Coupling of oceanic carbon and nitrogen facilitates spatially resolved quantitative reconstruction of nitrate inventories

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Anthropogenic impacts are perturbing the global nitrogen cycle via warming effects and pollutant sources such as chemical fertilizers and burning of fossil fuels. Understanding controls on past nitrogen inventories might improve predictions for future global biogeochemical cycling. Here we show the quantitative reconstruction of deglacial bottom water nitrate concentrations from intermediate depths of the Peruvian upwelling region, using foraminiferal pore density. Deglacial nitrate concentrations correlate strongly with downcore δ13C, consistent with modern water column observations in the intermediate Pacific, facilitating the use of δ13C records as a paleo-nitrate-proxy at intermediate depths and suggesting that the carbon and nitrogen cycles were closely coupled throughout the last deglaciation in the Peruvian upwelling region. Combining the pore density and intermediate Pacific δ13C records shows an elevated nitrate inventory of >10% during the Last Glacial Maximum relative to the Holocene, consistent with a δ13C-based and δ15N-based 3D ocean biogeochemical model and previous box modeling studies.

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Nitrogen (N) is a fundamental component of amino acids and thus, essential for all living organisms. The increasing use of chemical fertilizers to provide food for a growing global population and the burning of fossil fuels lead to a severe rise of fixed nitrogen in the biosphere. Nitrate (NO$_3^-$) is one of the main limiting nutrients in the modern ocean and nitrate fertilization is considered to contribute to the ongoing ocean deoxygenation. A strong climate sensitivity has been predicted for the global NO$_3^-$ inventory and feedbacks on climate by the coupling of the biogeochemical carbon (C) and nitrogen (N) cycles through the biological pump. A quantitative reconstruction of past reactive N inventories and feedbacks on other biogeochemical cycles throughout time might help us to predict scenarios for the future. Nevertheless, despite different estimates from numerical models, quantitative paleo-records for past reactive N budgets in the oceans are not yet available.

The main source for bioavailable N in the modern ocean is N$_2$ fixation, performed by cyanobacteria, while the main loss of mineralized N results from denitrification and anaerobic ammonium oxidation (Anammox) in oxygen deficient zones (ODZs) in the sediments as well as in the water column. Estimates of past inventories of reactive N species are mainly based on geological records of the fractionation between the N isotopes $^{15}$N and $^{14}$N (given as $\delta^{15}$N in $\%_o$) in bulk sedimentary organic matter ($\delta^{15}$N$_{bulk}$). The complexity of various Ncycle processes influencing $\delta^{15}$N (e.g. N$_2$ fixation, sedimentary or water column denitrification, NO$_3^-$ utilization, remineralization and nitrification) complicates a quantitative reconstruction of the N budget based on $\delta^{15}$N alone.

Models have used global $\delta^{15}$N$_{bulk}$ records for estimating changes in the past N budget. Box modeling studies agree that the inventory of reactive N was likely elevated during cold phases mainly due to a reduction of denitrification in the water column and seafloor sediments, related to enhanced O$_2$ solubility in colder seawater and decreased area of shelf sediments from lower sea level, respectively. Additionally, enhanced N$_2$ fixation from atmospheric iron deposition has been proposed. Estimated changes from box models based on $\delta^{15}$N$_{bulk}$ range from 5 to 100% between 100 kyr BP and the present. Another box model study, which is not based on $\delta^{15}$N$_{bulk}$, predicts changes in the global oceanic nutrient budgets due to changes in sea-level, dust deposition, and ocean circulation. This study estimates an increase in dissolved N (DN) of 16% during the late Holocene compared to the Last Glacial Maximum. This is generally consistent with a study representing glacial nitrogen cycling constrained by isotopes in a 3D global ocean biogeochemical model considering LGM boundary conditions that predicts a glacial N$_{bio}$ increase between 6.5 and 22%.

A main focus of our study is the reconstruction of past NO$_3^-$ concentrations ([NO$_3^-$]) using the pore density of benthic foraminifera. Foraminifera are one of the rare examples of eukaryotes which are able to use NO$_3^-$ as an electron acceptor when oxygen is depleted within their habitats and play an important role in the oceanic benthic nitrogen cycle. The density in the shells of Bolivina spissa is significantly correlated to the NO$_3^-$ in their habitats because the pores facilitate the uptake of electron acceptors for respiration. A comprehensive review about the functionality of pores in benthic foraminifera can be found in ref. 18. The functionality of pores in Foraminifera ranges from gas exchange for the uptake of electron acceptors and the release of metabolic waste products like CO$_2$ to the uptake of dissolved organic material. Foraminifera from oxygen depleted environments typically show an increased porosity and often a clustering of mitochondria under the pores. Several recent studies describe the influence of oxygen availability on foraminiferal pore characteristics. While some species adapt their porosity by changing the size of their pores, other species are adapting the numbers of pores (pore density) in their tests.

Benthic Foraminifera from oxygen depleted environments have recently been shown to use NO$_3^-$ as electron acceptor. At least one species, B. spissa, from the Peruvian ODZ, adapts its pore density to the availability of NO$_3^-$ in its habitat. A comparison of 232 measurements of the pore density in B. spissa to the bottom water nitrate concentrations ([NO$_3^-$]) from 8 different sampling locations at the Peruvian continental margin revealed a significant linear relationship between both parameters. Another species from the Peruvian ODZ, Bolivina seminuda, has been shown to have a high affinity to NO$_3^-$ and foraminiferal pore densities are highly porous. Every species of the genus Bolivina which has been analyzed so far, including B. seminuda, has the ability to denitrify, which implies that denitrification is a common strategy of Bolivinidae for survival under oxygen depleted conditions. This makes species from this genus in particular candidates for paleo NO$_3^-$ reconstruction by analyses of pore characteristics as an empirical proxy.

We determined the pore density of the benthic foraminiferal species B. spissa as a quantitative paleoproxy for [NO$_3^-$] in intermediate waters (1250 m) at the Peruvian continental margin over the last deglaciation. The foraminiferal pore density is providing a tool to reconstruct past [NO$_3^-$] in a high lateral and temporal resolution allowing to test model predictions. A comparison of the reconstructed [NO$_3^-$] to the stable carbon isotope ratio ($^{13}$C) in our sedimentary record shows the same correlation as in intermediate depths of the modern Pacific, enabling us to reconstruct regional differences in deglacial [NO$_3^-$]. A first analysis of deglacial $^{13}$C records reveals the same trend in deglacial [NO$_3^-$] change as reconstructed by the pore density and predicted by the different model studies.

Results

Deglacial changes in the oceanic reactive N inventory. We reconstructed bottom water NO$_3^-$ concentrations ([NO$_3^-$]$_{bw}$) using sediment core M77/2 52-2 (5°29′S; 81°27′W; 1250 m) from the Peruvian continental margin over the last deglaciation. Past [NO$_3^-$]$_{bw}$ was reconstructed using the pore density of the benthic foraminiferal species B. spissa (Fig. 1a, b; Supplementary Table 1) following the method published in ref. 18. The pore densities of 819 specimens were analyzed for this record to provide a statistically robust dataset in a sufficient temporal resolution (Fig. 1a). We distinguished between five different time intervals including the Last Glacial Maximum (LGM; 22–17 kyr BP), Heinrich Stadial 1 (H1; 17–15 kyr BP), Antarctic Cold Reversal (ACR; 15–12 kyr BP), Early Holocene (EH; 11.7–8.2 kyr BP) and Middle to Late Holocene (MLH; 8–0 kyr BP). The lowest pore densities (highest [NO$_3^-$]$_{bw}$) occurred during the LGM. This difference is highly significant compared to all other individual time intervals ($P<0.001$; $N=136$; two-sided heteroscedastic Student’s T-test). The highest pore densities, and thus lowest [NO$_3^-$]$_{bw}$, have been found for the MLH. This difference is also highly significant compared to all other time intervals ($P<0.001$; $N=353$).

A comparison with continuous transient global box model simulations covering the last deglaciation provided evidence that the NO$_3^-$ inventory at this location is driven by fluctuations of the global reactive N inventory. A plot which compares relative changes in the global reactive N budget over the last deglaciation from the different modeling approaches with our quantitative [NO$_3^-$]$_{bw}$ record is shown in Fig. 1c. The pore density derived NO$_3^-$ inventory during the LGM was elevated compared to the Holocene which corroborates estimations from
previous biogeochemical model studies\textsuperscript{7,10,11,13} although it also reveals fluctuations in $[\text{NO}_3^-]_{\text{BW}}$ in a much higher temporal resolution. A 50-100\% higher reactive N inventory is suggested for the LGM by another box model study by Eugster et al.\textsuperscript{11} and thus probably overestimates this change by one order of magnitude according to our reconstruction.

The $\delta^{15}\text{N}_{\text{bulk}}$ record of our sediment core (Fig. 1d) showed trends similar to other records from the Eastern Tropical South Pacific (ETSP) and the Eastern Tropical North Pacific (ETNP)\textsuperscript{10,28}. It depicted the typical maximum of $\delta^{15}\text{N}_{\text{bulk}}$ in these regions during the last deglaciation, which was caused by an acceleration in water column denitrification relative to the LGM\textsuperscript{10,28}. The increase in benthic denitrification at the shallow shelf due to sea level rise and increased shelf area was slower than the increase of denitrification in the water column. The balancing between enhanced denitrification in the water column and sedimentary denitrification by N\textsubscript{2} fixation, which introduces low $\delta^{15}\text{N}$ into the ocean, at the onset of the Holocene leads to a subsequent reduction in $\delta^{15}\text{N}_{\text{sed.org}}$\textsuperscript{29}.

Deglacial coupling of $\delta^{13}\text{C}$ and $\text{NO}_3^-$ in intermediate depths. A comparison between the reconstructed $[\text{NO}_3^-]_{\text{BW}}$ and $\delta^{13}\text{C}$ measured on Uvigerina peregrina in the same sediment core
(δ¹³C_FORAM, Fig. 1b) showed a strong coupling starting from the LGM and persisting over deglaciation until the Late Holocene. The mean δ¹³C signature of dissolved inorganic carbon (δ¹³C_DIC) in seawater is controlled by the balance between terrestrial and marine carbon sources and sinks13,30-32, while the spatial distribution of δ¹³C_DIC is mainly controlled by photosynthesis, respiration, and the ventilation and mixing between different water masses30-33. Autotrophic organisms preferably take up the lighter isotope ¹³C during photosynthesis. Thus, surface water masses have more positive δ¹³C_DIC and are depleted in DIC, since ¹²C-carbon is preferably exported as organic matter. In intermediate to deep water masses organic matter is readily remineralized by respiration, which leads to an increase in DIC and a decrease of δ¹³C_DIC within these water masses. An increase in photosynthesis leads to a higher export productivity and thus a stronger gradient in δ¹³C_DIC between surface and deep water masses established through the biological carbon pump.

Since photosynthesis and respiration both influence the distribution of major nutrients in the ocean, there is an inverse relationship between δ¹³C_DIC and [NO₃⁻] and [PO₄³⁻] in the modern ocean with a stronger correlation to [NO₃⁻] than [PO₄³⁻]13. The distributions of [NO₃⁻] and δ¹³C_DIC in water masses of the modern Pacific, taken from the GLODAPv2 database34, are shown in Fig. 2a, b. Both distributions are similar since the main processes affecting δ¹³C also affect the NO₃⁻ distribution. Surface water masses show high δ¹³C_DIC and low [NO₃⁻] through primary productivity, while the intermediate to deep water masses show low δ¹³C_DIC and higher [NO₃⁻] through remineralization of exported organic matter. All these processes define the endmembers of δ¹³C_DIC and [NO₃⁻] in different water masses and thus the mixing processes between different water masses follow the same trend.

A comparison of the correlation of downcore [NO₃⁻]₆W and δ¹³C_FORAM and the correlation of dissolved NO₃⁻ and δ¹³C_DIC in intermediate water depths (700–2000 m) of the recent Pacific34, is shown in Fig. 2c. Both linear regressions were highly significant (P < 0.0001) and neither slopes nor intercepts significantly differed from each other (Slope: P = 0.15; Intercept: P = 0.13). Thus, [NO₃⁻]₆W and δ¹³C in our downcore record showed basically the same correlation over the last 22 kyrs as [NO₃⁻] and δ¹³C of DIC in intermediate water depths of the modern Pacific. We propose that the linear regression between [NO₃⁻] and δ¹³C_DIC (eq. 1 and eq. 2) can be used to quantitatively reconstruct past [NO₃⁻].

\[
\delta^{13}C_{FORAM} = -0.093( \pm 0.001) \cdot [NO_3^-] + 3.568( \pm 0.038)
\]  
(1)

Alternatively solved for [NO₃⁻]:

\[
[NO_3^-] = -\frac{\delta^{13}C_{DIC} - 3.568( \pm 0.038)}{(0.093( \pm 0.001))}
\]  
(2)

### 3D Biogeochemical model on deglacial δ¹³C_DIC-[NO₃⁻] coupling

The distribution of δ¹³C and [NO₃⁻] has been modeled for the modern ocean, the pre-industrial Holocene and the LGM (Fig. 3) using a coupled 3D ocean circulation-biogeochemical isotope model. The model system used here is an improved version of Somes et al. by including the carbon isotope cycling following Schmittner and Somes35,36 and optimizing LGM iron deposition patterns to better reproduce δ¹⁵N bulk observations (see Supplementary Figure 1). The modeling results indicated no significant difference in the relationship of the δ¹³C_DIC-[NO₃⁻] correlation in the deep intermediate Pacific at our core location (i.e. [NO₃⁻]₆W; Supplementary Figure 2) during the different climatic time intervals. This supported our comparison of the M77/2-52-2 sediment record to the modern δ¹³C_DIC-[NO₃⁻] distribution. The [NO₃⁻]₆W reconstruction using our pore density proxy during the LGM and MLH at our sampling location corresponded well to our independent global biogeochemical model based on sedimentary δ¹⁵N bulk records. The predictions of our global 3D biogeochemical model for the sampling location of M77/2 52-2 are shown in Fig. 1b for the LGM and the pre-industrial Holocene. The best prediction from this model of 7.4% (uncertainty range 2.7–11%; Supplementary Table 2), was generally consistent with the relative offset in the nitrate inventory between the LGM and MLH of ~10% from our pore density record. It has to be noted that the model predicted that the increase to the global [NO₃⁻] inventory was 1.5 µM larger than at our core location.

### Intermediate Pacific [NO₃⁻] records by the use of δ¹³C FORAM

The reconstructed relative [NO₃⁻]₆W changes from the pore density of B. spissa and another [NO₃⁻]₆W reconstruction based on the δ¹³C FORAM Record on U. peregrina and equation 2 are showing the same trends and magnitude (Fig. 1c). The
\[ \delta^{13}C_{\text{DIC}} = -0.093(\pm 0.001)x + 3.568(\pm 0.038) \]
\[ R^2 = 0.63, F = 8363; P < 0.001 \]
\[ y = -0.110(\pm 0.014)x + 4.299(\pm 0.606) \]
\[ R^2 = 0.59, F = 60; P < 0.001 \]

\( y = -0.093(\pm 0.001)x + 3.568(\pm 0.038) \)
\[ R^2 = 0.63, F = 8363; P < 0.001 \]
\[ y = -0.110(\pm 0.014)x + 4.299(\pm 0.606) \]
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\[ R^2 = 0.63, F = 8363; P < 0.001 \]
\[ y = -0.110(\pm 0.014)x + 4.299(\pm 0.606) \]
\[ R^2 = 0.59, F = 60; P < 0.001 \]

**Fig. 2** Distribution of \([\text{NO}_3^-]\) and \(\delta^{13}C_{\text{DIC}}\) in the modern Pacific and \([\text{NO}_3^-] - \delta^{13}C_{\text{DIC}}\)-coupling in the intermediate Pacific - modern and downcore. All data for the modern Pacific have been taken from the GLODAPv2 database. **a** Distribution of \([\text{NO}_3^-]\) in the modern Pacific. **b** Distribution of \(\delta^{13}C\) of dissolved inorganic carbon (DIC; \(\delta^{13}C_{\text{DIC}}\)) in the modern Pacific. The Ocean Data View software has been used to compile these plots. **c** Correlation between \([\text{NO}_3^-]\) and \(\delta^{13}C_{\text{DIC}}\) in intermediate water depths (700–2000 m) of the modern Pacific (red, \(N = 4779\)) and between \([\text{NO}_3^-]_{\text{BW}}\) and \(\delta^{13}C_{\text{FORAM}}\) in the sediment record of M77/2 52-2 (black, \(N = 44\)). Both linear regressions neither differ significantly in slope \((P = 0.15)\) nor in intercept \((P = 0.13)\). Due to graphical reasons all \(\delta^{13}C\) below \(−1\%\) have been cut in this plot, although they were included into the fit. For a complete plot of all data points see Supplementary Figure 4B.
Discussion

In this study, we show the application of a new quantitative NO$_3^-$ paleoproxy using pore density of the benthic foraminiferal species *B. spissa*. Furthermore, we propose that $\delta^{13}$C$_{FORAM}$ in benthic foraminifera from Pacific intermediate water depths is directly coupled to [NO$_3^-$] (Fig. 1). A first comparison of different available $\delta^{13}$C$_{FORAM}$ records measured on tests of the epibenthic *Cibicidoides* from the Pacific at intermediate water depths show similar trends as the pore density record and global biogeochemical model predictions (Fig. 1c).

We found a distinct offset of [NO$_3^-$]$_{BW}$ between the LGM and the MLH (Fig. 1b, c). The depletion of reactive N during warm periods compared to glacial periods can be explained by lower denitrification activity during the glacials but $\delta^{13}$N$_{sed.org}$ may have also been enhanced by iron deposition, although $\delta^{15}$N$_{sed.org}$ from the tropical North Pacific and Atlantic indicate reduced N$_2$ fixation during glacials in response to reduced N loss, consistent with our 3D biogeochemical model predictions (Fig. 1c).

A stronger stratification of Antarctic water masses due to decreased meridional overturning during the LGM probably supported the storage of remineralized nutrients in sluggish Antarctic Bottom Water and thus supported the decrease of preformed NO$_3^-$ during the LGM. This led to a decreased transport of preformed NO$_3^-$ to the tropics limiting productivity, which reduces the volume of ODZs and thus denitrification. Furthermore, the low sea level during the LGM led to a reduction of shelf seafloor area from 0 to 100 m water depths by 73% and shelf and hemipelagic sediments are the main contributors to sedimentary N loss processes today. Both processes, water column denitrification in ODZs and sedimentary denitrification, the main sinks for reactive N, were dampened during the LGM compared to the MLH. The most distinctive offset to the global model predictions appears during H1, when [NO$_3^-$]$_{BW}$ was depleted for ~4 kyr (Fig. 1b). This offset most probably represents local dynamics not accounted for in the coarse resolution of box model studies which are discussed in the Supplementary Note 2 together with local O$_2$ fluctuations and their possible influence on local [NO$_3^-$]$_{BW}$.

A comparison between the reconstructed [NO$_3^-$]$_{BW}$ and $\delta^{15}$N$_{bulk}$ (Fig. 1b, d) in our sediment core shows a phase shift at the beginning of the last deglaciation (~18 kyr BP): High [NO$_3^-$]$_{BW}$ during the LGM corresponds to more isotopically light $\delta^{15}$N$_{bulk}$ while [NO$_3^-$]$_{BW}$ and $\delta^{15}$N were in phase during the deglaciation and the Holocene. At first glance, this might appear contradicting since heavier $\delta^{15}$N$_{bulk}$ indicates higher water column denitrification, which would result in NO$_3^-$ depletion. However, sediment core M77/2 52-2 is located in intermediate water depths well below the most oxygen (O$_2$) depleted center of the ODZ near the thermocline. Deglacial water column denitrification mainly occurred in ODZs, and was probably stimulated by an enhanced supply of preformed nutrients that led to an increase in export production. As such, more organic N was transferred to intermediate water depths by the biological pump where it was decomposed to NO$_3^-$ and increased ambient [NO$_3^-$]$_{BW}$ despite the N loss at shallower water depths.

Our comparison of $\delta^{13}$C$_{FORAM}$ to the reconstructed [NO$_3^-$]$_{BW}$ using the pore density proxy show how closely the oceanic carbon and nitrogen cycle were coupled over the last glacial/interglacial cycle in the Pacific. $\delta^{13}$C$_{FORAM}$ has extensively been used as a proxy of paleoproductivity but also as proxy for ventilation and oxygenation. Nevertheless, our study shows that the ratio between [NO$_3^-$]$_{BW}$ and $\delta^{13}$C$_{FORAM}$ over the last 22 kyr at our sampling location remained unchanged and implies the possibility that $\delta^{13}$C$_{FORAM}$ might also be used as a quantitative NO$_3^-$ proxy at intermediate water depths. Several locations of the modern Pacific show relatively low $\delta^{13}$C$_{DIC}$ values (Supplementary Figure 4). The positions of these locations mainly follow the distribution of anthropogenic CO$_2$ in the Pacific (Supplementary Note 3 and Supplementary Figure 5). Since the deglacial correlation between $\delta^{13}$C$_{FORAM}$ and reconstructed [NO$_3^-$]$_{BW}$ is not influenced by anthropogenic CO$_2$ deviations from this correlation could even be used to trace anthropogenic CO$_2$ in the modern ocean.

A factor controlling the mean $\delta^{13}$C$_{DIC}$ in seawater is the exchange of atmospheric CO$_2$ with the ocean surface. A change in atmospheric pCO$_2$ would also mediate disequilibrium in the surface ocean. However, a recent study showed that this pCO$_2$ effect would cause a maximum $\delta^{13}$C$_{DIC}$ offset in subsurface waters of the Southern Ocean of ~0.2‰. This deglacial offset is even smaller in other parts of the oceans and close to zero at our sampling location and thus cannot explain the changes of $\delta^{13}$C$_{FORAM}$ in our downcore record. Despite this low deglacial offset in $\delta^{13}$C$_{DIC}$ by the pCO$_2$ effect the authors of named study caution to interpret $\delta^{13}$C$_{FORAM}$ as a nutrient proxy. The pCO$_2$ effect might mask the influence of the biological pump on $\delta^{13}$C$_{DIC}$ if the pCO$_2$ gradient is very strong at times of high atmospheric pCO$_2$ such as during the early Cenozoic.

The fact that the correlation between $\delta^{13}$C$_{DIC}$ and NO$_3^-$ in intermediate water depths of the Pacific was stable over the last deglaciation is unexpected at a first glance. Indeed, the main processes which control the distribution of $\delta^{13}$C$_{DIC}$ and NO$_3^-$ in the oceans all influence both parameters as discussed above. However, the main factors controlling the oceanic NO$_3^-$ budget (e.g. denitrification and N$_2$ fixation) do not individually influence $\delta^{13}$C$_{DIC}$ in the same direction. It is possible that the main background driver controlling both processes is the deglacial change in sea level. The decreased area of continental shelves during the LGM in comparison to interglacial conditions led to a lower benthic denitrification and thus higher [NO$_3^-$] and a lower burial rate of organic carbon and thus a lower mean
oceanic $^{13}$C. Strong nitrogen cycle feedbacks are required to realistically model deglacial $^{13}$N$^\delta$10]. In this case, the main factor controlling the oceanic NO$_3^-$ budget would indeed be the change in benthic denitrification due to the extension of shelf seafloor. The mean oceanic $^{13}$N is controlled by the ratio of pelagic to benthic denitrification$^{28}$ and the balance from N$_2$ fixation. The decrease of $^{15}$N$_{bulk}$ in the Eastern Tropical North and South Pacific starting ~12 kyr BP can indeed be modeled by increasing the ratio of benthic to pelagic denitrification$^{28}$ since benthic denitrification fractions $^{13}$N much less than pelagic denitrification.

Another factor, controlling both $^{13}$CDIC and [NO$_3^-$] in different water masses is the ventilation and thus their reservoir age. Consistent evidence from different studies indicates a poorly ventilated deep Pacific during the LGM45-47. Data from the Eastern Equatorial Pacific (EEP) is very scarce, though, and shows some strong contrasts between different sampling locations and approaches$^{48-49}$. Nevertheless, it is likely that deep water masses at the EEP were also poorly ventilated during the LGM. This older water mass would increase [NO$_3^-$] and reduce $^{13}$CDIC by remineralization, as well as reduce oxygen concentration ([O$_2$]) at these depths.

Contrarily, redox proxy records from the EEP indicate higher [O$_2$] during the LGM at depths similar to our sampling location50. This is consistent with other redox proxy records from shallower depths in the Peruvian upwelling region, which indicated a less pronounced ODZ and lower primary productivity during the LGM51. Indeed, the accumulation rates of organic carbon (Acc. Rate, C$_{org}$) at our sampling site were lower during the LGM52 which also indicates a lower primary productivity above this sampling site (Fig. 1d). The elevated [O$_2$] during the LGM are in disagreement with poorly ventilated water masses and thus cannot directly explain the tendencies within our record due to local changes in water mass ventilation. This suggests that local changes to overlying productivity have a strong impact on [O$_2$]$_{BW}$, whereas [NO$_3^-$]$_{BW}$ is more influenced by the global NO$_3^-$ inventory that is determined by the large-scale balance between N$_2$ fixation and denitrification. It might well be, though, that total changes in the nutrient budget of the Pacific are partly related to an increased reservoir age of the deep water masses, related to decreased meridional overturning.

The comparison of our record to the other deglacial $^{13}$C$_{FORAM}$ records is considered as evidence, that coupling of [NO$_3^-$] and $^{13}$CDIC was mainly controlled by the biological carbon pump at our sampling location in the intermediate Eastern Equatorial Pacific, and possibly at other regions of the intermediate Pacific. The situation might be different in the Atlantic Ocean, at greater depths or further back in Earth’s history. Independent calibrations are thus substantial to extend the application of $^{13}$C$_{FORAM}$ as a quantitative [NO$_3^-$] proxy. Furthermore, it is unlikely that this proxy would work at shallow depths where the pCO$_2$ effect might predominate the effect of the biological carbon pump.

Our 3D biogeochemical modeling results support that [NO$_3^-$] at our sampling location records changes in the global budget (predicted at our location: ANO$_3^-$ = 3.0 µM), but also is affected by iron fertilization at high latitudes. Iron fertilization decreases preformed nutrients in SAMW and shallow Antarctic Intermediate Water (AAIW), where our core location exists, of the Pacific due to the transfer of more remineralized nutrients to the deep Pacific. This process is observationally constrained in the 3D model by direct comparison to $^{15}$N$_{bulk}$ across the Southern Ocean (Supplementary Figure 1), which records changes to surface [NO$_3^-$] utilization in response to dust deposition6. Sensitivity simulations associated with Southern Ocean iron fertilization uncertainties cause [NO$_3^-$] changes at our location of ±0.7 µM on top of the direct impact on global [NO$_3^-$] (Supplementary Table 2). The increase to global [NO$_3^-$] in the model was 1.5 µM larger than bottom water [NO$_3^-$] change at our core location, which suggests that our sampling location underestimates changes to the global [NO$_3^-$] inventory.

Nevertheless, in order to prove coupling between $^{13}$CDIC and [NO$_3^-$] in intermediate water depths at different locations on glacial/interglacial timescales, a systematic downcore comparison of benthic $^{13}$C$_{FORAM}$ and the pore density of B. spissa needs to be extended. Although the presence of B. spissa is limited to the Pacific, it occurs both on the Eastern and Western Pacific continental margin17,23–25. The biogeochemical model results of our study revealed no significant difference of the $^{13}$CDIC-[NO$_3^-$] correlation between the LGM and the pre-industrial Holocene at intermediate water depths of the Pacific. Whereas all evidence is pinpointing that the $^{13}$CDIC-[NO$_3^-$] correlation remained stable at Pacific intermediate depths on Glacial-Interglacial timescales, the validity of this correlation in other basins, on different timescales or greater water depths is not yet constrained. We therefore caution to use this correlation on a global scale before additional work has been done on testing this proxy approach in different oceanic basins.

Methods

Stratigraphy of sediment core M77/2 52-2. Core M77/2-52-2 was recovered during RV Meteor cruise M77/2 in 200886. The age model and $^{3}$He and $^{3}$H data of sediment core M77/2-52-2 has already been published56 and added to the appendix. Volume defined samples were taken using cuffed syringes at 10 cm intervals. The samples were wet sieved on a 63–µm screen. The remaining >63 µm fraction of the samples was dried at 50 °C, weighed and stored for further analysis. Stable oxygen isotope ($^{18}$O$_{FORAM}$) measurements of the cores were done with three to six individuals of benthic foraminiferal species Uvigerina pergrina. The tests of single species were crushed. Isotopic measurements were done with a Thermo Scientific MAT253 mass spectrometer equipped with an automated Carbo Kiel IV carbonate preparation device at GEOMAR, Kiel. Isotope values were reported in per mil (‰) relative to the VPDDB (Vienna Pee Dee Belemmite) scale and calibrated vs. NBS 19 (National Bureau of Standards) as well as to an in-house standard (Solnhofen limestone). Long-term analytical accuracy (1-sigma) for $^{18}$O$_{FORAM}$ and $^{13}$CDIC was better than 0.06‰ and 0.03‰ on the VPDDB scale. The data for $^{3}$H and $^{3}$He is listed in the Supplementary Table 1.

For the stable nitrogen isotope ($^{15}$N$_{FORAM}$) measurements, 10–15 mg of dried freeze dried bulk sediments were analyzed using a Thermo Scientific Flash 2000 Elemental Analyzer coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) at NIOZ, Texel. Results were expressed in standard δ notation relative to atmospheric N$_2$ and the precision as determined using laboratory standards calibrated to certified international reference standards were <0.3‰. The data for $^{15}$N, $^{3}$He and $^{3}$H are listed in the Supplementary Table 1.

The already published age model is based on five $^{14}$C AMS dating measurements performed at Beta Analytic, Inc., Florida, USA, on the planktonic foraminiferal species Neogloboquadrina dutertrei$^{57}$. Conventional radiocarbon datings were calibrated applying the marine calibration set Marine 13$^{58}$ and using the software Calib 7.0$^{46}$. Reservoir age of 102 yrs was taken into account according to the marine database (http://calib.qub.ac.uk/marine/). Ages are expressed in thousands of years (kyr) before 1950 AD (abbreviated as cal kyr BP). The radiocarbon based chronology of the core was supplemented and tuned using Analysesy software with $^{13}$C$_{FORAM}$ record from a nearby core M77/2-059-160 and the Antarctic EPICA $^{18}$O reference stack64.

Quantitative [NO$_3^-$] record using foraminiferal pore density. Depending on the availability 7–22 Bolivina spissa specimens were picked of the >63 µm fraction from each sample of sediment core M77/2-52-2. All of the 819 specimens were mounted on aluminum stubs by the use of adhesive carbon pads. They were not sputtered to coat them for future geochemical analyses. Scanning electron micrographs were produced for every single individual using a Hitachi table top scanning electron microscope (TM3000 accelerating voltage of 5–15 kV and using back-scattered electrons (BSE) detector. Following the method published in ref.17 scanning electron microscope (TM3000 accelerating voltage of 5–15 kV and using back-scattered electrons (BSE) detector. Following the method published in ref.17 819 specimens were crushed. Isotopic measurements were done with a Thermo Carbon Prep System coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) and Uvigerina peregrina species. Isotopic measurements were done with a Thermo Carbon Prep System coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) and Uvigerina peregrina species. Isotopic measurements were done with a Thermo Carbon Prep System coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) and Uvigerina peregrina species. Isotopic measurements were done with a Thermo Carbon Prep System coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) and Uvigerina peregrina species. Isotopic measurements were done with a Thermo Carbon Prep System coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) and Uvigerina peregrina species. Isotopic measurements were done with a Thermo Carbon Prep System coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) and Uvigerina peregrina species. Isotopic measurements were done with a Thermo Carbon Prep System coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) and Uvigerina peregrina species.
Supplementary Figure 6. The resulting function (Eq. 4) has been used to quantitatively reconstruct [NO3] bw.

\[
[NO_3]_{bw} = -3853 \pm 390 \text{ µmol/kg} + 60.6 \pm 2.2
\]  \hspace{1cm} (4)

For the calculation of the errors for the reconstructed [NO3] bw complete error propagation has been done including both the uncertainty of the mean PD within the samples and the uncertainties of the calibration function. The error propagation has been applied to Eq. 3 in the form of equation 5:

\[
\sigma_{[NO_3]_{bw}} = \sqrt{\left(\frac{\delta[NO_3]_{bw}}{\delta a}\sigma_{a}\right)^2 + \left(\frac{\delta[NO_3]_{bw}}{\delta b}\sigma_{b}\right)^2 + \left(\frac{\delta[NO_3]_{bw}}{\delta \sigma}\sigma_{\sigma}\right)^2}
\]  \hspace{1cm} (5)

where \(\sigma_{a}\) is the uncertainty (1σd) of the corresponding parameter \(x\) (in this case [NO3] bw, a, b and PD). Considering Eq. 4 this results in Eq. 6 for the calculation of \(\sigma_{[NO_3]_{bw}}\).

\[
\sigma_{[NO_3]_{bw}} = \sqrt{(90 \pm PD)^2 + (-3853 \pm 390\mu \text{mol/kg})^2 + (2.2)^2}
\]  \hspace{1cm} (6)

The standard error of the mean (SEM) for one sample was then calculated according to Eq. 7:

\[
\text{SEM}_{[NO_3]_{bw}} = \frac{\sigma_{[NO_3]_{bw}}}{\sqrt{n}},
\]  \hspace{1cm} (7)

where \(n\) is the number of specimens analyzed in each sample. The results for each sample are summarized in Supplementary Table 1.

Recent δ13C on DIC and [NO3] in the intermediate Pacific. All data for recent δ13CDIC and [NO3] are taken from the GLODAPv2 database34. The Ocean Data View (ODV) software has been used to compile the plots for Fig. 2a, b. The dataset, which is shown in Fig. 2 and has been used to calculate equation 1 of the main manuscript, includes all data from 700–2000 m the recent Pacific, including parts of the Southern Ocean. Longitudinal boundaries were set to 118°E and 73°S, while latitudinal boundaries were set to 63°N and 79°S (Supplementary Figure 4A). This dataset includes 4956 measurements of both δ13C on DIC and [NO3] . Due to graphical reasons, all δ13C below -1‰ have been cut Fig. 2c of the main manuscript. Nevertheless, all data were included into the linear fit shown in Fig. 2c and eq. 1. A complete plot of all data points can be found in Supplementary Figure 4B. Stations with low δ13C mainly follow the distribution of anthropogenic CO2 in the Pacific (Supplementary Note 3). The recent [NO3] shown in Fig. 1b has been taken from the station within the GLODAPv2 database34 which was located closest to the location and within the same water depth of M77/2-52-2 (Station ID: 33205; Cruise: 316N19930222; Station: 356; 5°31'S; 85°50'W; 1278 m; [NO3] = 41.1 µmol/l). This concentration was also used to calculate the δ13C for the downcore data from the pore density shown in Fig. 1c.

Biogeochemical modeling results on δ13C DIC−[NO3] coupling. We use an improved model version of Somes et al.7 which is based on the UVic Earth System Climate Model33 with a version of Kiel biogeochemistry34. The physical ocean-atmosphere–sea ice model includes a three-dimensional (1.8 x 3.6°, 19 vertical levels) general circulation model of the ocean (Modular Ocean Model 2) with parameterizations such as diffusive mixing along and across isopycnals, eddy-induced tracer advection36, computation of tidally-induced diapycnal mixing over rough topography including sub-grid scale66, as well as anisotropic viscosity67 and enhanced zonal isopycnal mixing schemes in the tropics to mimic the effect of zonal equatorial undercurrents68. A two-dimensional, single level energy-moisture parameterizations such as diffusive mixing along and across isopycnals, eddy-atmosphere-sea ice model includes a three-dimensional (1.8 x 3.6°, 19 vertical layers) simulations assume global PO43−, available online or within the Supplementary material. The foraminiferal pore water [NO3] concentration was also used to calculate the δ13C for the downcore data from the pore density shown in Fig. 1c.

Data availability. All data which support the findings of this study are either available online or within the supplementary material. The foraminiferal pore density, reconstructed [NO3] bw, δ13C DIC and δ13N for sediment record M77/2-52-2 is available in Supplementary Table 1. The data for δ13C FORAM and the reconstructed deglacial [NO3] bw for all records from the intermediate Pacific is available in Supplementary Table 3. The model code and output for the 3D Biogeochemical modeling on deglacial δ13C DIC−[NO3] coupling are available on the GEOMAR Thredds Server (https://thredds.geomar.de).

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Author contributions

N.G. analyzed and interpreted the foraminiferal pore density data, did the database investigation, main interpretation of δ¹³C records and core-writing of the manuscript. Z. E. provided the age model and stratigraphy and performed the δ¹⁵N analyses for core M77/2-55-2. K.W. provided the continuously modeled, global reactive N-inventory and contributed to the interpretation of the δ¹³C records. C.J.S. did the 3D Biogeochemical modeling on deglacial δ¹³C([NO₃]⁻) [NO₃]⁻ coupling. V.L. contributed to the initial interpretation of the nitrate record. J.S. provided additional information about available δ¹³C records. S.G. provided access to the electron microscope for the determination of foraminiferal pore densities. A.E. contributed to the discussion of data and interpretation.

Additional information

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