

Similar glacial-interglacial $\delta^{15}\text{N}$ variations in two MIS 13-10 sediment sequences in the western North Atlantic Ocean: Changes in nitrogen sources, denitrification, or diagenesis?

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Abstract

We have determined TOC-MARs and $\delta^{15}\text{N}$ values in MIS 13-10 sediments from two oligotrophic parts of the western North Atlantic Ocean - ODP Site 1063 on the Bermuda Rise and Site 1058 on the Blake Outer Ridge. Both TOC-MARs and $\delta^{15}\text{N}$ values vary significantly in these depositional records. TOC-MARs are highest in sediments deposited at Site 1063 during MIS 12 and MIS 10, implying marine productivity or TOC preservation increased at this location during glacial stages, and low TOC-MARs during most of MIS 11 in Site 1063 sediment imply low rates during this warm interval. In contrast to the Site 1063 record, productivity or preservation appears to have been greater at Site 1058 during parts of the MIS 11 interglacial than during the glacial intervals. Unlike the TOC-MAR records, $\delta^{15}\text{N}$ values at both locations exhibit similar glacial-interglacial alternations. Values peak during substage 11.3 and gradually decrease towards the terminations of MIS 12 and MIS 10. The similarity of the $\delta^{15}\text{N}$ patterns at these two sites implies that nitrogen cycling at these locations is largely independent of changes in local surface production of organic matter, and the higher $\delta^{15}\text{N}$ values are not likely to result from denitrification. Instead, the $\delta^{15}\text{N}$ alternations likely result from glacial-interglacial alternations between higher rates of sediment delivery to these western North Atlantic locations during glacial periods that favored TOC preservation, and lower rates during interglacials that allowed more TOC degradation and associated diagenetic alteration of its nitrogen isotopic composition, leading to higher sediment $\delta^{15}\text{N}$ values.

Keywords: Glacial-interglacial cycles, Denitrification, Diagenesis, Sediment accumulation rates, Blake Outer Ridge, Bermuda Rise

1. Introduction

Nitrogen in its bioavailable forms in seawater is essential to all marine life and is the major limiting nutrient in most of the modern ocean (Dugdale and Goering, 1967; Codispoti, 1989). The amount of bioavailable nitrogen is consequently important to marine productivity and the associated removal of dissolved inorganic carbon from the surface ocean. The principal sources of bioavailable N, which is predominantly dissolved nitrate (NO_3^-), to the oceans are continental runoff, atmospheric delivery, and *in situ* bacterial nitrogen fixation. Of these sources, nitrogen fixation is by far the dominant (e.g., Wang *et al.*, 2019). After biological utilization, denitrification is the largest sink of NO_3^- , which occurs in suboxic ($<5\mu\text{M}$ O_2) water columns and sediments where NO_3^- becomes the primary electron acceptor for the oxidation of organic matter.

The $\delta^{15}\text{N}$ values of dissolved nitrate and of sedimentary nitrogen provide insights into the processes that affect these compartments of the nitrogen cycle. Nitrogen fixation imparts little fractionation on the $^{15}\text{N}/^{14}\text{N}$ ratio of dissolved dinitrogen and leads to nitrate with low $\delta^{15}\text{N}$ values that lie between 0‰ to -2‰ relative to the atmosphere (Wada and Hattori, 1979). These low values provide a useful indicator of the importance of nitrogen fixation to local biological productivity. Denitrification of nitrate changes the $^{15}\text{N}/^{14}\text{N}$ ratio of the residual NO_3^- , selectively recycling ^{14}N and leading to $\delta^{15}\text{N}$ values that become progressively larger as the proportion of NO_3^- that has been denitrified becomes greater (e.g., Brandes *et al.*, 1998; Altabet *et al.*, 1999). Uptake and utilization of newly fixed or partially denitrified bioavailable nitrogen by marine organisms will produce organic matter with $\delta^{15}\text{N}$ values that reflect their nitrogen sources and can indicate changes over time in their relative importance to oceanic processes. During biological uptake, an additional factor that can impact the nitrogen isotopic composition of marine organic matter is selective assimilation of $^{14}\text{NO}_3^-$ over $^{15}\text{NO}_3^-$ by photoautotrophs (Wada and Hattori, 1979) as observed by Thunell *et al.* (2004) in the upper photic zone of the Cariaco Basin. However, this process is unlikely to be significant in most parts of the ocean because of the low availability and hence complete utilization of dissolved nitrate. Finally, early diagenesis of sedimentary organic matter can selectively remove ^{14}N and increase the $^{15}\text{N}/^{14}\text{N}$ ratio of the residual material (Altabet and Francois, 1994; Freudenthal *et al.*, 2001; Robinson *et al.*, 2012; Möbius, 2013).

Marine sedimentary $\delta^{15}\text{N}$ records for the past 200 ky at multiple locations show a generally consistent pattern of higher $\delta^{15}\text{N}$ values during interglacial periods and lower ones during glacial times (Altabet *et al.*, 1995; Ganashram *et al.*, 2000, 2002; Kienast *et al.*, 2002; Galbraith *et al.*, 2004; Meissner *et al.*, 2005; Robinson *et al.*, 2007; Martinez and Robinson, 2010; Galbraith *et al.*, 2013; Robinson *et al.*, 2014). This alternation has been shown to extend as far back as 4 Ma in sediments deposited under the California Margin upwelling system (Liu *et al.*, 2008). However, the pattern of higher interglacial $\delta^{15}\text{N}$ values and lower glacial ones is not universal. For example, the $\delta^{15}\text{N}$ values of sediment cores recovered from six locations in the South China Sea show no or little variation over the past 30 ky (Keinast, 2000). A particularly dramatic exception to the general pattern is provided by the MIS 13-1 sediment sequence captured by ODP Site 1002 in the Cariaco Basin off Venezuela. Interglacial $\delta^{15}\text{N}$ values drop below 2‰ whereas glacial values are consistently higher than 4‰ and sometimes exceed 5‰ (Haug *et al.*, 1998). The inconsistencies in the glacial-interglacial patterns of variation in $\delta^{15}\text{N}$ values imply that local factors strongly affect the processes important to nitrogen isotopic compositions of sediments at each location.

The higher interglacial $\delta^{15}\text{N}$ values documented at the locations that have high modern primary productivity rates imply greater degrees of denitrification related to elevated production rates of marine organic matter during interglacial periods and subsequent greater drawdown of dissolved oxygen during its decomposition. Conversely, the lower glacial $\delta^{15}\text{N}$ values imply lower degrees of denitrification related to lower production of organic matter during glacial times. However, the existence of similar glacial-interglacial patterns in the $\delta^{15}\text{N}$ values of sediments under areas of low productivity is not likely to derive from changes in organic matter production and subsequent denitrification. Instead, it may imply changes in oceanic circulation that advected either surface waters with lower nitrate $\delta^{15}\text{N}$ values or deeper water masses with more dissolved oxygen that depressed denitrification during glacial times. As an example of the latter possibility, Meissner *et al.* (2005) estimated that increased delivery of cold, oxygen-rich intermediate water masses depressed denitrification by half in the eastern tropical Pacific Ocean during the Last Glacial Maximum (LGM). An alternative explanation is presented by Galbraith *et al.* (2013), who calculated that post-glacial benthic denitrification as much as doubled between 15 and 8 ka as rising sea

level flooded the formerly subaerially exposed continental shelves of the world and raised the $\delta^{15}\text{N}$ values of the residual dissolved nitrate.

Most glacial-interglacial sedimentary $\delta^{15}\text{N}$ records are from areas of elevated modern primary productivity associated with equatorial and eastern boundary currents, but Poli *et al.* (2010) present a record of glacial-interglacial changes in $\delta^{15}\text{N}$ values from ODP Site 1058 on the Blake Outer Ridge, an oligotrophic area offshore eastern North America. This record, which spans MIS 13-10, shows the classic pattern of lower glacial $\delta^{15}\text{N}$ values and higher interglacial ones found in younger sequences. Poli *et al.* (2010) postulate that subtle changes in marine productivity led to changes in benthic denitrification rates that produced the changes in $\delta^{15}\text{N}$ values. However, increases in delivery of oxygen-rich southern water masses could have depressed denitrification and led to the lower glacial values in this record. As a contribution to improving understanding of the processes important to $\delta^{15}\text{N}$ records in marine sediments and their possible relation to changes in paleoproductivity, we report a pattern of glacial-interglacial change in the $\delta^{15}\text{N}$ values of a MIS 13-10 sediment sequence from ODP Site 1063 on the Bermuda Rise in the oligotrophic central North Atlantic Ocean that closely resembles the same-age pattern reported in the western North Atlantic by Poli *et al.* (2010). We compare the two records to consider the relative importance of possible changes in surface productivity vs. water mass ventilation in affecting the $\delta^{15}\text{N}$ values in sediments at these locations. Finally, we consider the potential impact of glacial-interglacial changes in their sediment accumulation rates on the benthic diagenetic alteration of $\delta^{15}\text{N}$ values.

2. Study settings and sampling

2.1. Site 1063 – Bermuda Rise

ODP Site 1063 (33°41'N, 57°37'W) is at 4595 m present water depth in a sediment drift on the northeastern flank of the Bermuda Rise (Fig. 1). This site lies within the present mixing zone between the Antarctic Bottom Water and the lower limb of the North Atlantic Deep Water (LNADW, 2500-4100 m). Sedimentation rates are high at this location, especially during glacial intervals, owing to advection of clay and silt into the region by deep recirculating gyres (Keigwin and Jones, 1989, 1994). Site 1063 is presently located under the North Atlantic subtropical gyre, which is a pool of warm, low-nutrient water

with low marine productivity. However, occasional injections of cold-core rings that are formed by Gulf Stream meanders evidently have created short episodes of higher productivity during the Holocene (Gil *et al.*, 2009). Furthermore, southward repositioning of the Gulf Stream (Fig. 1) and iceberg migrations during the most recent glacial and deglacial intervals delivered nutrient-rich water that promoted higher productivity over this sector of the Bermuda Rise (Gil *et al.*, 2009).

Advanced piston coring (APC) during ODP Leg 172 in 1997 recovered sediment from Site 1063 for this study. The MIS 12-11 interval was initially identified from the shipboard magnetic susceptibility record and the extinction of the calcareous nannofossil *Pseudoemiliania lacunosa*, which occurred within MIS 12 (Thierstein *et al.*, 1977). The 31 m long core section corresponding to MIS 13-10 consists of alternating nannofossil-rich and clay-rich sediments with variable silt contents (Keigwin *et al.*, 1998). Samples were collected at 7 cm intervals throughout this interval of the core as described by Poli *et al.* (2000).

2.2. Site 1058 – Blake Outer Ridge

ODP Site 1058 (31°41'N, 75°25'W) is at 2996 m present water depth on the crest of the Blake Outer Ridge and under the Gulf Stream (Fig. 1). This site presently lies within the well-oxygenated LNADW and above the Western Boundary Undercurrent high velocity core (Stahr and Sanford, 1999). Healey and Thunell (2004) investigated paleoceanographic changes at nearby Site 1059 (2985 m) that occurred during the MIS 12-10 interval. They found evidence of significant variability in the flow of NADW during this interval, which was stronger during MIS 11 and weaker during MIS 12 and 10.

APC coring at Site 1058 during ODP Leg 172 provided samples for this study. The MIS 12-11 interval was initially identified from the shipboard magnetic susceptibility record and the extinction of the calcareous nannofossil *Pseudoemiliania lacunosa*. The corresponding 17.5 m long section consists of alternating nannofossil-rich and clayey sediments with variable silt contents (Keigwin *et al.*, 1998). Samples were collected at 6 cm intervals throughout this interval of the core after adjusting for a 1.5 m

slump feature that had been identified from its unusual carbonate content. Details of the total number of samples and related time-resolution of each of them are provided by Poli *et al.* (2010).

3. Procedures

3.1. Site 1063 age-scale and foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ stratigraphy

The age model for the Site 1063 MIS 13-11 interval was developed by Poli *et al.* (2000) based on the $\delta^{18}\text{O}$ stratigraphy of the benthic foraminifer *Cibicidoides wuellerstorfi*. (Fig. 2). Stable isotope (oxygen and carbon) analyses were done at the University of South Carolina using a VG Optima isotope ratio mass spectrometer equipped with an automated carbonate carousel. Samples were reacted at 90°C in phosphoric acid. The isotope data are reported relative to Vienna Pee Dee belemnite via the Carrara marble working standard. Seven time-control points were derived from the Lisiecki and Raymo (2005) stacked $\delta^{18}\text{O}$ record (Fig. 2). From these oxygen isotope data, Poli *et al.* (2000) concluded that the record of the Site 1063 extends from the upper part of MIS 13 (~500 ka) to the lower part of MIS 10 (~340 ka). Estimated sedimentation rates based on this chronology are high and extremely variable, ranging from ~7 cm/kyr during MIS 11 and up to 36 cm/kyr during MIS 10 (Poli *et al.*, 2012), resulting in sample temporal spacing ranging from 1,000 to 200 years. By analogy to the elevated sedimentation rates documented by Keigwin and Jones (1989, 1994) during the LGM on the Bermuda Rise, glacial-age sediment rates are magnified by resuspension and transport of terrigenous sediment from the Canadian continental margin by deep circulating gyres

3.2. Site 1058 age-scale and foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ stratigraphy

We used the benthic foraminifera oxygen isotope data presented by Poli *et al.* (2010) for the Site 1058 MIS 13-10 interval. Stable isotope (oxygen and carbon) analyses were done at the University of South Carolina using a VG Optima isotope ratio mass spectrometer equipped with an automated carbonate carousel. Samples were reacted at 90°C in phosphoric acid. The isotope data are reported relative to Vienna Pee Dee belemnite via the Carrara marble working standard. For correlation purposes, we developed a revised age model using the Lisiecki and Raymo (2005) stacked isotope record, which is the same used for Site 1063. Ten time-control points were derived from Lisiecki and Raymo (2005). A

bipartite $\delta^{18}\text{O}$ decrease corresponding to MIS 11 was tuned to the 65°N insolation curve of Berger and Loutre (1991). Poli *et al.* (2010) concluded from these data that the record for Site 1058 extends from the upper part of MIS 13 (~490 ka) to the upper part of MIS 10 (~340 ka). Estimated sedimentation rates based on this chronology are extremely variable, ranging from ~4 cm/kyr during MIS 11 to greater than 17 cm/kyr during MIS 12 (Poli *et al.*, 2010). The elevated glacial-age sedimentation rates reflect erosion of continental margin sediments during lowstands and their transport to the Blake Outer Ridge by the deep western boundary current system (Keigwin and Jones, 1989, 1994)

3.3. Organic carbon analyses of Site 1063 and Site 1058 sediment samples

Dried sediment samples were ground to a homogeneous powder with an agate mortar and pestle. Subsamples were treated with excess 3N HCl to remove their calcium carbonate contents in preparation for organic carbon analyses. The carbonate-free residue was recovered by centrifugation, rinsed to remove chlorides, and dried. The amounts of total organic carbon (TOC) in the carbonate-free residue were determined with a Carlo Erba 1108 elemental analyzer in the Marine Geochemistry Laboratory of The University of Michigan. The absolute precision of this method is better than 0.05 weight percent, based on replicate analyses of sulfanilamide. TOC concentrations are expressed on a whole-sediment basis after adjusting for the carbonate content of each sample, and the TOC mass accumulation rate (MAR) of each sample was estimated from its TOC concentration, its linear sedimentation rate, and shipboard density determinations (Keigwin *et al.*, 1998). The latter two determinations may have introduced some uncertainty into the TOC-MAR values, but it likely would have been consistent between closely spaced sediment samples and thus would not have compromised comparison of their values.

3.4. Organic carbon and nitrogen isotopic analyses of Site 1063 and Site 1058 sediment samples

Portions of the carbonate-free sediment were analyzed for their organic carbon and total nitrogen isotopic compositions in the Laboratory of Isotope Geochemistry at the University of Arizona using a Costech elemental analyzer interfaced directly with a Finnigan Delta Plus XL mass spectrometer.

Analytical precisions for N and C were measured by performing six replicate analyses of acetanilide at the beginning, middle, and end of each batch of sample analyses. The $\delta^{15}\text{N}$ of each sample is expressed relative to atmospheric dinitrogen with an analytical precision better than $\pm 0.2\text{‰}$. The $\delta^{13}\text{C}_{\text{org}}$ is given relative to the Vienna PeeDee Belemnite (VPDB) standard. Precision is better than $\pm 0.06\text{‰}$. We are cognizant of the possibility that decarbonation of sediment samples can impact their absolute $\delta^{15}\text{N}$ values, yet studies have documented that the $\delta^{15}\text{N}$ values differences between bulk and decarbonated samples are generally within the analytical precision (e.g., Meyers and Bernasconi, 2006). Moreover, comparison of $\delta^{15}\text{N}$ values obtained from suites of samples that span the same age interval and that were analyzed by the same procedure as done here should minimize the potential bias of any analytical artifacts on relative patterns in the $\delta^{15}\text{N}$ values of these sediment intervals.

4. Results

4.1. Glacial-interglacial alternations of $\delta^{15}\text{N}$ values

The $\delta^{15}\text{N}$ records of the MIS 13-10 sequences at both locations track the glacial and interglacial cycles recorded in the carbonate isotopic stratigraphy (Figs. 2 and 3). The sediment sections at Site 1063 having lower $\delta^{15}\text{N}$ values ($\sim 4.0\text{‰}$) roughly correspond to the glacial sections having higher $\delta^{18}\text{O}$ values and lower $\delta^{13}\text{C}$ values, whereas the sections with the higher $\delta^{15}\text{N}$ values ($\sim 6.5\text{‰}$) fall within the part of MIS 11 having lower $\delta^{18}\text{O}$ values and higher $\delta^{13}\text{C}$ values (Fig. 2). The highest $\delta^{15}\text{N}$ values at Site 1063 are present in MIS 11.3b between 421-410 ka, which is just before the period of global peak warmth (410-400 ka) recorded by benthic oxygen isotopes. Relatively high values ($\sim 5.5\text{‰}$) are also found in substages 13.1a, 11.23, and 11.1, which were periods of global cooling. The lowest $\delta^{15}\text{N}$ values ($\sim 4.0\text{‰}$) are in substages 12.33 and 10.3, which closely preceded the times of maximum sea ice based on the oxygen isotope record (Fig. 2).

Similar well-developed patterns of lower ($\sim 3.5\text{‰}$) and higher ($\sim 5.5\text{‰}$) $\delta^{15}\text{N}$ values exist between glacial and interglacial intervals in the Site 1058 MIS 13-10 sequence (Fig. 3). Like the sequence at Site

1063, the glacial sections have the lower $\delta^{15}\text{N}$ values. The highest value (6.6‰) occurs in substage 11.3b and follows closely the beginning of MIS 11 at ~425 ka. Similar to Site 1063, the lowest $\delta^{15}\text{N}$ values are present in substages 12.33 (~3.5‰) and 10.3 (~4.0‰).

4.2. Glacial-interglacial alternations of organic $\delta^{13}\text{C}$ values and TOC-MARs

The $\delta^{13}\text{C}$ records of the MIS 13-10 sequences at the two locations alternate between lower and higher values with the glacial and interglacial cycles, but in different ways. The values at Site 1063 vary narrowly between ~-24.0‰ in glacial substages 12.2 and 10.3 to ~-22.5‰ in the lower part of glacial substage 12.33 and in interglacial substage 11.1 (Fig. 2). In contrast, the glacial and interglacial $\delta^{13}\text{C}$ values at Site 1058 differ widely. The glacial values are as low as ~-26.0‰ in substage 12.2 and ~-24.5‰ in substage 10.3, whereas the interglacial values increase to as much as ~-22.0‰ in substage 11.23 (Fig. 3).

TOC-MARs at both locations are generally lower during interglacial MIS 13 and 11 than during glacial MIS 12 and 10, yet they have very different variation patterns. At Site 1063, the interglacial TOC-MAR values are ~0.2 g m⁻² yr⁻¹, but they climb to ~2.8 g m⁻² yr⁻¹ in substage 11.1 (Fig. 2). The patterns exhibited by this productivity proxy differ between the two Site 1063 glacial intervals. The values progressively increase through MIS 12 to reach their peak of 3.8 g m⁻² yr⁻¹ in substage 12.2, whereas they remain between 2.2 and 3.2 g m⁻² yr⁻¹ in substage 10.3 (Fig. 2). Like Site 1063, the smallest TOC-MARs (~0.4 g m⁻² yr⁻¹) are found in the interglacial interval of Site 1058 sediments, but unlike Site 1063, the highest TOC-MARs (~2.6 g m⁻² yr⁻¹) exist in interglacial substage 11.3b, and MIS 12 and 10 TOC-MARs remain between 0.5 and 1.1 g m⁻² yr⁻¹ (Fig. 3). Most of these values are significantly higher than under present-day open-ocean gyres (3 mg m⁻² yr⁻¹; Suess and Müller, 1980), and many of the glacial-stage TOC-MARs are greater than under the zone of modern Atlantic equatorial upwelling (0.1 to 0.8 g m⁻² yr⁻¹, Verardo and McIntyre, 1994). However, only a few of the glacial values from Site 1063 and interglacial values from Site 1058 reach as high as values in the lower part of the range of the elevated TOC-MARs

reported for the early Pleistocene Benguela Current Upwelling System (1 to 10 g m⁻² yr⁻¹; Robinson and Meyers, 2002).

5. Discussion

The systematic pattern of lower $\delta^{15}\text{N}$ values in MIS 12 and 10 and higher ones in MIS 13 and 11 sediments at both Site 1063 on the Bermuda Rise and Site 1058 on the Blake Ridge (Figs. 2 and 3) indicates significant differences in nitrogen cycling between glacial and interglacial intervals in the western North Atlantic Ocean. Both sites are located under low-productivity areas of the ocean, yet their glacial-interglacial $\delta^{15}\text{N}$ alternations closely resemble those in younger sequences from sites under areas of high productivity. Because biological uptake of nitrogen and primary production of organic matter occur in the photic zone, it is possible that the processes that are responsible for the glacial-interglacial $\delta^{15}\text{N}$ sedimentary variations are active in the surface and near-surface waters of the ocean. However, Robinson *et al.* (2012, 2014) and Galbraith *et al.* (2013) present compelling arguments that differences in glacial and interglacial denitrification rates at and near the sea floor are the principal control on the $\delta^{15}\text{N}$ values of marine sediments in the high productivity areas. The similarities between the MIS 13-10 cycles at sites 1058 and 1063 and those from MIS 2-1 at other locations suggest that that differences in denitrification may have functioned in low productivity areas as well, although it is difficult to understand how denitrification could occur without sufficient organic matter to create suboxic conditions.

5.1. Photic zone processes

Consideration of the three processes that affect the isotopic composition of the bioavailable nitrogen that is assimilated by marine primary producers might offer possible explanations for the glacial-interglacial pattern that we observe. The first possibility is related to the $\delta^{15}\text{N}$ value of the nitrate that is mixed into the photic zone from deep waters. The open ocean $\delta^{15}\text{N}$ value of NO_3^- typically ranges between ~4-6‰ (Sigman *et al.* 2000), which essentially encompasses the range of glacial-interglacial values at sites 1058 and 1063 (Figs. 2 and 3). Other areas of the ocean provide examples of delivery of deep water with different nitrate $\delta^{15}\text{N}$ values to the photic zone. For example, Robinson and Meyers

(2002) document a shift in $\delta^{15}\text{N}$ values of sediment deposited under the Benguela Current Upwelling System from 1‰ at 2.3 Ma to 4‰ at 2.0 Ma that they attribute to a change in the origin of the upwelling water mass. The glacial-interglacial $\delta^{15}\text{N}$ pattern in the MIS 13-10 sediment sequences at sites 1058 and 1063 may reflect similar changes in the origins of the water masses that delivered dissolved nitrate during glacial and interglacial times, which would imply large scale changes in the subsurface circulation of the North Atlantic. The $\delta^{15}\text{N}$ values at Site 1063 are routinely 0.5‰ larger than those at equivalent intervals at Site 1058 (Figs. 2 and 3), which may record a systematic difference between the surface waters at these two locations that are indeed sensitive to glacial-interglacial changes.

The second possibility does not require such large scale changes, although they are not excluded. Water column denitrification commonly takes place at relatively shallow depths (100-500 m) in the upper part of the oxygen minima of the oceans (*e.g.* Brandes *et al.*, 1998; Altabet *et al.*, 1999; Ganeshram *et al.*, 2000). The residual nitrate is enriched in ^{15}N relative to the dissolved dinitrogen that is fixed by marine bacteria and relative to the $^{15}\text{N}/^{14}\text{N}$ composition of the local nitrate supply. Variations in the development of the local oxygen minimum zone modify the extent of ^{15}N enrichment during denitrification and hence the amount of increase in the $\delta^{15}\text{N}$ values of the residual nitrate that remains available for assimilation by primary producers and eventual sedimentation. The pattern shared by both Site 1058 and Site 1063 is for $\delta^{15}\text{N}$ values to reach minima of ~4‰ in substage 12.2, increase to 6-7‰ in substage 11.3, and then drop again to ~4‰ in substage 10.3 (Figs. 2 and 3). Similar alternations between lower glacial and higher interglacial $\delta^{15}\text{N}$ values have been reported in sediments from the Arabian Sea (Altabet *et al.*, 1995, 1999), the eastern equatorial Pacific (Ganeshram *et al.*, 1995, 2002; Ganeshram and Peterson, 1998; Kienast *et al.*, 2002; Thunell and Kepple, 2004), and the California Margin (Pride *et al.*, 1999; Emmer and Thunell, 2000), where they have been interpreted as evidence of decreased denitrification during glacial periods because of better ventilation of intermediate water masses. Evidence for better glacial-stage thermocline ventilation also exists closer to sites 1058 and 1063. Slowey and Curry (1995) show that thermocline waters on the Bahama Bank originate in the subtropical gyre that bathes Site 1063 and likely influences Site 1058. Benthic foraminifera isotopic compositions indicate the absence of an oxygen

minimum zone on the Bahama Bank during the LGM, presumably because of more vigorous wind mixing of the upper ocean. Slowey and Curry (1995) further postulate that southward migration of the northern edge of the subtropical gyre resulted in a shallower thermocline region that contributed to more effective wind mixing.

Greater surface productivity generally leads to greater oxygen drawdown during organic matter oxidation in the thermocline regions of the ocean. Consequently, the higher productivity implied by the larger TOC-MARs during the onsets of MIS 12 and 10 (Figs. 2 and 3) would seem to predict existence of more strongly developed oxygen minima and more water column denitrification at these times. This is contrary to the $\delta^{15}\text{N}$ signal that we find in the Site 1063 record and in parts of the Site 1058 record. As shown in Figure 4, larger TOC-MARS at Site 1063 are associated with smaller $\delta^{15}\text{N}$ values, which would suggest less denitrification during times of elevated surface productivity. Although some of the TOC-MARs at Site 1058 have a weak positive correlation with the $\delta^{15}\text{N}$ values, most exhibit little or no relation to them (Fig. 4). The inconsistent relation between TOC-MARs and $\delta^{15}\text{N}$ values at the two locations implies that surface productivity has little or no influence over denitrification over glacial-interglacial cycles in the oligotrophic western North Atlantic Ocean.

The third and most important process that affects the isotopic composition of bioavailable nitrogen is nitrogen fixation (e.g., Wang *et al.*, 2019). This bacterial process converts dissolved dinitrogen to dissolved ammonia that is quickly oxidized in seawater to form dissolved nitrate having an isotopic signature that is essentially the same as atmospheric nitrogen (0‰ to -2‰) and distinctively lower than the oceanic average of ~5‰ of sub-thermocline nitrate (Sigman *et al.*, 2000). Nitrogen fixation is limited by the availability of phosphorus. Most parts of the world ocean have adequate dissolved nitrate to sustain healthy algal communities, and the algae out-compete bacteria for phosphorus and thus limit local nitrogen fixation. However, oligotrophic areas have little nitrate, and nitrogen-fixing bacterial can out-compete algae for the limited phosphorus in such areas. The western North Atlantic is one of those areas. As shown by Knapp *et al.* (2005), thermocline dissolved nitrate $\delta^{15}\text{N}$ values between 2‰ and 3‰ indicate

significant contributions of newly fixed nitrogen to the bioavailable supply in this region. These values are preserved in foraminifera-bound $\delta^{15}\text{N}$ values in Holocene sediments from the western North Atlantic (Ren *et al.*, 2009; Straub *et al.*, 2013). The interglacial $\delta^{15}\text{N}$ values between 2‰ and 3‰ that are documented by Haug *et al.* (1998) in sediments of the Cariaco Basin suggest that this is another area in which nitrogen fixation is important (see Thunell *et al.* 2004). It seems reasonable that nitrogen fixation should have been as important to Pleistocene interglacial productivity as it is in the modern western North Atlantic. However, the MIS 11 $\delta^{15}\text{N}$ values of ~6‰ at Site 1063 (Fig. 2) and ~5‰ at Site 1058 (Fig. 3) are significantly higher than the modern thermocline nitrate values of 2‰ and 3‰ reported by Knapp *et al.* (2005) and in Holocene foraminifera by Ren *et al.* (2009) and Straub *et al.* (2013). This difference suggests that the sediment values could have been enhanced by denitrification, but the inconsistencies between TOC-MARs and $\delta^{15}\text{N}$ values in the interglacial sediments do not support denitrification as being likely. Consequently, their $\delta^{15}\text{N}$ values have evidently been increased by a process that mimics the isotopic effects of denitrification but cannot be denitrification.

Unlike the interglacial values, the glacial $\delta^{15}\text{N}$ values that lie between 3‰ and 4‰ (Figs. 2 and 3) are closer to modern thermocline nitrate values and lower than the modern oceanic average of ~5‰ (Sigman *et al.*, 2000). Although these relatively low values suggest that nitrogen fixation was as important to glacial-age marine productivity in the western North Atlantic as it is today, foraminifera-bound $\delta^{15}\text{N}$ values of ~6‰ reported by Ren *et al.* (2009) and Straub *et al.* (2013) suggest that nitrogen fixation was depressed in the western North Atlantic during the Last Glacial Maximum. The difference between their foraminifera-bound $\delta^{15}\text{N}$ values and our bulk sediment glacial-age values is close to the 3‰ to 4‰ increase that occurs with each trophic level (e.g., Peterson and Fry, 1987), and hence it is possible that the MIS 12 and 10 sediments preserve a record of the isotopic composition of photic zone nitrate that was captured by primary producers. If this is true, then it is principally the interglacial sediments in MIS 11 that have had their nitrogen isotopic compositions altered by the process that mimics the effects of denitrification.

5.2. Pelagic processes

Poli *et al.* (2010, 2012) note that similar patterns of lower glacial and higher interglacial values exist in the $\delta^{13}\text{C}$ values of organic matter and benthic forams in the MIS 13-10 sequences of Site 1058 and Site 1063 (Figs. 2 and 3). A possible explanation for the parallel glacial-interglacial excursions in organic $\delta^{13}\text{C}$ values, the benthic foram $\delta^{13}\text{C}$ values, and the $\delta^{15}\text{N}$ values in the MIS 13-10 sequences of both sites 1058 and 1063 is offered by an hypothesis put forward by Bertrand *et al.* (2000). They observe that similar excursions exist in $\delta^{15}\text{N}$ values of continental margin sediments deposited at multiple locations during the latest deglaciation, and they interpret these patterns as consequences of the early postglacial sea level rise that shifted nutrient recycling from oceanic areas towards continental margins. One impact of this shift would be increased denitrification during interglacial stages, as also hypothesized by Galbraith *et al.* (2013), and another is diminished export of metabolizable organic carbon to the deep ocean.

The excursions to higher $\delta^{15}\text{N}$ values that appear in the substage 11.3b intervals in both the Site 1063 and Site 1058 sequences (Figs. 2 and 3) are consistent with an increase in denitrification, but they are not consistent with the measured decreases in delivery of organic carbon at both sites, which would depress denitrification. Instead, the increases in $\delta^{15}\text{N}$ values that are evident in substage 11 in both sequences and that are concordant with depressed TOC-MARs (Figs. 2 and 3) might indicate that denitrification increased even though organic matter delivery decreased during the interglacial stages. This change in mode of nitrogen recycling is possible if seawater at these locations held less dissolved oxygen during interglacial intervals than during glacial times. This possibility might be supported by several tempting lines of evidence for greater deep-water oxygenation in the glacial-age North Atlantic. First, Poli *et al.* (2000) postulate that the lower CaCO_3 concentrations in the glacial intervals of the Site 1063 sections we have studied here as evidence of increased penetration of corrosive, well oxygenated Antarctic Bottom Water to the western North Atlantic location. Second, Dubois-Dauphin (2016) interpret higher ϵNd values in cold-water corals in the Gulf of Cadiz as evidence of enhanced northward penetration of Eastern Antarctic Intermediate Water into the eastern North Atlantic during the LGM. The

deeper penetration of cold and oxygen-rich Antarctic water masses into the North Atlantic would depress pelagic denitrification during the glacial periods (e.g., Galbraith *et al.*, 2004). The opposite phenomenon, diminished penetration of Antarctic water masses into the North Atlantic during interglacial periods, would have encouraged denitrification. In partial support of this possibility, Galbraith *et al.* (2013) estimate from a survey of multiple core records that seafloor denitrification increased 30-120% during the end of the LGM. However, the presence of diverse benthic foraminiferal communities at both site 1063 and 1058 throughout the MIS 13-10 sequence (Poli *et al.*, 2010, 2012) argues against poor oxygenation at the seafloor of the western North Atlantic and by association throughout most of the pelagic water column. Hence, unlike under regions of high-productivity, fluctuations in pelagic denitrification seem unlikely to be responsible for the alternations between lower glacial $\delta^{15}\text{N}$ values and higher interglacial ones in the site 1063 and 1058 sequences.

5.3. Benthic processes

As summarized by Galbraith *et al.* (2008) and Robinson *et al.* (2012), comparisons of the bulk $\delta^{15}\text{N}$ values of sinking particles and the underlying surface sediments in areas of the ocean having low sedimentation rates and low sediment TOC concentrations generally find an increase of 1‰ to 5‰ in core tops relative to the sinking particles. This finding contrasts with ocean margin areas, especially those with high productivity, where $\delta^{15}\text{N}$ values of surface sediments are typically close to those of the sinking particles (e.g., Galbraith *et al.*, 2008). The difference is generally attributed to partial degradation of sedimented organic matter in which components enriched in ^{14}N are preferentially remineralized, and it appears to become significant in settings in which delivery of organic matter is low. Its impact on the $\delta^{15}\text{N}$ values of sediments interestingly mimics that of denitrification – an increase in the values of the residual nitrogen – but the process is very different because it is oxidizing organic matter instead of reducing nitrate and it is favored by an aerobic environment instead of a suboxic one. The length of the exposure time to oxygen seems to be important to the organic matter alteration, inasmuch as Robinson *et al.* (2012) find a relation between water depth and the amount of increase in sediment $\delta^{15}\text{N}$ values in the low sedimentation rate areas. From this observation, differences in sediment accumulation rates would seem

also to be very important to this process; organic matter in locations with higher sedimentation rates would be exposed to oxygenated bottom water for shorter times than in locations with lower rates.

Poli *et al.* (2010, 2012) have estimated the sedimentation rates for the MIS 13-10 sequences at sites 1063 and 1058. They report that the sedimentation rates drop from an average of 33 cm/ky in MIS 12 to average 5 cm/ky in MIS 11 and then increase to average 35 cm/ky in MIS 10 at Site 1063. The respective changes at Site 1058 are 15 cm/ky to 5 cm/ky and then to 18 cm/ky. Explanations for the much higher sediment accumulation rates at both sites during the glacial stages are provided by analogy to similar differences between MIS 2 and MIS 1 sedimentation rates that occurred at these locations (Keigwin and Jones, 1989, 1994). The elevated rates reflect increased delivery of clastic sediments during the LGM from the subaerially exposed North American continental shelf and from the St. Lawrence River at Site 1063 (Keigwin and Jones, 1994) and from the Mississippi River at Site 1058 (Keigwin and Jones, 1989) and transport to these locations by deep-water gyres. Low atomic TOC/TN ratios (Poli *et al.*, 2010, 2012) and virtually unchanging organic $\delta^{13}\text{C}$ values (Fig. 3) throughout both the site 1058 and 1063 sequences indicate that the clastic sediments entrained little to no land-derived organic matter. The TOC-MARs reach their lowest during the interglacial intervals in the MIS 13-10 sequences at both sites and are accompanied by $\delta^{15}\text{N}$ values that are at their highest (Figs. 2 and 3). Both the low TOC-MARs and the relatively high $\delta^{15}\text{N}$ values are consistent with a greater degree of degradation of the sediment organic matter and diagenetic alteration of its isotopic composition during the MIS 11 intervals of low sediment accumulation and associated increased exposure to oxygenated bottom water at both sites. We therefore conclude that the principal process responsible for the MIS 13-10 alternations in the $\delta^{15}\text{N}$ values of the sediments at sites 1063 and 1058 in the oligotrophic western North Atlantic is variations in the degree of diagenesis of sedimented organic matter that are a consequence of glacial-interglacial variations in sediment burial rates. Consistent with the conclusion of Robinson *et al.* (2012), MIS 11 $\delta^{15}\text{N}$ values that are ~1‰ higher in the Site 1063 sequence than in the Site 1058 record suggest that the 1600 m greater water depth and probable longer settling time at Site 1063 allowed for a greater degree of oxidation of settling organic matter and therefore more diagenetic alteration of its $^{15}\text{N}/^{14}\text{N}$ composition at this location.

6. Summary and Conclusions

We have determined organic carbon mass accumulation rates (TOC-MARs) and nitrogen isotopic values ($\delta^{15}\text{N}$) in sediments deposited from 500 to 340 ka at ODP sites 1063 on the northeastern Bermuda Rise and 1058 on the Blake Outer Ridge of the western North Atlantic. This time interval encompasses Marine Isotope Stages (MIS) 13 to 10 and includes MIS 11, an especially warm interglacial period from about 423 to 360 ka, and MIS 12, a particularly severe glacial period from approximately 487 to 423 ka. Both the TOC-MARs and the $\delta^{15}\text{N}$ values vary significantly with the glacial-interglacial cycles in the depositional records from these two locations. Sediment accumulation rates also vary significantly, being markedly greater at both sites during MIS 12 and 10 than during MIS 13 and 11.

TOC-MARs are highest in sediments deposited at Site 1063 during MIS 12 and MIS 10, implying either that marine productivity was higher at this location during glacial stages or that organic matter preservation was better during these intervals of higher sediment rates. Low TOC-MARs during most of MIS 11 in Site 1063 sediment imply low rates of marine productivity or poor preservation of organic matter during this warm interval. In contrast to the Site 1063 record, productivity or preservation appears to have been greater at Site 1058 during intervals of the MIS 11 interglacial than during the preceding and following glacial intervals. TOC-MARs peaked at the onset of MIS 11, dropped to low values from 410 to ~390 ka, and then recovered to relatively high levels during the remainder of MIS 11 and the early part of MIS 10.

Unlike the TOC-MAR records, $\delta^{15}\text{N}$ values at both locations vary in closely similar glacial-interglacial ways. Values peak during Interval 11.3 and gradually decrease towards the terminations of MIS 12 and MIS 10. In addition, both records contain similar short-lived inflections to lower values near the end of Interval 11.3. Moreover, two features of the Site 1063 and 1058 records make them especially interesting. First, these records provide the first open-ocean documentation of glacial-interglacial $\delta^{15}\text{N}$ variations associated with the MIS 12-11 transition. Second, the two $\delta^{15}\text{N}$ records exhibit a systematic offset of about 1‰, with the Bermuda Rise location having the higher values.

The differences in TOC-MARs of the Site 1063 and Site 1058 records imply that surface productivity and organic matter preservation at these two locations responded differently to the glacial and the interglacial conditions that changed at these locations during the MIS 13-10 time period. Because the $\delta^{15}\text{N}$ patterns of change at these two sites are like each other, they appear to be largely independent of changes in local surface production of organic matter at these low-productivity locations. Instead, sedimentation rates that are markedly less in the interglacial stages than in the glacial states at both sites likely allowed greater postdepositional diagenetic alteration of the nitrogen isotopic composition in the MIS 11 sediments during their longer burial times. This change is probably responsible for the larger interglacial $\delta^{15}\text{N}$ values. Moreover, the systematic offset to $\delta^{15}\text{N}$ values that are about 1‰ higher on the Bermuda Rise than on the Blake Outer Ridge suggests that a greater amount of diagenetic alteration occurred during the longer settling time at Site 1063, which is 1600 m deeper than Site 1058.

The closely similar patterns of glacial-interglacial changes in the $\delta^{15}\text{N}$ values at sites 1063 and 1058 in the oligotrophic western North Atlantic Ocean indicate that nitrogen cycling in areas of the ocean characterized by low rates of productivity and low rates of sediment accumulation is likely to be sensitive to diagenesis in and at the seafloor that can alter its isotopic composition. Partial degradation of sediment organic matter evidently removes ^{14}N -enriched components and results in larger $\delta^{15}\text{N}$ values of the residual bulk nitrogen in a way that mimics the effects of denitrification but is a very different process. Therefore, cautious interpretations of bulk $\delta^{15}\text{N}$ values in sedimentary sequences from low-productivity areas of the ocean are likely to yield valuable site-specific information about processes important to nitrogen cycling in these oligotrophic regions.

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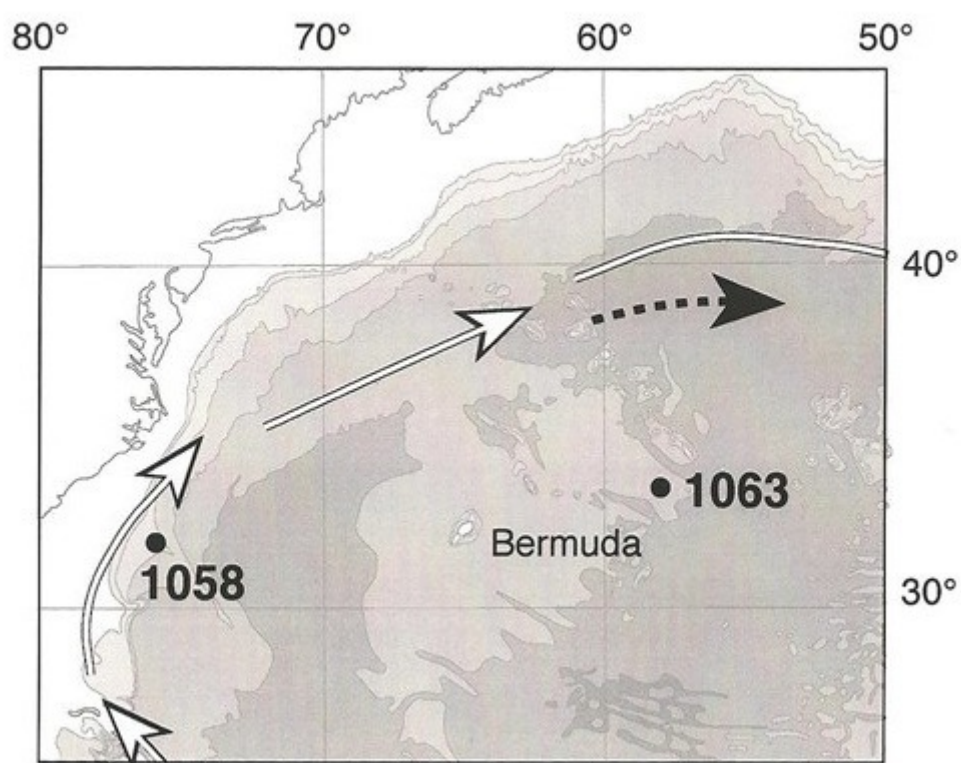
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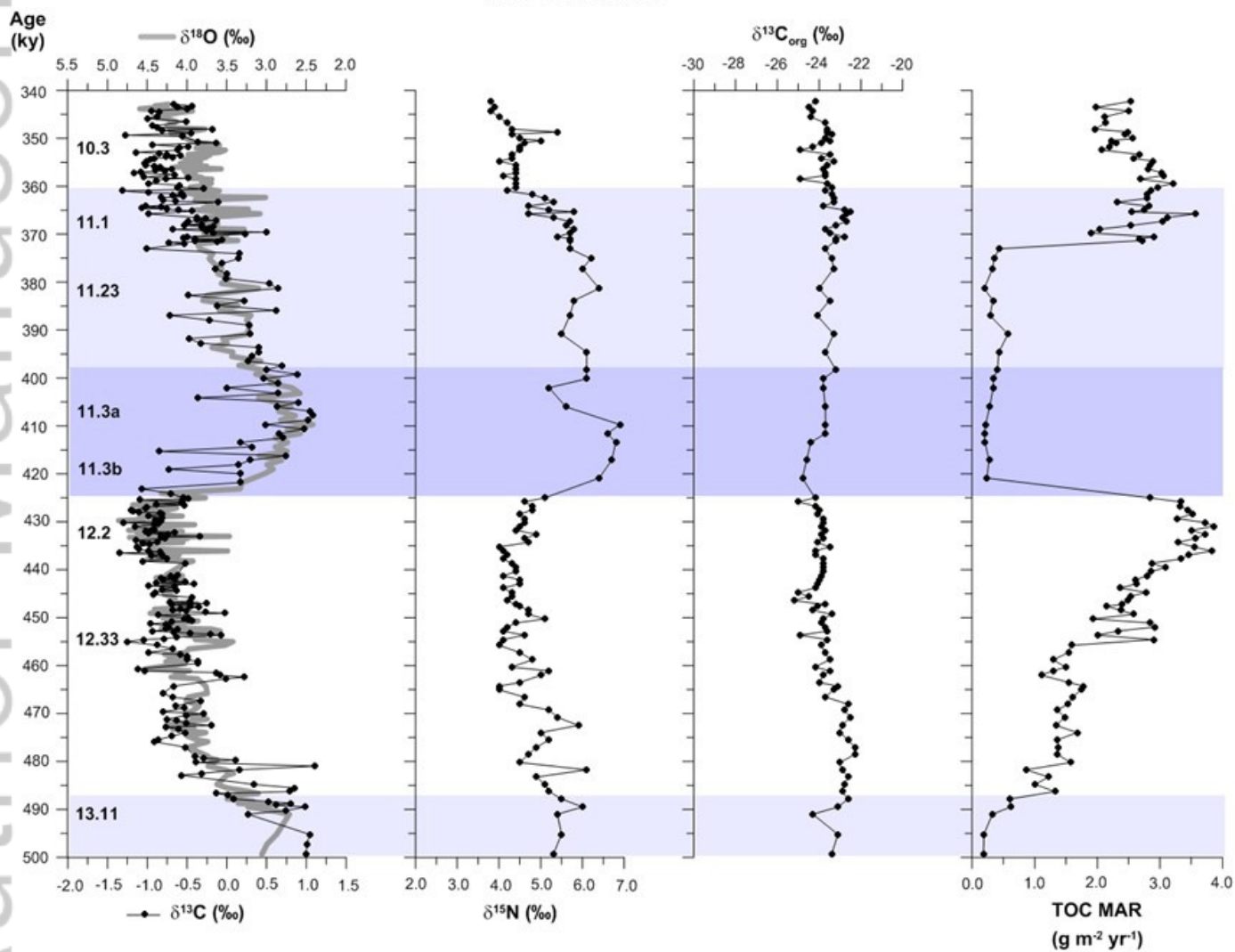
Figures

1. Locations of ODP Site 1063 at 4595 m present depth on the Bermuda Rise and ODP Site 1058 at 2996 m present depth on the Blake-Bahama Ridge. General surface flow patterns of the modern and last glacial western North Atlantic Ocean are shown as solid lines and dashed lines, respectively.
2. Glacial-interglacial patterns of changes in benthic foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and in organic matter $\delta^{13}\text{C}$ and total $\delta^{15}\text{N}$ values relative to changes in organic carbon mass accumulation rates in Site 1063 sediments deposited from 500 ka to 340 ka on the Bermuda Rise. Late interglacial periods MIS 13.1 and MIS 11.1 and 11.2 are indicated by light shading, and the peak interglacial period MIS 11.3 is indicated by dark shading. Note that the scale of the $\delta^{18}\text{O}$ variations has been inverted to conform to variations in the companion isotope plots.
3. Glacial-interglacial patterns of changes in benthic foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and in organic matter $\delta^{13}\text{C}$ and total $\delta^{15}\text{N}$ values relative to changes in organic carbon mass accumulation rates in Site 1058 sediments deposited from 500 ka to 340 ka on the Blake-Bahama Ridge. Late interglacial periods MIS 13.1 and MIS 11.1 and 11.2 are indicated by light shading, and the peak interglacial period MIS 11.3 is indicated by dark shading. Note that the scale of the $\delta^{18}\text{O}$ variations has been inverted to conform to variations in the companion isotope plots. Data are from Poli *et al.* (2010).
4. Relation between TOC-MARs and total $\delta^{15}\text{N}$ values at sites 1063 and 1058. Correlations are negative to poor, respectively.



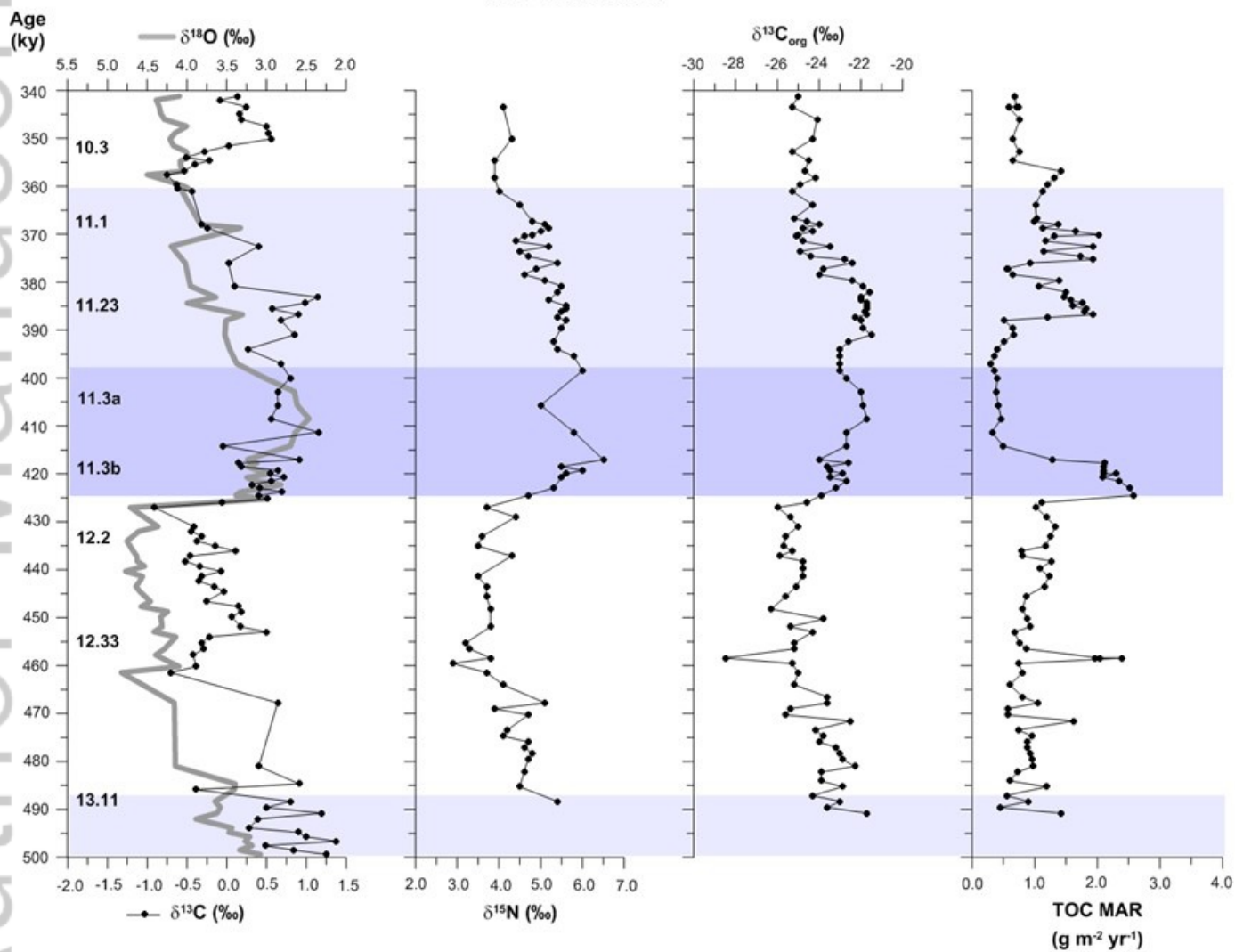
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ODP Site 1063

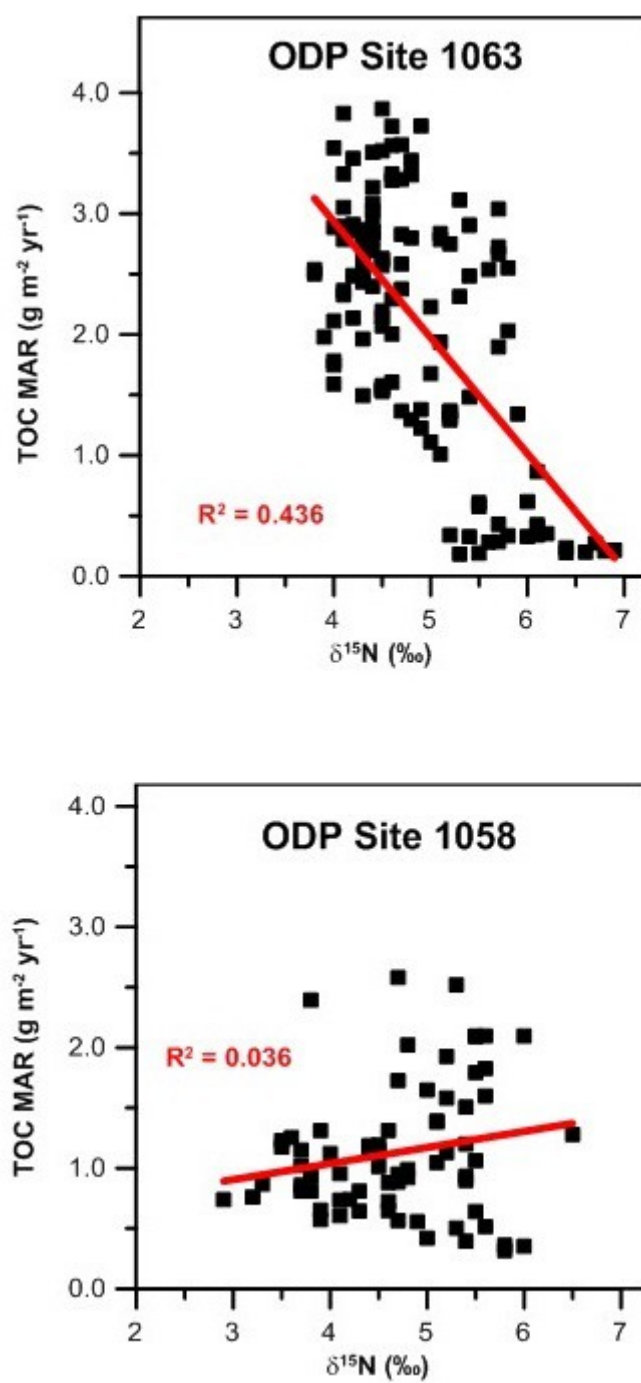


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ODP Site 1058



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