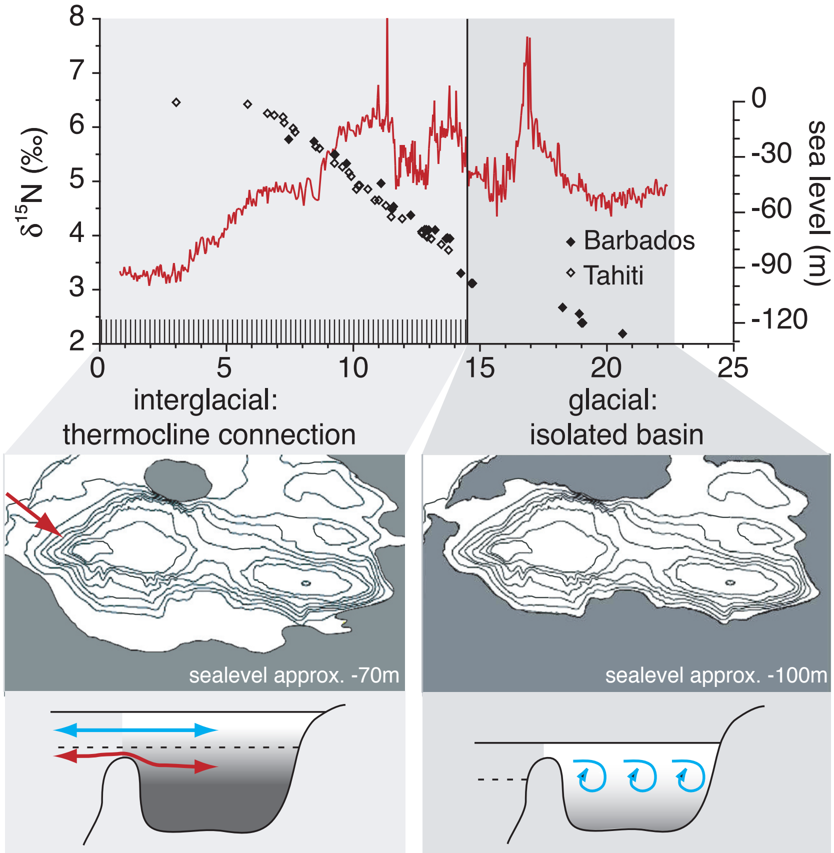
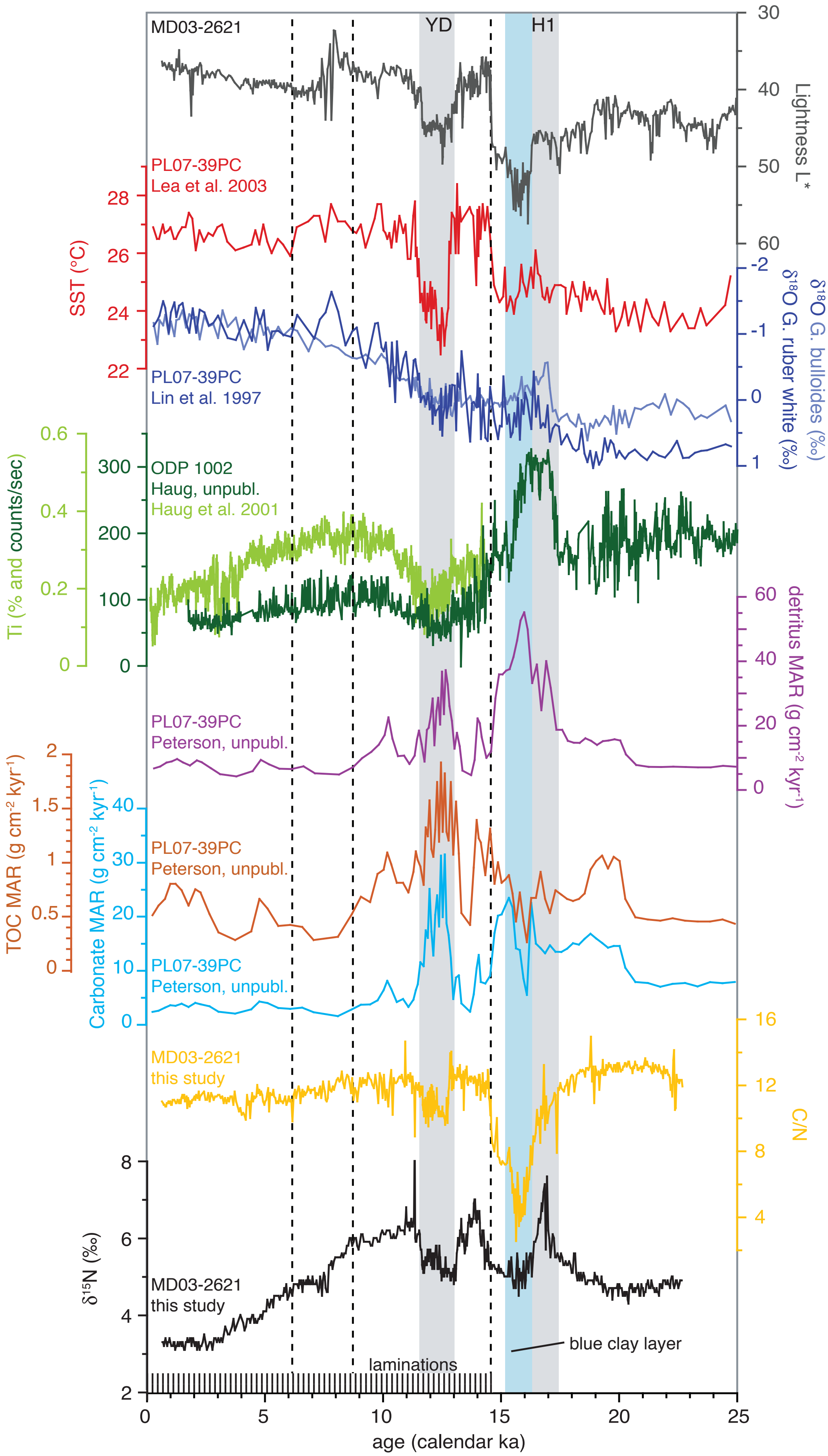


Figure 5. Deglacial change of the local conditions in Cariaco Basin due to sea level rise. Sea level data are from *Fairbanks* [1989] and *Bard et al.* [1990] (Barbados) and *Bard et al.* [1996] (Tahiti). Isobath spacing is 200 m except for upper 300 m, where spacing is 100 m (c.f. Figure 1). The hatched bar indicates laminated sediments, reflecting the prevalence of anoxic bottom water.

increases abruptly, it has been thought that the main reason for the anoxia was increased productivity after nutrients became abundant *[e.g., Haug et al., 1998]*. This is supported by a sudden increase in the relative abundance of the foraminifera species *G. bulloides* [*Peterson et al.*, 1991]. However, the increase of TOC mass accumulation rate [*L. Peterson*, unpublished data], an alternative proxy for productivity, is not so clear at this time (Figure 6). In any case, a second effect of the tapping of thermocline water was probably that water masses of higher density filled the basin. Together with reduced wind strength due to northern hemisphere warming, this could have suddenly increased stratification in the basin, leading to anoxia and denitrification. Increased stratification is also consistent with the sudden increase in sea surface temperature [*Lea et al.*, 2003]. High $\delta^{15}N$ values indicate that denitrification was not complete at that time, resulting in heavy residual nitrate being upwelled to the photic zone. The residence time of deep water in the basin was probably short during the Bølling/Allerød interval [*Piper and Dean*, 2002], which could be due to frequent flushing events, because continuing sea level rise led to tapping of increasingly dense water.

During the Younger Dryas, sediment accumulation rates peaked, which was due to increases in both terrigenous input (detritus MAR) and productivity (TOC MAR, carbonate MAR)[*L. Peterson*, unpublished data]. In many places, this interval was characterized by a return to (near-) glacial conditions. Around Cariaco Basin, it became drier again [*Haug et al.*, 2001; *Hughen et al.*, 2004] and sea surface temperatures were colder [*Lea et al.*, 2003] (Figure 6). Stronger winds probably resulted in increased upwelling, which is indicated by faunal assemblage shifts [*Peterson et al.*, 1991]. It is unclear whether the increased terrigenous input despite overall drier conditions was caused by increased wind transport or whether single runoff events mobilized the material. Despite high detrital inputs, biomarker analyses showed that terrigenous organic matter contribution was low during the Younger Dryas [*Werne et al.*, 2000], which would be supported by the lower C/N ratios if they are due to a stronger contribution of marine organic matter. However, it is also possible that the C/N ratios again reflect input of clay-bound nitrogen. If so, the comparison with the clay layer values shows that in the Younger Dryas this could only explain a small portion of the $\delta^{15}N$ decrease. Instead, the low $\delta^{15}N$ is better explained by peak organic matter flux leading to increased oxygen demand and increased denitrification rates until complete transformation of nitrate at depth. Thereby the influence of local denitrification on sinking flux $\delta^{15}N$ would have diminished. In addition, we cannot exclude increased N_2 fixation as a contributing factor, which will be further discussed in section 5.3.

After the Younger Dryas, both upwelling strength and organic matter flux decreased, which could have resulted in decreasing denitrification strength, temporarily restoring its influence on the isotopic composition of the sinking flux. This could explain the higher $\delta^{15}N$ values, especially the very brief peak exceeding 8 ‰ at around 11.5 ka. If so, part of the decrease in $\delta^{15}N$ after 11 ka would have to be caused by a subsequent strengthening of denitrification until completeness, as observed today. The only way such a Holocene increase in denitrification strength could be explained is an increase in the residence time of the deep water, because productiv-



MD03-2621
YD
H1
Lightness L*
30
40
50
60
PL07-39PC
Lea et al. 2003
SST (°C)
28
26
24
22
PL07-39PC
Lin et al. 1997
δ18O G. bulloides (‰)
δ18O G. ruber white (‰)
-2
-1
0
1
ODP 1002
Haug, unpubl.
Haug et al. 2001
Ti (% and counts/sec)
0.6
0.4
0.2
0
300
200
100
0
detritus MAR (g cm-2 kyr-1)
60
40
20
0
PL07-39PC
Peterson, unpubl.
TOC MAR (g cm-2 kyr-1)
2
1.5
1
0.5
0
Carbonate MAR (g cm-2 kyr-1)
40
30
20
10
0
PL07-39PC
Peterson, unpubl.
PL07-39PC
Peterson, unpubl.
MD03-2621
this study
C/N
16
12
8
4
δ15N (‰)
8
6
4
2
MD03-2621
this study
blue clay layer
laminations
0
5
10
15
20
25
age (calendar ka)

Figure 6. Compilation of proxy data for the last deglaciation from Cariaco Basin. MAR is mass accumulation rate, YD is Younger Dryas and H1 indicates the time of Heinrich event 1. Dashed lines are for better comparison. Lightness is a mixed signal of carbonates (bright) and organic and terrigenous matter (dark). SST is based on foraminiferal Mg/Ca. Foraminiferal $\delta^{18}O$ is a signal of salinity and/or temperature, superimposed on the global ice volume effect. Ti reflects terrigenous input, as does detritus (= 100% - %TOC - %opal - %$CaCO_3$). Note the differences in MAR of detrital material and TOC compared to the respective concentrations (Ti and TOC, c.f. Figure 3) due to a large increase in sedimentation rate during the YD. Low C/N in the blue clay layer is probably due to inorganic N.

ity was decreasing. Such a decrease in ventilation could have been due to the decreased wind strength and upwelling in the Preboreal/early Holocene. We therefore assume that a possible return to complete consumption of nitrate by denitrification occurred within the early Holocene.

Despite the likely influence of variations in local denitrification strength, a striking similarity can be observed between the Cariaco Basin record and data from denitrification zones in the east Pacific and the Arabian Sea (Figure 7) with regard to the Bølling/Allerød and Preboreal/early Holocene peaks and the Younger Dryas minimum. By this time, a thermocline connection with the open Caribbean had already been established. A rapid transfer of changes in the isotopic composition of thermocline nitrate in other areas to Cariaco Basin could therefore potentially be invoked, assuming thermocline waters of different ocean basins communicated without involving the deep ocean. Even if this was the case, however, the shifts in Cariaco Basin are more abrupt than one would expect if they were reflecting thermocline signals from distant areas. Furthermore, in the denitrification areas of the southern hemisphere, the timing of the deglacial changes was different from the northern hemisphere sites (Figure 7), as exemplified by opposite signals during the Younger Dryas period. If the Cariaco Basin signal was imported, it should be influenced by both southern and northern hemispheric changes. For these reasons it is currently unclear how much of the rapid deglacial variations in the Cariaco Basin are imported from denitrification regions, but it seems likely that local changes in denitrification strength played a more important role.

It should be noted that this finding does not preclude an imprint of changes in the mean ocean nitrate isotopic composition, as discussed before in the context of the low-resolution records. Such a signal, due to changes in the relative importance of water column and sedimentary denitrification, would be expected to have the shape of a broad peak, reflecting the different timing of denitrification increases (and decreases). The initial part of the Holocene decrease in Cariaco Basin is similar to decreasing trends observed in all records from the denitrification zones (Figure 7). This agreement of records from very different environments is an indication for a global component in the records. While the onset of such a peak is difficult to determine in the Cariaco Basin record, it is most probably responsible for at least part of the early Holocene decrease. In contrast, the second portion of the Holocene decrease does not appear to be a global signal, and consequently has to be due to local or regional processes (see section 5.3).

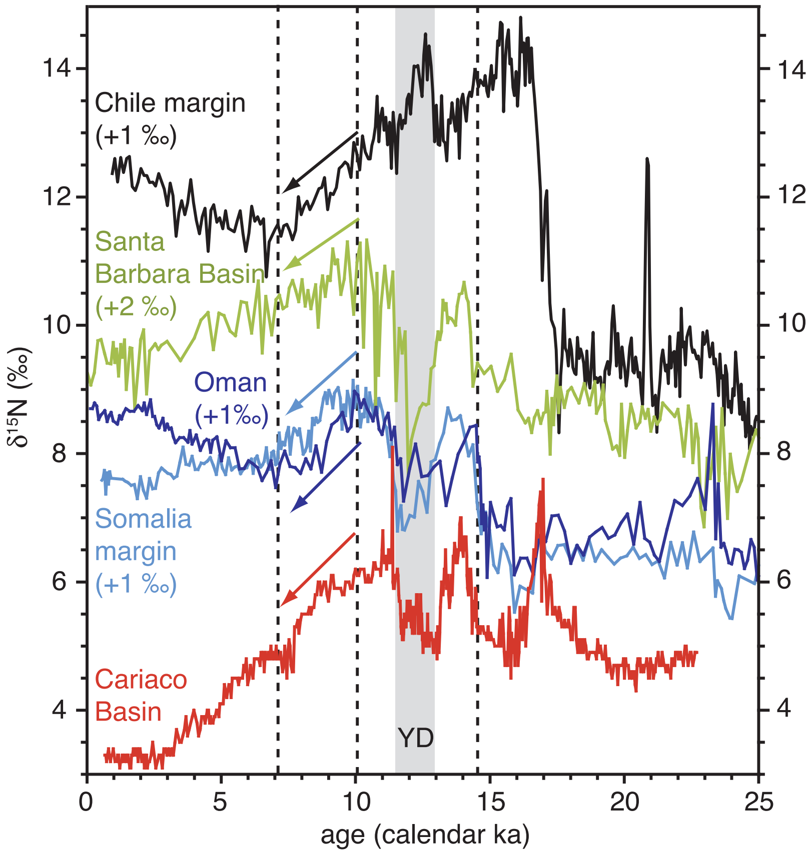


Figure 7. Global comparison of $\delta^{15}N$ records for Termination I. Shown are records from denitrification zones in the east Pacific off Chile [*De Pol-Holz et al*., 2006] and off California (Santa Barbara Basin) [*Emmer and Thunell*, 2000], and the Arabian Sea off Oman [*Altabet et al.,* 2002] and off Somalia [*Ivanochko et al.*, 2005] in comparison with the data from Cariaco Basin (this study). Some records are shifted for better comparison. The gray bar indicates the Younger Dryas and dashed lines the rapid increase in denitrification in the northern hemisphere as well as the early Holocene decrease (arrows) common to all records.

Based on the above considerations, we propose the deglacial part of the Cariaco Basin $\delta^{15}N$ record reflects mainly changes in local denitrification strength, in response to changes in density stratification and productivity, as well as variations in mean ocean nitrate $\delta^{15}N$. Our current best estimate of the extent of these influences is depicted in Figure 8. Uncertainties remain as to the influence of inorganic N input in specific parts of the record (Figure 8A, 1) and the occurrence of changes in mean ocean or thermocline nitrate $\delta^{15}N$ during the Younger Dryas period (Figure 8A, 2).

5.3. Timing of the N_2 fixation increase

As discussed before, the overall decrease in Cariaco Basin $\delta^{15}N$ between glacials and interglacials is probably due to increasing N_2 fixation. It is therefore most likely that this process was responsible for the mid-Holocene decrease in $\delta^{15}N$, implying that much of the increase in N_2 fixation recorded in Cariaco Basin occurred later than the influence of the transient global $\delta^{15}N$ signal. The step-like character of the interglacial $\delta^{15}N$ decrease, including a plateau at $\delta^{15}N$ values similar to those of the last glacial maximum, supports this interpretation. However, what could have caused this delayed increase in N_2 fixation?

The onset of the mid-Holocene $\delta^{15}N$ decrease coincides with climatic changes in the region, which could have stimulated N_2 fixation. Over the course of the Holocene, northern hemispheric summer insolation decreased, which resulted in a southward movement of the Intertropical Convergence Zone (ITCZ) [*Haug et al.*, 2001]. This caused declining Caribbean precipitation as indicated by decreasing Ti concentrations in Cariaco Basin (Figure 6) [*Haug et al.*, 2001]. A noticeable effect was the re-establishment of the Saharan desert after an early Holocene humid period [*deMenocal et al.*, 2000; *Adkins et al.*, 2006]. In the context of this change, transport of dust to the (sub)tropical North Atlantic and the Caribbean probably increased greatly in the mid-Holocene (Figure 8B), facilitated by stronger trade winds and a less prevalent ITCZ rain curtain in this region. In the tropical North Atlantic, N_2 fixation appears to be closely connected to the dust input, as suggested both by geographical correlations [*Mahaffey et al.*, 2003; *Tyrrell et al.*, 2003] and by dust addition experiments [*Mills et al.*, 2004], probably due to its iron content. Therefore, an increased mid-Holocene iron input by dust potentially stimulated N_2 fixation at times when high interglacial denitrification had decreased the N:P ratio of nutrients in the thermocline (Figure 8A, 3). The latter stimulation was absent in glacial times, preventing high N_2 fixation rates despite a Saharan dust input that was probably higher than today [*Mahowald et al.*, 1999; *Yarincik et al.*, 2000]. In contrast, while the deglacial increase in global denitrification created a global surplus of phosphate, we propose that Atlantic N_2 fixation was limited by iron and therefore only increased after the dust input recommenced. An exception might be the Younger Dryas, where increased terrigenous flux is recorded off Africa, coinciding with a $\delta^{15}N$ minimum in Cariaco Basin, which might reflect a brief period of stronger N_2 fixation.

This mechanism leaves us with the question of whether the Cariaco Basin records a signal of locally increasing N_2 fixation or instead represents a change in the whole region of the (sub)tropical North Atlantic and the Caribbean. We consider the latter as much more likely since the coastal areas receive iron by riverine input and therefore probably do not depend on the dust-bound iron source.

In summary, we propose that the step-wise Holocene decrease in $\delta^{15}N$ in Cariaco Basin is due to 1) an early Holocene decrease in mean ocean nitrate $\delta^{15}N$ as part of a deglacial peak, possibly in combination with local changes in denitrification strength as discussed above, and 2) a mid-Holocene increase in regional N_2 fixation due to an increase in Saharan dust input. Mid-Holocene changes also occurred in denitrification zones, albeit in varying ways (Figure 7). At the Oman and Chile margins, increasing denitrification after 7 ka has been inferred from increasing $\delta^{15}N$ values [*Altabet et al.*, 2002; *De Pol-Holz et al.*, 2006], whereas at the Somalia margin and in the Santa Barbara Basin, the Holocene decrease in $\delta^{15}N$ continued, suggesting decreasing denitrification [*Emmer and Thunell*, 2000; *Ivanochko et al.*, 2005]. Although the impact of these different changes on the overall global denitrification rate is yet to be determined, a mid-Holocene increase in global denitrification could have played an additional role in the stimulation of North Atlantic N_2 fixation. Either way, the data suggest that the nitrogen cycle as sensed by the Cariaco Basin did not reach stability until at least the late Holocene (around 3 ka).

5.4. Comparison of Terminations I and V

The pattern of $\delta^{15}N$ changes observed for the last deglaciation in Cariaco Basin is very similar to the trends during Termination V, except for the larger millennial-scale excursions during the last deglaciation. The reduced signal of such deglacial peaks during the earlier termination could be due to less pronounced shifts between different redox conditions, which is supported by the laminations being less clear in that earlier interval. However, the redox conditions during Termination V are not well constrained at present. In any case, the fact that the remaining trends are similar in timing and magnitude during the two terminations studied here indicates that the shifts represent systematic changes in the nitrogen cycle. During Termination V, a slow increase of around 1 ‰, followed by a decrease of similar magnitude, could represent the transient change in mean ocean nitrate $\delta^{15}N$, similar to that proposed for the last deglaciation. Furthermore, the interglacial $\delta^{15}N$ decrease seems to occur in two steps, analogous to the Holocene decrease.

Unfortunately, there is presently neither a high-resolution $\delta^{15}N$ record for Termination V from another part of the ocean, nor detailed control on changes in climate during the interglacial period following Termination V (MIS 11) to put these changes into context. The desertification of the Sahara in the mid-Holocene and the southward shift of the ITCZ were likely due to decreasing summer insolation linked to the 23-kyr precessional cycle. The fact that during MIS11 $\delta^{15}N$ stayed low for around 25 kyrs, during which summer insolation exhibited both a minimum and a maximum, would seem to contradict the dust trigger hypothesis. However, other factors could be important in addition to precession, and there is presently no detailed information on changes in dust input within this earlier interglacial period.

MIS 11 was an exceptionally long interglacial period, with interglacial climate conditions lasting around 30 kyrs [*McManus et al.*, 1999; *Siegenthaler et al.*, 2005]. This interglacial can therefore be used to assess the stability of the nitrogen cycle in the absence of deglacial perturbations. The constant $\delta^{15}N$ values in the Cariaco Basin record after 417 ka indicate long-term regional and probably also global stability of the nitrogen cycle for much of this interglacial period. As the Holocene is characterized by similar orbital configurations, with reduced amplitudes of insolation changes due to a minimum in eccentricity, the stability inferred for the

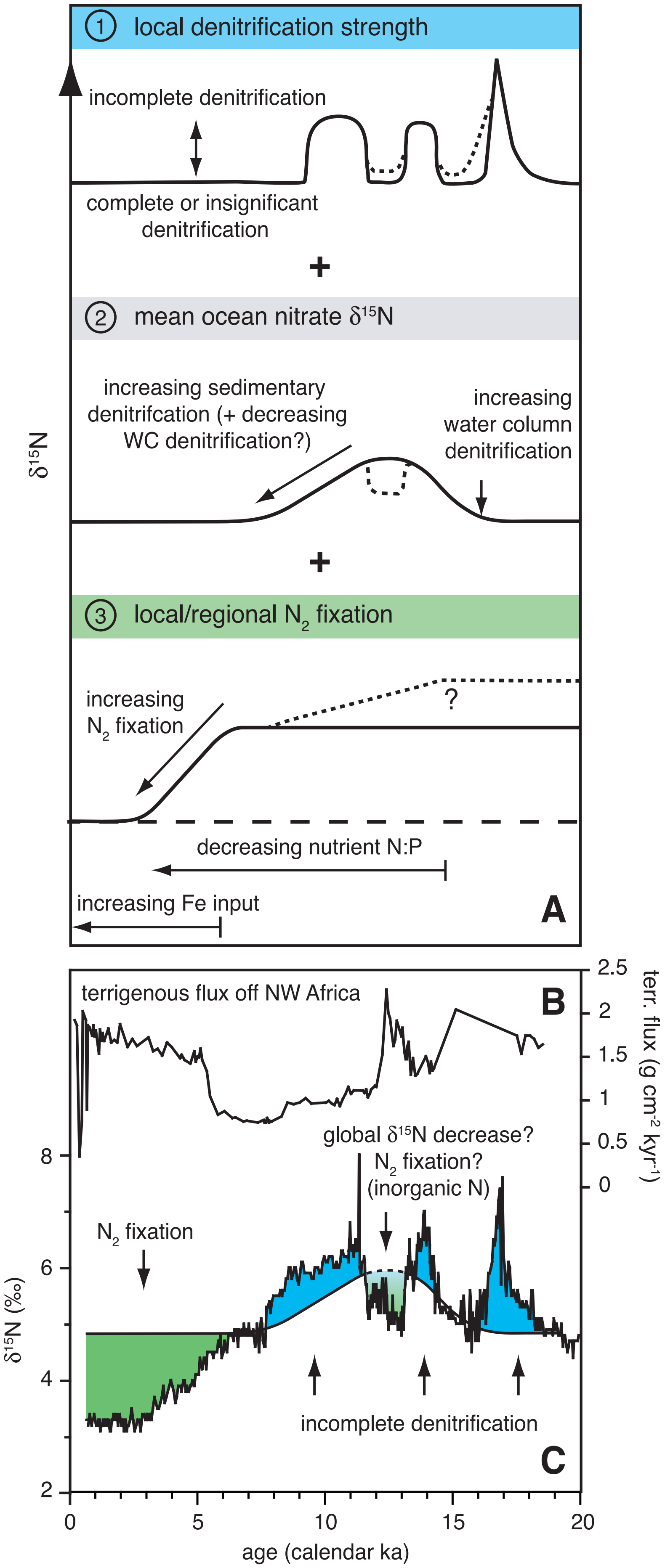


Figure 8. A. Conceptual drawing of the effects thought to cause the observed $\delta^{15}N$ trends in Cariaco Basin during terminations. Due to the variety of influences, the shape of different signals is not always clear: Potential inorganic N input would cause overestimation of the denitrification effect (dashed lines in 1); the timing and shape of the mean ocean nitrate signal (2) as well as potentially rapid changes in thermocline nitrate $\delta^{15}N$ are currently not well constrained; if N_2 fixation increased before the mid-Holocene (dashed line in 3), processes 1 and 2 would have obscured this signal. B. Excess ^{230}Th normalized terrigenous flux off NW Africa (ODP core 658C) [*Adkins et al.,* 2006], potentially representing Fe input to the tropical North Atlantic and the Caribbean. C. Graphic representation of proposed influences on Cariaco Basin $\delta^{15}N$, subject to the uncertainties outlined above.

last 3 kyrs could potentially last for some thousand years into the future, in absence of human perturbations of the nitrogen cycle.

6. Conclusions

The high-resolution $\delta^{15}N$ data obtained for two terminations in Cariaco Basin allowed a more detailed assessment of changes in the nitrogen cycle at that site than previously possible. An observed time lag of up to 6 kyrs between local changes in productivity and anoxia and the deglacial decreases in $\delta^{15}N$ confirm that the overall decreases are neither related to redox-driven changes in diagenetic alteration of the signal nor are they due to changes in local processes such as nutrient utilization or denitrification. However, local processes do play a role in the millennial-scale variability superimposed on the glacial-interglacial trends; specifically, a comparison with other available proxy data suggests that variations in the strength of denitrification in Cariaco Basin drove several abrupt $\delta^{15}N$ changes during the deglacial interval (Figure 8A, 1). This local influence was apparently more pronounced during the last deglaciation than during Termination V.

The overall deglacial decreases in $\delta^{15}N$ observed in Cariaco Basin were most likely due to increasing N_2 fixation. The Cariaco Basin record therefore adds to the growing evidence that N_2 fixation responds to the higher rates of global denitrification during interglacials [*Deutsch et al.*, 2004; *Galbraith et al.*, 2004]. However, a significant time lag was observed between global increases in denitrification and the Cariaco Basin $\delta^{15}N$ decreases. In the Holocene, the $\delta^{15}N$ decrease occurred in two steps, whereby the earlier part of this signal likely represents a decrease in mean ocean nitrate $\delta^{15}N$ as part of a deglacial peak (Figure 8A, 2). This is supported by the similarity of the Cariaco Basin data with $\delta^{15}N$ records from various denitrification zones during this interval. Furthermore, deglacial peaks in mean ocean nitrate $\delta^{15}N$ are suggested by records from the South China Sea [*Kienast*, 2000].

Much of the Holocene decrease in $\delta^{15}N$ occurred after around 6 ka, coinciding with a change in regional climate and, most importantly, the re-establishment of the Saharan desert. We propose that a concurrent increase in dust input triggered a mid-Holocene increase in N_2 fixation in the (sub)tropical North Atlantic, relieving iron limitation that hindered N_2 fixation in the early Holocene (Figure 8A, 3). In glacial times, high $\delta^{15}N$ values in the Cariaco Basin indicate reduced N_2 fixation despite large dust input [*Mahowald et al.*, 1999]. Our hypothesis therefore calls for two requirements to be met in order to trigger N_2 fixation in the North Atlantic: a decreased nutrient N:P ratio and sufficient availability of the micronutrient iron.

The good agreement of the $\delta^{15}N$ signal during the two terminations studied here, regarding the timing, shape and magnitude of the deglacial decreases, suggests a similar sequence of influences during Termination V. However, the long-lasting stability of low $\delta^{15}N$ values during

MIS11 seems to contradict the dust trigger mechanism if dust input varied with the 23-kyr precessional cycle. Future work on dust input and climate variability during this interval will allow further testing of the proposed mechanisms. The observed stability of the $\delta^{15}N$ values after the late decrease in both the MIS 11 and the Holocene data suggest that the nitrogen cycle reaches a balance when interglacial conditions prevail adequately long.

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