Ice Age-Holocene Similarity of Foraminifera-Bound Nitrogen Isotope Ratios in the Eastern Equatorial Pacific

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Abstract  Bulk sediment δ15N records from the eastern tropical Pacific (ETP) extending back to the last ice age most often show low glacial δ15N, then a deglacial δ15N maximum, followed by a gradual decline to a late Holocene δ15N that is typically higher than that of the Last Glacial Maximum (LGM). The lower δ15N of the LGM has been interpreted to reflect an ice age reduction in water column denitrification. We report foraminifera shell-bound nitrogen isotope (FB-δ15N) measurements for the two species Neogloboquadrina dutertrei and Neogloboquadrina incompta over the last 35 ka in two sediment cores from the eastern equatorial Pacific (EEP), both of which have the typical LGM-to-Holocene increase in bulk sediment δ15N. FB-δ15N contrasts with bulk sediment δ15N by not indicating a lower δ15N during the LGM. Instead, the FB-δ15N records are dominated by a deglacial δ15N maximum, with comparable LGM and Holocene values. The lower LGM δ15N of the bulk sediment records may be an artifact, possibly related to greater exogenous N inputs and/or weaker sedimentary diagenesis during the LGM. The new data raise the possibility that the previously inferred glacial reduction in ETP water column denitrification was incorrect. A review of reconstructed ice age conditions and geochemical box model output provides mechanistic support for this possibility. However, equatorial ocean circulation and nitrate-rich surface water overlying both core sites allow for other possible interpretations, calling for replication at non-equatorial ETP sites.

Plain Language Summary  The 15N/14N ratio of sediments provides information on the past marine nitrogen (N) cycle through the production of N-bearing organic matter in the surface ocean and its burial in the sediments. Previous measurements of the sedimentary 15N/14N ratio in the eastern equatorial Pacific (EEP) indicate lower values during the last ice age compared to the Holocene (the current warm period). This has been interpreted to reflect an ice age reduction in the oceanic N loss process known as “denitrification” that occurs between 200 and 500 m depth in this region of the ocean. However, the 15N/14N ratio measured on the whole sediment can be biased by biological and chemical processes in the sediments and by foreign N inputs. To avoid these complications, we measured the 15N/14N ratio of organic N embedded in the calcite shell of unicellular zooplankton (foraminifera) in two sediment cores from the EEP. We found similar foraminifera-bound 15N/14N ratios during the last ice and the Holocene. This may argue against the long-held interpretation of a reduction in denitrification during the last ice age. However, the oceanographic setting of these equatorial cores leaves open alternative interpretations, calling for further work at other eastern tropical Pacific sites.

1. Introduction

The eastern tropical Pacific (ETP) is important in climate and biogeochemical cycles. It hosts three upwelling systems: the equatorial upwelling, the coastal upwelling off California in the eastern tropical North Pacific (ETNP), and the Peru-Chile coastal upwelling in the eastern tropical South Pacific (ETSP) (Figure 1). In these regions, cold, nutrient-rich waters upwell to the surface, fueling productivity. In addition, slow circulation through the thermocline in these regions isolates the mid-depths waters from ventilation by the high latitudes. Due to the combination of slow ventilation and the abundance of sinking organic matter, respiration completely consumes the supply of dissolved oxygen (O₂), producing O₂-deficient zones (ODZs),...
one in the ETNP and one in the ETSP. Within the ODZs, denitrification reduces nitrate to N₂, providing the oxidant for the respiration of organic matter. This water column denitrification is a major driver of fixed N loss from the ocean (Deutsch et al., 2001), and it can also produce nitrous oxide, a potent greenhouse gas, as a side-product (Pierotti & Rasmussen, 1980). Moreover, reconstruction of the history of denitrification may provide insight into past changes in ocean circulation and the strength of the global ocean’s biological carbon pump (Altabet et al., 1995, 2002; Ganeshram et al., 1995; Martinez et al., 2006; Robinson et al., 2007).

During denitrification, ^14N-nitrate is preferentially lost from the ocean water column, elevating the residual nitrate in δ^15N (Cline & Kaplan, 1975; Liu & Kaplan, 1989) (with δ^15N = [(15N/14N)sample/(15N/14N)atm - 1]*1000‰). This ^15N-enriched nitrate is then transported laterally in the subsurface, spreading this isotopic signal through the mid-depth ocean. The high-δ^15N nitrate is also supplied to the surface by upwelling, resulting in the production of high-δ^15N organic matter. This organic N is then exported to depth, possibly after significant lateral transport in the surface. Regeneration back to nitrate in the subsurface represents an additional mechanism for spreading the high-δ^15N signal of denitrification both laterally and vertically (Sigman et al., 2009).

The water from the ETNP with its ^15N-enriched nitrate is transported northward in the subsurface with the California Undercurrent (CUC) and southward at the surface with the California Current (CC) (Figure 1) (S.S. Kienast et al., 2002; Sigman et al., 2005). In the tropical Pacific, the CC flows into the North Equatorial Current (NEC), which itself recirculates into the North Equatorial Counter Current (NECC). The NECC is one of a number of inputs to the Equatorial Undercurrent (EUC), and the EUC is a major source water for equatorial upwelling (Goodman et al., 2005; Kessler, 2006; Talley et al., 2011; Wyrtki, 1966). Water from the ETSP with its elevated nitrate δ^15N is transported southward in the subsurface with the Peru-Chile Undercurrent (PCUC) (De Pol-Holz et al., 2009) and northward in the surface with the Peru-Chile Current (PC)
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(Lukas, 1986; Silva & Neshyba, 1979). The high-$\delta^{15}N$ signal of ETSP denitrification is thus advected to the southern part of the eastern equatorial Pacific (EEP) upwelling, and it may also be transported further west with the South Equatorial Current (SEC) (Peters et al., 2018; Rafter et al., 2012; Rafter & Sigman, 2016). A second N isotope signal that pertains to the EEP (as well as to the central equatorial Pacific) is that of partial nitrate consumption in surface waters (Altabet, 2001; Altabet and François, 1994). The preferential consumption of $^{14}N$ nitrate by phytoplankton produces low-$\delta^{15}N$ organic matter above the upwellings and leaves the residual nitrate enriched in $^{15}N$. The high-$\delta^{15}N$ nitrate is then advected away from the upwelling, with continued consumption leading to the production of high-$\delta^{15}N$ organic matter (Altabet & François, 1994). This pattern is reflected in the $\delta^{15}N$ of bulk organic matter and foraminifera shell-bound organic matter on the seabed (Costa et al., 2016; Farrell et al., 1995). Sediment records of the N isotopes in the EEP are thus expected to record changes in both water column denitrification and the spatial pattern of surface nitrate consumption.

A third potential influence is the $\delta^{15}N$ of shallow subsurface nitrate imported into the EEP by the equatorial system. Nitrate $\delta^{15}N$ data are lacking in the EEP east of the Galapagos Islands. West of Galapagos, the $\delta^{15}N$ of nitrate in the EUC proper is $\sim 7.1\%$, similar to that of Subantarctic Mode Water, which is the ultimate nitrate source to much of the tropical Pacific thermocline (Rafter et al., 2012). Strengthening in the flow of the EUC has the potential to lower the $\delta^{15}N$ of the nitrate supply to the EEP relative to that supplied from the denitrification zones. However, the caveat must be added that the EUC flow is interrupted by the Galapagos, and thus its nitrate isotopic signature may not persist east of the islands. This must be clarified by future nitrate isotope studies.

A water mass known as the subsurface equatorial “thermostad” just below the EUC as well as the eastward-flowing Southern Subsurface Counter Current (SSCC) have a nitrate $\delta^{15}N$ that can reach below $6\%$ (Rafter et al., 2012; Rafter & Sigman, 2016). This lower nitrate $\delta^{15}N$ results from the remineralization of low-$\delta^{15}N$ sinking N associated with the upwelling and incomplete consumption of nitrate that upwells along the equator and its southern margin. Thus, rather than being a distinct signal of nitrate source from the west, the lower nitrate $\delta^{15}N$ of the thermostad and SSCC is an additional aspect of the signal of incomplete nitrate consumption in the equatorial Pacific. Accordingly, its likely effect is to amplify the $\delta^{15}N$ lowering of sinking N due to incomplete nitrate consumption in the region.

Existing bulk sediment $\delta^{15}N$ records from the ETNP, ETSP, and EEP typically show low glacial $\delta^{15}N$ that is followed by a deglacial $\delta^{15}N$ rise (De Pol-Holz et al., 2006; Dubois et al., 2011; Emmer & Thunell, 2000; Farrell et al., 1995; Ganeshram et al., 1995, 2000; Hendy et al., 2004; Hendy & Pedersen, 2006; Higginson & Altabet, 2004; S. S. Kienast et al., 2002; Pichelin et al., 2010; Pride et al., 1999; Robinson et al., 2007, 2009; Thunell & Kepple, 2004). This $\delta^{15}N$ increase is widely interpreted as a deglacial rise in water column denitrification across the ETP, an interpretation supported by a comparable deglacial $\delta^{15}N$ rise in the Arabian Sea of the Indian Ocean (Altabet et al., 2002; Ganeshram et al., 2000). Typically, in the ETSP, the $\delta^{15}N$ rise is observed to begin at $\sim 17–18 \text{ ka}$, in step with southern hemisphere warming (De Pol-Holz et al., 2006; Higginson & Altabet, 2004; Robinson et al., 2007), whereas the $\delta^{15}N$ rise in the ETNP (and downstream of it) occurs with the first abrupt northern hemisphere warming at $\sim 14–15 \text{ ka}$, associated with the Northern Hemisphere’s Bolling-Allerod Warm Period (Chang et al., 2014, 2008; Emmer & Thunell, 2000; S. S. Kienast et al., 2002; Pride et al., 1999). The deglacial rises in water column denitrification in the ETNP and ETSP, with their respective timings, are often interpreted as the result of a tendency for warming to enhance water column suboxia and denitrification, through the decreased solubility of O$_2$ and/or slower ventilation of intermediate waters and the thermocline under warmer climate (Galbraith et al., 2004). A deglacial rise in nutrient supply to the thermocline has also been implicated, the concept being that increased thermocline nutrients would drive higher lower latitude export production and thus more oxygen demand for respiration in the thermocline (Robinson et al., 2005). Millennial scale variations during the deglaciation are largely consistent with these interpreted mechanisms (Robinson et al., 2007).

In many ETP records, the later deglaciation and Holocene is characterized by a subsequent decline in bulk sediment $\delta^{15}N$. In some records, the decline is minor; in others, the decline almost completely compensates for the more abrupt early deglacial $\delta^{15}N$ rise. There have been multiple plausible interpretations of this decline: as part of a whole-ocean trend in nitrate $\delta^{15}N$, a late deglacial decline in water column denitrification,
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The deglacial δ15N maximum is often accompanied by deglacial maxima in redox sensitive trace metals and/or sediment lamination (Pride et al., 1999; Y. Zheng et al., 2000). These parallel changes support the interpretation of the deglacial δ15N maximum as due to an associated temporal peak in water column denitrification. However, as with the δ15N records, the Holocene evolution of trace metal concentrations and lamination varies among sediment cores, declining back to baseline in some but not in others (Chang et al., 2014; Murati et al., 2010; Y. Zheng et al., 2000). Finally, the deglacial δ15N maximum itself has significantly different temporal structure in different regions and sediment cores (De Pol-Holz et al., 2006; Dubois et al., 2011; Emmer & Thunell, 2000; Ganeshram et al., 2000; Hendy & Pedersen, 2006; Higginson & Altabet, 2004; S. S. Kienast et al., 2002; Pichevin et al., 2010; Robinson et al., 2009, 2007; Thunell & Kepple, 2004).

In the EEP, the LGM-to-Holocene δ15N rise in the first sediment δ15N records was initially interpreted as a lower degree of nitrate consumption during the ice ages (Farrell et al., 1995). However, the change was very similar to that reconstructed from the ETP (Ganeshram et al., 1995); as described above, that change has been interpreted as deriving from an increase in water column denitrification. The LGM-to-Holocene sediment δ15N rise in the EEP is now most often interpreted as a shared ETP/EEP signal, reflecting a rise in the δ15N of subsurface nitrate as a result of an LGM-to-Holocene increase in water column denitrification (Dubois et al., 2011). Further west in the EEP, studies have revealed no LGM-to-Holocene rise in sediment δ15N but rather a deglacial maximum, which is also apparently observed in the western equatorial Pacific (Rafter & Charles, 2012). This sediment δ15N signal might be linked to the deglacial δ15N maximum that is apparent in some records from the ETP. Differencing of western and eastern equatorial Pacific sediment δ15N records yields a signal with orbital periodicities, dominantly of precession; this has been interpreted as a changing degree of nitrate consumption that results from insolation-driven EEP upwelling changes (Rafter & Charles, 2012). Interpretations aside, sediment δ15N records from the EEP appear to hold signals of both an LGM-to-Holocene sediment δ15N rise and, further westward, a deglacial δ15N maximum.

The existing δ15N records mentioned above are all based on N isotopic measurement of the bulk sediment (δ15Nbulk). However, the primary N isotopic signals acquired in the surface ocean may be obfuscated in δ15Nbulk. Two causes for this are (1) diagenetic alteration during sinking in the water column and early burial in the sediment (Altabet and François, 1994), and (2) the contribution of organic and inorganic N derived from terrestrial or distal marine (e.g., shelf) sources (Meckler et al., 2011; Schubert & Calvert, 2001). To avoid these biases, recent work has focused on measuring the δ15N of organic matter bound within and protected by the tests of microfossils, such as foraminifera and diatoms (Ren et al., 2009; Robinson et al., 2004).

Here, we report measurements of foraminifera shell-bound δ15N (FB-δ15N) on the two species Neogloboquadrina dutertrei and Neogloboquadrina incompta (formerly named Neogloboquadrina pachyderma (dextral); Darling et al., 2006) in two sediment cores extending back to the last ice age. These cores (ME0005-24JC and ME0005-27JC) fall within the nutrient-rich EEP (Figure 1). They both have abundant foraminifera and a rich set of previous measurements. Of particular interest, each core shows a LGM-to-Holocene increase in bulk sediment δ15N similar to that observed at other EEP and ETP sites, which has most often been interpreted as indicating that ETP water column denitrification was reduced during the LGM (De Pol-Holz et al., 2006, 2007; Dubois & Kienast, 2011; Ganeshram et al., 1995, 2000; Robinson et al., 2007).

2. Materials and Methods

Sediment cores ME0005-24JC and ME0005-27JC (hereafter abbreviated as ME-24 and ME-27) were retrieved from the EEP. ME-24 is located north of Carnegie Ridge (0°1.3’ N, 86°27.8’ W, 2941 m), while ME-27 is located south of Carnegie Ridge (1°51.2’ S, 82°47.2’ W, 2203 m) (Figure 1). The age models for both sediment cores have been updated by Dubois et al. (2014) and are based on (1) radiocarbon ages measured on the planktonic foraminifera N. dutertrei by accelerator mass spectrometry (S. S. Kienast et al., 2007; Kusch et al., 2010), (2) correlation of benthic foraminifera oxygen isotopes to the LR04 stack, and (3) the identification of the Los Chocoyos Ash Layer (Drexler et al., 1980) in the sediment cores. In core ME-27, we have included three additional 14C dates on N. dutertrei at 0.5 cm, 80.5 cm, and 125.5 cm depth from Meik (2014). All radiocarbon ages were calibrated with Calib 7.1 and the marine calibration curve MARINE13 (Reimer et al., 2013; Stuiver & Reimer, 1986), assuming a reservoir age of 467 years as given in Dubois
et al. (2014). Ages were linearly interpolated between the stratigraphic tie points, which are given in Supplementary Table 1.

Foraminifera-bound δ15N was measured with the “persulfate-denitrifier” technique (Knapp et al., 2005; Ren et al., 2009; Straub et al., 2013). In brief, ∼3–5 mg of foraminifera (N. dutertrei and N. incompta from the 300–600 µm size fraction) were picked, were cut open with a scalpel (rather than being crushed, to minimize sample loss), and underwent a chemical cleaning (Ren et al., 2009; Straub et al., 2013). The organic N bound within the calcite was then released by dissolution with HCl and converted to nitrate in a basic potassium persulfate solution (Nydahl, 1978). The nitrate concentration of the solution was determined by chemiluminescence (Braman & Hendrix, 1989), and an aliquot of the nitrate solution equivalent to 5 nmol N was converted to nitrous oxide (N2O) by denitrifying bacteria (Sigman et al., 2001). The N isotopic composition of the N2O was measured with a custom continuous-flow system for N2O extraction and purification on-line to a Thermo MAT253 stable isotope mass spectrometer and referenced to air N2 using the international nitrate standards IAEA-N3 and USGS-34 (Weigand et al., 2016). The FB-δ15N data were then corrected for the contribution of the oxidation procedural blank with an in-house aminocaproic acid standard of known isotopic composition.

After the blank correction, we found linear offsets in FB-δ15N of up to 0.5–0.6‰ among the individual batches analyzed. The origin of this linear offset may be an additional blank introduced during the cleaning process that was not monitored by the procedural blanks at the time of these analyses. Since we analyzed almost all samples in duplicate across separate batches of analyses, we were able to correct for the artifact by applying offsets to whole batches (Supplementary Figures 1 and 2). Replicate FB-δ15N analyses for each depth were then averaged, yielding species-specific FB-δ15N records for both N. dutertrei and N. incompta in each sediment core. The offset correction does not impact the interpretation of the data.

3. Results

In the δ15Nbulk records measured in ME-24 and ME-27 by Dubois et al. (2011), δ15Nbulk is lowest (4–5‰) during the last ice age, increases to 6–7‰ during the deglaciation, and then slightly increases (ME-24) or decreases (ME-27) during the Holocene (Figure 2).

FB-δ15N is almost always higher than δ15Nbulk, a common finding when the foraminifera species analyzed lacks dinoflagellate endosymbionts (Martinez-Garcia et al., 2014; Ren et al., 2012; Smart et al., 2018). In terms of downcore change, FB-δ15N is notably different from δ15Nbulk at both core sites. Most importantly, unlike δ15Nbulk, FB-δ15N during the last ice age (6–8‰) is similar to or higher than that of the late Holocene (6–7.5‰). At both sites, FB-δ15N gradually increases during deglaciation and shows a deglacial maximum during the HS1 and early Bolling-Allerod (BA). At ME-27, FB-δ15N then gradually declines throughout the YD and the Holocene. At ME-24, FB-δ15N declines abruptly during the second half of the BA and is at a minimum during the YD, peaks again during the early Holocene, and then declines into the middle Holocene. Another difference between the two core sites is that at ME-27, FB-δ15N of N. dutertrei and N. incompta are very similar, while at ME-24, FB-δ15N of N. dutertrei is on average 0.6‰ higher than FB-δ15N of N. incompta. Despite this difference, the two species show the same down-core changes within each core.
4. Discussion

4.1. Disagreement Between $\delta^{15}$N$_{bulk}$ and FB-$\delta^{15}$N

The similarity among the $\delta^{15}$N$_{bulk}$ records from ME-24 and ME-27 and other cores in the region (Figure 3) appears consistent with a coherent change in nutrient dynamics in the EEP. Furthermore, the location close to the continent and in proximity to two upwelling systems promises high primary productivity that in turn leads to rapid biogenic fluxes and sediment accumulation, which are expected to minimize the influence of diagenetic alteration at the seafloor (Ganeshram et al., 2000; Thunell et al., 2004; Thunell & Kepple, 2004). However, the disagreement with the trends in FB-$\delta^{15}$N indicates a bias in either $\delta^{15}$N$_{bulk}$ or FB-$\delta^{15}$N.

More ground-truthing of FB-$\delta^{15}$N is called for, especially in dynamic environments such as upwelling systems. Observed species-associated offsets point to influences from symbiosis and possibly also from feeding habits, seasonality, and depth habitat (Costa et al., 2016; Ren et al., 2012; Smart et al., 2018, 2020). Moreover, the two species measured here, N. dutertrei and N. incompta, show an offset in ME-24 of 0.6‰ on average but have no clear offset in ME-27 (Figure 2). N. dutertrei are non-spinose and pelagophyte symbiont-bearing, whereas N. incompta are non-spinose and asymbiotic (Bird et al., 2018; Takagi et al., 2019). Modern studies indicate that asymbiotic and/or non-spinose species have a distinctly higher FB-$\delta^{15}$N than spinose, dinoflagellate-bearing species, by as much as 4‰ (Ren et al., 2012; Smart et al., 2018). These studies indicate that pelagophyte symbiont-bearing species, including N. dutertrei, cluster with asymbiotic species such as N. incompta, consistent with their similar FB-$\delta^{15}$N in ME-27. We suggest that the $\delta^{15}$N offset between the two species in ME-24 speaks to a stronger affinity of N. incompta for upwelling, which may cause N. incompta to be biased toward periods and locations of maximal upwelling, resulting in a lower $\delta^{15}$N for its food source. Above ME-27, the strong flow of surface waters from the South and their pervasive nutrient-richness may preclude seasonal or small-scale spatial variations in food source $\delta^{15}$N, leading to more similar FB-$\delta^{15}$N for the two species.

However, a glacial-to-interglacial bias in the FB-$\delta^{15}$N records is unlikely, lacking a clear mechanism. Supporting this view, the two species show similar changes within each core, including the pronounced $\delta^{15}$N minimum during late deglaciation in ME-24. Thus, we question the primary nature of the bulk sediment $\delta^{15}$N records, in particular, their glacial-to-interglacial $\delta^{15}$N increase. We point to two processes that may bias the bulk sediment $\delta^{15}$N records to indicate an artificially low $\delta^{15}$N for sinking N during the last ice age.

First, given the proximity of the South American continent, significant input of organic and inorganic nitrogen from terrestrial sources to the core sites may be occurring. Linear regression of bulk sediment total nitrogen (TN) against total organic carbon (TOC) yields a non-zero intercept (Figure 4a), suggesting the presence of clay-bound N with a low C/N, such as clay-bound ammonium and amino acids (Meckler et al., 2011; Muller et al., 1977; Schubert & Calvert, 2001). If the intercept is entirely due to inorganic N, then it accounts for ~23 ± 14% of the average TN in ME-24 and ME-27. Inorganic N, likely present as ammonium bound in clay minerals, is reported to have a low $\delta^{15}$N, for example, of 2–4‰ (Schubert & Calvert, 2001). The $\delta^{15}$N of terrestrial organic N probably depends strongly on the region and environment of the source. Nevertheless, given the relatively high $\delta^{15}$N of marine organic matter in this region, the combined contributions of terrestrial organic and inorganic N would likely work to lower $\delta^{15}$N$_{bulk}$; $\delta^{15}$N$_{bulk}$ is indeed mostly lower than FB-$\delta^{15}$N at both ME-24 and ME-27, even after subtracting 1–2‰ from FB-$\delta^{15}$N to account for
the typical elevation of asymbiotic and/or non-spinose foraminifera δ¹⁵N relative to the δ¹⁵N of the nitrate consumed in the euphotic zone (Ren et al., 2012; Smart et al., 2018).

Second, weaker diagenetic alteration during the last ice age may have caused or contributed to the glacial-to-interglacial δ¹⁵N difference. The majority of studies indicate that bulk sediment δ¹⁵N increases during oxic organic matter diagenesis (Robinson et al., 2012 and references therein). Oxic diagenesis appears to be strongly affected by oxygen exposure time, which is in turn controlled by bottom water oxygen concentrations, sediment burial rate, and the flux of organic matter to the sediment (Hartnett et al., 1998). Compared to the Holocene, ice age bottom water oxygen concentrations were lower in the deep EEP and ETP, including in the depth range of ME-24 (2941 m) and ME-27 (2203 m) (R. F. Anderson et al., 2019; Bradtmiller et al., 2010; Hoogakker et al., 2018; Jacobel et al., 2020; Loveley et al., 2017). This may have worked to minimize diagenetic loss, and thus, δ¹⁵N elevation, of bulk sedimentary N. Consistent with this possibility, in both ME-24 and ME-27, N content and N flux were higher during the last glacial and HS1 periods relative to the Holocene (Dubois et al., 2011; S. S. Kienast et al., 2007). Moreover, there is a correlation between the difference between δ¹⁵Nbulk and FB-δ¹⁵N and the N content of the sediments, with a greater difference during the last glacial (Figure 4b). This is as expected if glacial-age sediment underwent less oxic diagenetic N loss. The slope of correlation in δ¹⁵N against ln(% TN) space provides a Rayleigh model-based estimate of the net isotope effect of diagenetic N loss of 3.0 ± 0.5‰ (Figure 4c) that is consistent with previous estimates (Lehmann et al., 2002; Moebius, 2013). However, we caution that, as discussed above, this trend may alternatively (or additionally) result from exogenous N inputs being more important during the LGM.

### 4.2. Interpretation of EEP δ¹⁵N Change: Denitrification versus Surface Nitrate Consumption

At EEP sites, both the δ¹⁵N of the nitrate supply and the degree of nitrate consumption may influence the δ¹⁵N of export production. Accordingly, δ¹⁵Nbulk records have been scrutinized for changes in both. Differences among EEP records and between EEP and ETP records during deglaciations and interglacials have
been recognized, and these have been interpreted as arising from changes in the degree of nitrate consumption in the EEP (Dubois & Kienast, 2011; Robinson et al., 2009). However, the deglacial $\delta^{15}N_{\text{bulk}}$ rise and the higher $\delta^{15}N_{\text{bulk}}$ during interglacials are largely shared between the EEP and ETP records (as well as among EEP records), leading to the view that the $\delta^{15}N$ of the nitrate supply in the EEP changes in parallel with the ETP, with water column denitrification being the major driver of these changes (Dubois et al., 2011).

Modern ocean data should provide some insight into the degree to which the EEP should share changes in the $\delta^{15}N$ of the nitrate supply with the ETP. Data from 95°W suggest that the subsurface nitrate being upwelled along the equator has a $\delta^{15}N$ of $\sim 7.1\%$ or slightly lower (Rafter et al., 2012; Rafter & Sigman, 2016). At this longitude, the lowest $\delta^{15}N$ of shallow subsurface nitrate is associated with the SSCC, which also underlies the highest nitrate concentrations at the surface. The low nitrate $\delta^{15}N$ of the SSCC likely derives from the remineralization of low-$\delta^{15}N$ sinking N under the region of upwelling (Rafter & Sigman, 2016). These modern observations do not support a dominant role for the intensity of the EUC or other zonal subsurface flows on the $\delta^{14}N$ of subsurface nitrate, at least this far east in the EEP. Rather, the biogeochemical dynamics of the region, both the water column denitrification of the ETP and the incomplete nitrate consumption in the EEP surface, appear to most strongly influence the $\delta^{15}N$ of the nitrate being upwelled in the EEP. On the basis of prior studies of equatorial circulation and biogeochemical dynamics, a similar interpretation was put forward by Robinson et al. (2009). Thus, EEP sites should detect a significant reduction in ETP denitrification during the LGM. Such an influence is even more likely east of the Galapagos, due to the proximity to the suboxic zones and the interference of the islands with the eastward subsurface flows along the equator.

In summary, modern ocean data support prior interpretations of shared $\delta^{15}N_{\text{bulk}}$ changes among EEP and ETP records as deriving from changes in ETP denitrification.

Thus, based in part on the evidence above, the deglacial rise and Holocene elevation of bulk sediment $\delta^{15}N$ from ME-24 and ME-27 have been interpreted as dominantly reflecting reduced water column denitrification during the last ice age (Dubois et al., 2011), consistent with the previous conclusion of such a change on the basis of non-equatorial ETP records (Emmer & Thunell, 2000; Ganeshram et al., 2000, 1995; S. S. Kienast et al., 2002; Robinson et al., 2009). From this perspective, the FB-$\delta^{15}N$ records, lacking such an LGM-to-Holocene $\delta^{15}N$ difference, would appear to cast doubt on this overarching interpretation of an LGM reduction in ETP denitrification. We address this question next.

### 4.3. LGM-to-Holocene History of ETP Water Column Denitrification

As discussed in the prior section, the low glacial $\delta^{15}N_{\text{bulk}}$ observed at both ETP and EEP sites has been interpreted as a reduction in water column denitrification during the last ice age (Dubois et al., 2011; Dubois & Kienast, 2011; Emmer & Thunell, 2000; Ganeshram et al., 2000, 1995; S. S. Kienast et al., 2002; Robinson et al., 2009). However, not all $\delta^{15}N_{\text{bulk}}$ records in the ETP indicate an LGM-to-Holocene $\delta^{15}N$ rise. For example, $\delta^{15}N_{\text{bulk}}$ records from the Gulf of Tehuantepec indicate a deglacial maximum in $\delta^{15}N$ but no glacial-to-interglacial change, consistent with the FB-$\delta^{15}N$ measurements (Figure 3b; Hendy & Pedersen, 2006; Pichevin et al., 2010; Pride et al., 1999; Thunell & Kepple, 2004). More broadly, in specific records from both further North and South in the ETP, bulk sediment $\delta^{15}N$ is observed to return to glacial values over the Holocene (Figure 3a,c; Emmer & Thunell, 2000; Higginson & Altabet, 2004; S. S. Kienast et al., 2002; Pride et al., 1999). Thus, the FB-$\delta^{15}N$ data are not alone in casting doubt on an LGM-to-Holocene rise in $\delta^{15}N$ in the ETP and EEP. We propose that the “true” $\delta^{15}N$ signal for the ETP is a deglacial maximum, with the low glacial $\delta^{15}N$ observed at some ETP sites being a consequence of higher exogenous N input and/or reduced diagenetic alteration during the ice ages.

Suggested explanations for the gradual Holocene decline in $\delta^{15}N_{\text{bulk}}$ have ranged widely, including a decline in ETP water column denitrification, a rise in $N_2$ fixation, and/or a decline in mean ocean nitrate $\delta^{15}N$ (Deutsch et al., 2004; Galbraith et al., 2013; Thunell & Kepple, 2004). In other proxies that are sensitive to suboxia, the dominant signal appears to be of a deglacial maximum in ETP suboxia, rather than a secular rise in suboxia from the last glacial to the interglacial (Hendy & Pedersen, 2006; Hoogakker et al., 2018; Y. Zheng et al., 2000). These data favor the interpretation of a deglacial maximum in ETP water column denitrification, with the possibility that denitrification rates were comparable between the LGM and the late Holocene. However, other records suggest a more durable shift to suboxia (Chang et al., 2014; Muratli et al., 2010).
Addressing this question further is warranted from multiple perspectives. First, the history of ETP water column denitrification is central to the operation of the global ocean N budget over glacial cycles. Second, denitrification reflects thermocline suboxia, the extent of which is an important aspect of the ocean's environmental conditions. Third, the extent of suboxia is impacted by ocean circulation and the cycling of carbon and nutrients; thus, it provides an important constraint on changes in these processes over the glacial cycles. Next, we consider the plausibility that ETP suboxia was similar between the LGM and the latter Holocene, in comparison to the prevailing interpretation that suboxia was reduced during the LGM.

### 4.4. Suboxia in the EEP and ETP During the Last Ice Age

The interpretation of a reduction in ETP water column denitrification during ice ages has been argued to be consistent with expectations given other characteristics of the ice age ocean (Galbraith et al., 2004). First, the water ventilating the thermocline was colder during the LGM, increasing preformed O$_2$ concentrations. Second, arguments have been made for faster thermocline ventilation during the ice ages (Galbraith et al., 2004). Third, enhanced nutrient consumption in polar and subpolar surface waters would have worked to reduce the preformed nutrient concentration of the thermocline, tending to reduce low latitude biological productivity and the rate of oxygen consumption from the respiration of the resulting sinking organic matter (Figure 5; Keir, 1988; Robinson et al., 2005; Sigman and Boyle, 2000). Finally, North Atlantic overturning has alternated between North Atlantic Deep Water (NADW) formation during interglacials and Glacial North Atlantic Intermediate Water (GNAIW) formation during glacials (Oppo & Lehman, 1993). In most configurations of their downstream circulations, switching from NADW to GNAIW works to raise mid-depth O$_2$ concentrations (Boyle, 1988; Hain et al., 2010; Sigman et al., 2003).

However, countering these changes is the evidence that the ocean's biological pump was more efficient during the ice ages. Broecker (1982a, b) first proposed a stronger global ocean biological pump as the cause of the lowering of atmospheric CO$_2$ during the last ice age. He recognized that such a strengthening in the biological pump should also have caused a decline in the average O$_2$ concentration of the ocean interior. Indeed, there is now strong evidence for lower O$_2$ in the glacial deep ocean (R. F. Anderson et al., 2019; Bradtmiller et al., 2010; François et al., 1997; Galbraith and Jaccard, 2015; Hoogakker et al., 2018; Jaccard et al., 2016, 2009; Jaccard and Galbraith, 2012; Jacobel et al., 2020; Loveley et al., 2017; Marcantonio...
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This glacial decline in deep ocean O₂, through mixing and diffuse interior upwelling, would also have worked to lower the O₂ concentration in overlying mid-depth waters (Figure 5).

To gain insight into these competing influences on mid-depth O₂, we turn to output from a geochemical box model that has been used to investigate the potential causes of the ice age reduction in atmospheric CO₂ (Hain et al., 2010). Here, we focus on the model-induced sensitivities of O₂ in the model’s deep and mid-depth South and North Pacific boxes (Figure 6). Considering first the solubility effects of an ice age ocean that was 3°C colder and 1 PSU saltier than modern, the ocean interior oxygen concentration increases modestly, by 14 µmol/kg at mid-depths and 22 µmol/kg in the deep ocean (Garcia & Gordon, 1992). The combined effects of Subantarctic iron fertilization (which reduced the nutrient content of Subantarctic surface water and Subantarctic Mode Water; Martinez-Garcia et al., 2014; Robinson et al., 2005) and the shift from NADW to GNAIW (Lynch-Stieglitz et al., 2007) cause a reduction in regenerated nutrient burden et al., 2020). This glacial decline in deep ocean O₂, through mixing and diffuse interior upwelling, would also have worked to lower the O₂ concentration in overlying mid-depth waters (Figure 5).

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and O\textsubscript{2} utilization in the Pacific that translates to an additional and more substantial rise in mid-depth O\textsubscript{2}. However, further strengthening of the ocean’s biological pump through an increase in the degree of nutrient consumption in Antarctic surface waters as well as a decline in Antarctic overturning (Ai et al., 2020; François et al., 1997; Sigman et al., 2021; Studer et al., 2015; Wang et al., 2017) leads to a buildup of regenerated nutrients and a strong decline in deep ocean O\textsubscript{2}, consistent with available O\textsubscript{2} reconstructions (see above) and indicative of a more efficient global biological pump (Hain et al., 2014). The circulation communicates some of this O\textsubscript{2} decline to the mid-depth Pacific boxes as well. Combining this full list of ice age changes, the net result is little change in mid-depth Pacific O\textsubscript{2} concentration (Figure 6). In short, increasing the efficiency of the global ocean’s biological pump so as to lower atmospheric CO\textsubscript{2} to ice age observations tends to offset other influences on mid-depth O\textsubscript{2}, calling for little difference in mid-depth O\textsubscript{2} between the LGM and the Holocene.

These large-scale impacts having been considered, we must recognize that changes in ODZ extent and volume may be partially decoupled from average mid-depth O\textsubscript{2} concentration. In addition to being affected by the preformed O\textsubscript{2} and nutrient concentrations and the rate of newly forming intermediate waters, the ODZs may be sensitive to the spatial pattern of thermocline ventilation and the wind-driven upwelling of thermocline waters into the surface, the former delivering O\textsubscript{2} and the latter causing focused O\textsubscript{2} consumption. However, there is as yet no clarity as to how these smaller scale processes would have changed between the LGM and the Holocene.

4.5. Deglacial Features

In the two cores studied, both bulk sediment and foraminifera-bound $\delta^{15}$N show deglacial features (Figure 2); we focus here on the shell-bound data. Our first concern is the overall deglacial $\delta^{15}$N maximum shared by the two records (Figure 2), which is also observed in many low latitude bulk sediment $\delta^{15}$N records within and beyond the ETP (Figure 3). Previous work suggests that the $\delta^{15}$N maximum includes both a global thermocline signal and an ETP-specific deglacial maximum in water column denitrification (e.g., De Pol-Holz, 2006; Deutsch et al., 2004; Galbraith et al., 2013; Hendy & Pedersen, 2006; Y. Zheng et al., 2000). These and other studies propose a range of plausible explanations for these global and/or local deglacial maxima. However, while the FB-$\delta^{15}$N records reported here are not completely clear on the point, there is a suggestion that the $\delta^{15}$N rise begins before the deglaciation. If so, this adds to a body of data suggesting that the EEP “deglacial” signal actually includes a change preceding deglaciation (M. Kienast et al., 2006). One possibility is a response to orbitally (e.g., precession) driven insolation change (Rafter & Charles, 2012).

Another possible origin for the putative deglacial peak in ETP suboxia, which may also explain its early onset, involves apparently distinct timings for different Southern Ocean changes. In the Subantarctic, the indicators of iron fertilization appear to begin their declines early in the deglaciation (Martinez-Garcia et al., 2014; Wang et al., 2017). In addition, ocean warming began quite early in the deglacial sequence (Bereiter et al., 2018). In contrast, the Antarctic surface “isolation” of the LGM appears to decrease somewhat later and more gradually, continuing through the deglaciation and Holocene (Ai et al., 2020; Wang et al., 2017). As outlined above, the Antarctic deglacial change should have caused a deglacial decline in suboxia while the other two (Subantarctic and temperature) deglacial changes should have caused a deglacial rise in suboxia (Figure 6). Accordingly, the relative timing of these components may be appropriate to have caused a deglacial/early Holocene peak in suboxia and thus in ETP/EEP nitrate $\delta^{15}$N. Evaluation of this hypothesis awaits additional records with strong chronological controls.

While our two records both share an overall deglacial $\delta^{15}$N maximum, there are significant differences between the FB-$\delta^{15}$N records from ME-24 and ME-27. The clearest distinction is the FB-$\delta^{15}$N minimum of ME-24 centered on the Younger Dryas. The two sediment cores are separated by only 2° of latitude and 4° of longitude (Figure 1). However, ME-24 is located immediately above the equator, where the $\delta^{15}$N of this subsurface nitrate may have a greater sensitivity to changes in denitrification in the ETNP (Rafter et al., 2012; Rafter & Sigman, 2016). ME-27, on the other hand, is located under the influence of the coastal upwelling off Peru as well as in the broad region of southern hemisphere-biased open ocean upwelling of the EEP (Figure 1) and may thus be more sensitive to changes in denitrification in the ETSP (Dubois et al., 2011, 2014; Robinson et al., 2009).
The Younger Dryas FB-$\delta^{15}$N minimum in ME-24 is accompanied by similar $\delta^{15}$N minima in bulk sediment records from the ETNP (Figure 3a; Emmer & Thunell, 2000; Hendy et al., 2004; S. S. Kienast et al., 2002), also coinciding with metal redox indicators of higher ETNP thermocline oxygen at this time (Cartapanis et al., 2011; Chang et al., 2014; Hendy & Pedersen, 2005; Y. Zheng et al., 2000). We thus tentatively interpret the $\delta^{15}$N minimum as the result of lower nitrate $\delta^{15}$N in the subsurface waters of ME-24, resulting from a reduction in ETNP denitrification. Consistent with this interpretation, the lack of such a minimum in ME-27 matches its corresponding lack in bulk sediment $\delta^{15}$N records from the ETSP margin of Peru and Chile (Figure 3c; Higginson & Altabet, 2004).

As for the physical cause of this putative YD decline in ETNP denitrification, one possibility is a southward shift in the Intertropical Convergence Zone (ITCZ) during the YD, driven by northern hemisphere cooling at the time (Lea et al., 2003). Such a shift may have reduced upwelling along the EEP as a result of reduced cross-equatorial southeast trade winds (Koutavas & Lynch-Stieglitz, 2005), decreasing denitrification in the ETNP. However, this fails to explain why a similar event did not occur during HS1, when there was also abrupt northern hemisphere cooling (Bond et al., 1993). Indeed, it appears that HS1 was associated with higher, not lower, upwelling in the EEP (M. Kienast et al., 2006), which has been explained as the result of intensified northeast trade winds during HS1 when the ITCZ appears to have been at its southernmost position (S. S. Kienast et al., 2013; Timmermann et al., 2007). These conflicts encourage consideration of larger scale causes for the putative YD decline in ETNP denitrification. In this category, a cooling-associated acceleration of North Pacific thermocline ventilation has been suggested for the YD (Mikolajewicz et al., 1997).

In our interpretation of the deglacial changes, we have assigned primary signal to bulk sediment $\delta^{15}$N records. Further above, the disagreement of bulk sediment and foraminifera-bound $\delta^{15}$N in ME-24 and ME-27 was interpreted to argue against a primary origin for the glacial/interglacial $\delta^{15}$N difference in bulk sediment. We do not see these interpretations as contradictory. In some cases, down-core changes in bulk sediment $\delta^{15}$N will dominantly reflect the primary isotopic signal of the N sinking out of the surface ocean; in other cases, bulk sediment $\delta^{15}$N and its changes may be heavily altered by exogenous N or changes in diagenesis. The latter case is most likely when substantial changes in sedimentary environment occur, such as between glacial and interglacial intervals (Meckler et al., 2011).

5. Conclusions

In two sediment cores from the EEP, we measured foraminifera-bound $\delta^{15}$N back to $\sim$35 ka during the last ice age. FB-$\delta^{15}$N values are similar during the Holocene and the last glacial, unlike bulk sedimentary $\delta^{15}$N, which is lower during the Last Glacial Maximum (LGM) relative to the Holocene. Our FB-$\delta^{15}$N data do not appear to agree with previous bulk sediment-based inferences of reduced water column denitrification during the last ice age. Instead, our FB-$\delta^{15}$N data imply similar rates of water column denitrification during the Holocene and the last glacial and thus no dramatic LGM-to-Holocene change in suboxia in the ETP. Mechanisms have previously been identified for reduced ETP suboxia during the ice ages (e.g., Galbraith et al., 2004). We suggest that these were offset by the documented ice age decline in oxygen concentration in the deep Pacific waters underlying the Pacific thermocline. Mixing with, and upwelling from, these deeper less-well oxygenated waters would have helped to maintain the suboxic zones during the ice ages (Figure 5).

We caution that the observation of lower bulk sediment $\delta^{15}$N during the LGM extends both northward and southward along the eastern Pacific margin (De Pol-Holz et al., 2006; Galbraith et al., 2004; Ganeshram et al., 2000; Hendy et al., 2004; S. S. Kienast et al., 2002; Robinson et al., 2007), and our data do not directly test the veracity of these higher latitude bulk sediment $\delta^{15}$N records. Moreover, in part due to our lack of spatial coverage, we have been unable to assess the possible role of variations in the degree of nutrient consumption in the reconstructed $\delta^{15}$N changes, and yet, core-top bulk sediment $\delta^{15}$N and FB-$\delta^{15}$N data indicate that this is a potentially significant variable in the nutrient-rich EEP (Costa et al., 2016; Farrell et al., 1995). In addition, the rate at which upwelling is modified by the ocean circulation patterns could also change. As discussed above, modern ocean data argue against this as a major driver of $\delta^{15}$N change, but it cannot be ruled out. Finally, mean ocean nitrate $\delta^{15}$N may have changed from the LGM to the deglaciation, and then through the Holocene (Galbraith et al., 2013). In net, the potential for overlapping of signals leaves open the possibility that the LGM-Holocene similarity in EEP FB-$\delta^{15}$N does not reflect similar
extents of suboxia during the LGM and Holocene. Generating additional FB-3\textsuperscript{15}N records from the ETP suboxic zones will not address all uncertainties; nevertheless, this is the obvious next step.

**Data Availability Statement**

Data from this study are deposited at the PANGAEA repository (https://doi.pangaea.de/10.1594/PANGAEA.925339).

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